

Developing Nitrogen-Containing Organic Cathode Materials for Lithium-Ion Batteries

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Abstract

Developing Nitrogen-Containing Organic Cathode Materials for Lithium-Ion Batteries

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Lithium-ion batteries (LIBs) underpin today's mobile and stationary storage, but cathodes based on transition-metal oxides face material-supply, cost, and sustainability constraints. Organic cathode materials (OCMs), composed of earth-abundant elements, offer low-temperature processing, structural diversity, and molecule-level tunability. Most prior progress has focused on carbonyl systems; by comparison, nitrogen-containing organics (azo, nitroso, and nitro aromatics) remain less explored even though a variation of their functional groups allows tuning of redox potential, kinetics, and intermolecular interactions. This thesis targets that gap by examining nitrogen-rich small molecules as LIB cathodes, identifying the main limits to performance, and developing practical routes to stabilize cycling.

The work begins with a critical review of working principles of LIBs including the development of electrodes and electrolytes. As promising cathode candidates, OCMs are reviewed with emphasis on their major classes and charge-storage mechanisms; we also consolidate strategies, including spanning molecular design, electrode and separator modification, and electrolyte engineering, that improve performance and advance OCMs toward practical use. Throughout the experimental chapters, electrochemical testing (cyclic voltammetry, galvanostatic charge–discharge, impedance spectroscopy) is coupled with structural *ex situ* characterization (Fourier-transform infrared (FTIR), Raman, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)) to track functional-group evolution and to connect spectral changes to voltage profiles, polarization, and Coulombic efficiency. Three types of nitrogen-based organic materials have been subsequently studied and evaluated for their electrochemical performances as OCMs for LIBs.

Firstly, commercially available azo dye materials were surveyed as OCMs, with methyl orange (MO) as a low-cost lead candidate. *Ex situ* XRD, Raman, FTIR, and XPS confirm reversible lithiation/delithiation centered on the --N=N-- group. To curb dissolution and enhance

conductivity, MO was confined within porous conductive carbon (BP2000). The MO@BP2000 composite showed improved cyclic stability and rate response, delivering an initial 150 mAh g⁻¹ and retaining 121 mAh g⁻¹ after 50 cycles at 30 mA g⁻¹.

Secondly, nitroso aromatics were probed to clarify their charge-storage pathways. Five representatives, including nitrosobenzene, 2-nitrosotoluene, 4-nitrosobenzoic acid and its lithium salt, and polymeric 1,4-dinitrosobenzene (DNSB), were examined. *Ex situ* FTIR/Raman/XPS revealed a common electrochemical reaction route: nitroso units dimerize and evolve toward azo-type linkages; small molecules convert rapidly and irreversibly, whereas DNSB proceeds gradually via azoxy intermediates with growing conjugation and slower kinetics. Encapsulation of DNSB in high-surface-area carbons (BP2000, Ketjenblack (KB)) improves utilization and interface stability. The DNSB@KB composite reaches a discharge capacity of 383 mAh g⁻¹ initially and retains 102 mAh g⁻¹ after 800 cycles at 150 mA g⁻¹; impedance analysis indicates reduced charge-transfer resistance and more stable interfaces.

Thirdly, two stabilization strategies were evaluated for mitigating dissolution and improving the cycling durability for a promising cathode material, *p*-dinitrobenzene (*p*-DNB): (i) replacing the conventional liquid electrolyte with a poly(ethylene oxide)-based solid polymer electrolyte (PEO-LiTFSI) and (ii) applying poly(vinyl alcohol) (PVA) surface coatings on slurry-cast electrodes. The PEO-LiTFSI electrolyte enables acceptable capacity only at elevated temperature owing to sufficient ionic conductivity, but it fails to suppress thermally driven dissolution. In contrast, PVA surface coatings effectively mitigate dissolution in liquid electrolyte and enhance cycling stability at room temperature. With an optimized coating, *p*-DNB delivers 178 mAh g⁻¹ after 150 cycles at 0.2 C. Electrochemical impedance spectroscopy reveals that excessively thick coatings increase interfacial resistance, highlighting the trade-off between interfacial protection and ion transport.

Overall, this thesis establishes a comprehensive understanding of how organic cathodes, with a particular focus on nitrogen-containing systems (azo, nitroso, and nitro aromatics), can be advanced toward practical application. It delineates the principal limitations that still hinder their deployment, including dissolution, intrinsically low conductivity, interfacial instability, and limited volumetric energy. At the same time, it demonstrates that strategies such as salt formation, controlled polymerization, carbon confinement, protective surface coatings, and electrolyte optimization can improve their electrochemical performances.

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Contribution of Authors

Throughout this thesis, Ximeng Zhang was responsible for conceptualization (with Professor Ye as the primary contributor), conducting experiments or data collection, designing research methods and strategies, computational work, results validation and analysis, statistical or mathematical analysis, data curation, writing original drafts, and visualization.

Professor Zhibin Ye was responsible for supervision, conceptualization, project administration, designing research methods and strategies, ensuring the accuracy and reliability of results, reviewing and revising manuscripts and the thesis, and funding acquisition.

Chapter 3: This chapter is adapted from an article titled *Electrochemical Performances of Azo Dyes as Organic Cathodes for Lithium-Ion Batteries* published in Journal of Power Sources. In this article, Ximeng Zhang designed the research methods and strategies, performed experiments and data collection, carried out formal analysis, validated results, and curated data. Liuqing Yang and Xudong Liu contributed to research design, formal analysis, and data validation. Jay Nejad engaged in result discussion and data interpretation, providing critical feedback that shaped the theoretical framework and final conclusions. Professor Zhibin Ye supervised the research, guided conceptual development, and revised the manuscript.

Chapter 4: This chapter is adapted from a manuscript titled *Revealing the electrochemical evolution of nitroso-to-azo cathodes for lithium-ion storage*, published in ***Journal of Energy Chemistry*** by Ximeng Zhang, Jay Nejad, and Zhibin Ye. In this article, Ximeng Zhang designed research strategies, conducted formal analysis, and validated results. Jay Nejad contributed to selected experiments, data collection, and result discussion, providing essential feedback that shaped the theoretical framework and final conclusions. Professor Zhibin Ye supervised the project, ensured research accuracy, and contributed to reviewing and revising the manuscript.

Chapter 5: Ximeng Zhang designed the research methods and strategies, carried out formal analysis, and validated the data. Jay Nejad contributed to data validation. Professor Zhibin Ye supervised the work, provided conceptual guidance, and reviewed and revised the outcomes.

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List of Abbreviations

AB	Azobenzene
ADALS	Azobenzene-4,4'-dicarboxylic acid lithium salt
ALD	Atomic layer deposition
AQ	Anthraquinone
AQC	AQ/CMK-3
AQDS	Anthraquinone-1,5-disulfonic acid
Azo-CTF	Azo-linked covalent triazine framework
BBQB	1,4-Bis(<i>p</i> -benzoquinonyl)benzene
BNQ	2,2'-Bi(1,4-naphthoquinone)
C4Q	Calix[4]quinone
C₆O₆	Cyclohexanehexone
C6Q	Calix[6]quinone
CDCl₃	Chloroform-d
CE	Coulombic efficiency
CEI	Cathode–electrolyte interphase
CF₃-BQ	2,5-Bis(trifluoromethyl)-1,4-benzoquinone
CMC	Sodium carboxymethyl cellulose
CMC-SBR	CMC-styrene butadiene rubber
CMP	Conjugated microporous polymer
CNT	Carbon nanotube
COF	Covalent organic framework
CQ	Calix[4]arene quinone
CR	Congo red
CV	Cyclovoltammetry
CVD	Chemical vapor deposition
D₂O	Deuterium oxide

DCA	Dichloroisocyanuric acid
DE	Diethyl ether
DEC	Diethyl carbonate
DES	Diethyl sulfide
DFT	Density functional theory
DI	Deionized
DMAQ	2,6-Dimethoxy-9,10-anthraquinone
DMC	Dimethyl carbonate
DME	1,2-Dimethoxyethane
DMS	Dimethyl sulfide
DMSO	Dimethyl sulfoxide
DNB	Dinitrobenzene
DNSB	1,4-Dinitrosobenzene
DOL	1,3-Dioxolane
EC	Ethylene carbonate
EIS	Electrochemical impedance spectroscopy
EMC	Ethyl methyl carbonate
EMS	Ethyl methyl sulfone
EOC	Ethylene-olefin-copolymer
FEC	Fluoroethylene carbonate
FGS	Functionalized graphene sheet
FTIR	Fourier-transform infrared
GCD	Galvanostatic charge–discharge
GDY	Graphdiyne
GO	Graphene oxide
GPE	Gel polymer electrolyte
H₂O₂	Hydrogen peroxide

HCE	High-concentration electrolyte
HLL	Hybrid polymer–LLZTO composite electrolyte
HOMO	Highest occupied molecular orbital
IC	Ion chromatography
IDAQ	1,1'-Iminodianthraquinone
IEFPCM	Polarizable Continuum Model
IL	Ionic liquids
KB	Ketjenblack
LATP	$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$
LGPS	$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$
LHCE	Localized high-concentration electrolyte
LIB	Lithium-ion battery
LLZO	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$
LPS	Li_3PS_4
LPSCI	$\text{Li}_6\text{PS}_5\text{Cl}$
LPSX	$\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br, I)
LTO	Lithium titanate
LTPO	LiTa_2PO_8
LUMO	Lowest unoccupied molecular orbital
Li-DHAQ	Lithiated 1,5-dihydroxyanthraquinone
Li-TCNQ	Lithium tetracyanoquinodimethane
Li₂Q	Lithiated quinone
Li₄-<i>p</i>-DHBDS	Tetralithium 2,5-dihydroxy-1,4-benzenedisulfonate
LiBF₄	Lithium tetrafluoroborate
LiBOB	Lithium bis(oxalato)borate
LiCoO₂	Lithium cobalt oxide
LiFSI	Lithium bis(fluorosulfonyl)imide

LiFePO₄	Lithium iron phosphate
LiNO₃	Lithium nitrate
LiNSBA	Lithium 4-nitrosobenzoate
LiOH	Lithium hydroxide
LiPF₆	Lithium hexafluorophosphate
LiPON	Li _x PO _y N _z
LiTFSI	Lithium bis(trifluoromethane)sulfonimide
MC	Mesoporous carbon
MLD	Molecular layer deposition
MO	Methyl orange
MOLS	MO lithium salt
MR	Methyl red
MWCNT	Multi-walled carbon nanotube
MoS₂	Molybdenum disulfide
NBHQ	Nonylbenzo-hexaquinone
NCA	LiNi _x Co _y Al _z O ₂
NMC811	LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂
NP	Nanoparticle
NQ	1,4-Naphthoquinone
NSB	Nitrosobenzene
NSBA	Nitrosobenzoic acid
NST	2-Nitrosotoluene
OCM	Organic cathode material
OG	Orange G
P14AQ	Poly(1,4-anthraquinone)
P15AQ	Poly(1,5-anthraquinone)
P4VC	Poly(4-vinyl catechol)

PAALi	Lithium polyacrylate
PANQ	Poly(5-amino-1,4-naphthoquinone)
PAQ	9,10-Phenanthrenequinone
PAQS	Poly(2,6-anthraquinonyl sulfide)
PAc	Polyacetylene
PBA	Poly(acrylic acid-butyl acrylate-AMPS-acrylonitrile)
PBALS	4-(Phenylazo) benzoic acid lithium salt
PBQS	Poly(benzoquinonyl sulfide)
PC	Propylene carbonate
PDA	Poly(dopamine acrylamide)
p-DPPZS	5-Phenyl-10-(4-(phenylthio)phenyl)-5,10-dihydrophenazine oligomer
PDMcT	Poly(2,5-dimercapto-1,3,4-thiadiazole)
PDTTA	Poly(5,8-dihydro-1 <i>H</i> ,4 <i>H</i> -2,3,6,7-tetrathia-anthracene)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PGVS	Polygalvinoxylstyrene
PI	Polyimide
PMA	Poly(methyl acrylate)
PP	Polypropylene
PPP	Poly(p-phenylene)
PQ	Phenanthrenequinone
PT	Pentacene-5,7,12,14-tetrone
PTAL	Lithium terephthalate
PTCAQ	Poly(etracyano-9,10-anthraquinonedimethane)
PTCDA	3,4,9,10-Perylenetetracarboxylic dianhydride

PTCDI	Perylenetetracarboxylic diimide
PTFE	Polytetrafluoroethylene
PTMA	Poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate)
PTO	Pyrene-4,5,9,10-tetraone
PTPAn	Polytriphenylamine
PTTCA	Poly(trithiocyanuric acid)
PTh	Polythiophene
PVA	Poly(vinyl alcohol)
PVDF	Poly(vinylidene fluoride)
PVK	Poly(N-vinylcarbazole)
PYT	Pyrene-4,5,9,10-tetraone
QDO	Benzoquinone dioxime
Rf4-BQ	2,5-Bis(perfluorobutyl)-1,4-benzoquinone
SA	Sodium alginate
SEI	Solid-electrolyte interphase
SMD	Solvation Model based on Density
SN	Succinonitrile
SOC	State of charge
SPE	Solid polymer electrolyte
SSE	Solid state electrolyte
SWCNT	Single-walled carbon nanotube
TABQ	2,3,5,6-Tetraamino-benzoquinone
TCNQ	7,7,8,8-Tetracyanoquinodimethane
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
TEP	Triethyl phosphate
TETD	Tetraethylthiuram disulfide

TG	Thermogravimetric
THF	Tetrahydrofuran
TMP	Trimethyl phosphate
TMS	Tetramethylene sulfone
TiS₂	Titanium disulfide
V₂O₅	Vanadium pentoxide
VC	Vinylene carbonate
VEC	Vinylethylene carbonate
VY	Vat Yellow 3RT
XPS	X-ray photoelectron spectroscopy

Chapter 1. Introduction

1.1. Background

The depletion of fossil resources and the acceleration of climate change have intensified the search for alternative energy technologies. Combustion of coal, oil, and natural gas not only consumes finite reserves but also remains the dominant source of global greenhouse gas emissions. As a result, renewable sources such as wind and solar are expanding rapidly. Their variability, however, makes reliable energy storage essential for stable supply.^[1,2]

Rechargeable lithium-ion batteries (LIBs) are the most established storage technology for this purpose. Since their first commercialization in 1991, they have supported the growth of portable electronics and more recently enabled the rise of electric vehicles and stationary storage systems. Their widespread adoption reflects high efficiency, long cycle life, and steady reductions in manufacturing cost. However, despite decades of optimization, LIB technology now faces intensifying pressures: global electricity demand continues to rise, battery formats are scaling to larger and more safety-critical systems, and supply risks associated with critical raw materials are becoming increasingly acute.^[3–5]

On the cathode side, conventional insertion-type transition-metal oxides and phosphates are approaching practical limits in both performance and scalability. Their reversible capacities typically remain below 200 mAh g⁻¹, which is insufficient to meet the growing requirements of high-energy applications.^[6,7] In addition to limited capacity, inorganic cathodes suffer from rigid lattice structures that restrict further design flexibility and a lack of chemical versatility.^[8] Beyond performance constraints, sustainability concerns further limit their long-term viability. The synthesis of these inorganic cathodes generally relies on high-temperature calcination, which consumes large amounts of energy and generates considerable CO₂ emissions. Moreover, their reliance on metals such as cobalt and nickel raises cost and supply-chain risks. At end of life, improper disposal can release toxic heavy metals into soil and water, posing long-term environmental risks.^[9–12] This mismatch between the capacity of today's cathodes and the performance targets of emerging applications underscores the urgent need for alternative electrode materials.

Organic cathode materials (OCMs) are increasingly recognized as promising alternatives to transition-metal compounds because they unite sustainability with a design flexibility that

inorganic lattices cannot provide. Built from earth-abundant elements such as C, H, O, N, and S, OCMs avoid dependence on cobalt and nickel while offering low-temperature and solution-based synthesis routes that reduce both manufacturing cost and carbon footprint.^[13–15] More importantly, their redox properties can be tailored at the molecular level: functional groups such as carbonyl, imine, nitro, azo, or sulfur-based moieties can be deliberately modified to shift operating potential, improve reversibility, and enhance charge-transfer kinetics.^[16,17] This tunability opens a much broader chemical space than rigid transition-metal frameworks, allowing performance to be optimized for specific electrochemical requirements. OCMs also display remarkable structural diversity. They can be realized as small molecules with simple design, as polymers with extended backbones that suppress dissolution, or as porous frameworks such as covalent organic frameworks that immobilize redox centers and facilitate ion transport.^[18,19] Collectively, these advantages underscore the potential of OCMs to combine sustainability, tunability, structural diversity, and processing flexibility, thereby establishing a versatile platform for next-generation LIBs.

However, despite these attractive features, OCMs still face critical challenges that hinder their widespread deployment. Many small organic molecules dissolve in conventional electrolytes, leading to active-material loss and shuttle effects; most organics possess intrinsically low electronic conductivity, which reduces utilization of redox sites and impairs rate performance; and their low bulk density, particularly in porous or framework structures, causes volumetric energy density to lag even when gravimetric capacity is promising.^[18,20,21] Work in the field has therefore converged on three complementary solution paths to mitigate these problems: i) molecular design strategies seek to stabilize redox centers by enlarging or immobilizing active units through oligomerization, polymerization, or framework construction, while rigid linkages, extended conjugation, and salt formation are employed to suppress dissolution and improve charge delocalization;^[16,22] ii) electrode and separator engineering enhances conductivity and confinement by embedding organics in conductive carbons, covalently anchoring them to the host matrix, applying thin protective coatings, or introducing functional separator layers to intercept dissolved species;^[23,24] iii) electrolyte innovation moves beyond conventional carbonate solutions toward tailored solvent-salt-additive chemistries, gel polymer systems, and solid-state electrolytes that reshape solvation environments, stabilize interfaces, and block dissolution pathways.^[23,25,26] Together, these approaches outline a practical roadmap for making OCMs safer, more durable, and more energy-dense, while retaining their intrinsic advantages

of sustainability and molecular tunability.

In addition, many redox-active motifs remain unexplored, and identifying new organic systems with reduced solubility and improved stability is crucial for advancing the field. Research so far has centered mainly on a limited number of frameworks. Carbonyl-based compounds, including quinones, carboxylates, and anhydrides, have dominated because of their well-defined two-electron reactions and relatively high reversibility.^[27,28] Imide-based polymers provide improved stability through rigid backbones that suppress dissolution.^[29,30] Sulfur- and disulfide-containing systems enable multi-electron transfers but often suffer from sluggish kinetics and shuttle effects.^[31,32] Radical polymers exhibit fast redox kinetics and excellent rate capability, though their energy density remains modest.^[33,34] More recently, azo and nitro compounds have attracted attention for their distinct N=N and –NO₂ redox chemistry, yet their development is still at an early stage compared with carbonyl-based systems.^[35,36] Therefore, expanding the diversity of functional groups under study is critical for uncovering new reaction mechanisms and unlocking the full potential of OCMs.

1.2. Research objectives

The central goal of this thesis is to systematically investigate the electrochemical behavior of nitrogen-containing organic compounds, including nitro, azo, and nitroso compounds, as cathode materials for LIBs and to develop strategies to overcome their intrinsic limitations. To date, research on organic cathodes has been dominated by carbonyl-centered systems, where extensive efforts have been devoted to structural modification, polymerization, salt formation, and electrolyte optimization.^[27] In contrast, nitrogen-based redox motifs remain far less developed. Although preliminary studies have clarified certain mechanistic aspects of nitro and azo compounds,^[35–38] broader exploration of molecular diversity, structure–property relationships, and performance optimization is still lacking. These gaps highlight the opportunity to expand the scope of OCMs by establishing design principles and stabilization strategies for nitrogen-containing families. Specifically, this research addresses the following objectives:

- i) Identifying the electrochemical performance of nitrogen-containing OCMs by evaluating voltage profiles, specific capacity, conductivity, cycling stability, and rate capability through systematic cell testing, and clarifying their reaction pathways through structural characterization including *ex situ* Fourier-transform infrared (FTIR), Raman,

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), where spectral features are correlated with charge states, intermediates, and electrochemical behavior.

- ii) Investigating molecular-level stabilization of nitrogen-containing compounds through salt formation, targeted functional substitution with specific substituents, and polymerization, aiming to suppress dissolution, adjust redox potential, and enhance reversibility, while clarifying the balance among capacity, voltage, kinetics, and synthetic complexity.
- iii) Designing electrode architectures by integrating nitrogen-containing OCMs with high-surface-area carbon materials to form conductive composites that provide continuous electron pathways and nanoscale encapsulation, and applying protective coating layers on the electrode surface to enhance mechanical integrity and suppress dissolution.
- iv) Refining liquid electrolytes by adjusting solvent and salt choices to shape stable interphases and mitigate dissolution, and exploring solid-state options, especially solid polymer electrolytes (SPEs), to further suppress crossover and stabilize electrode-electrolyte contact.

Through these objectives, the thesis aims to contribute both mechanistic understanding and applied design strategies for nitrogen-containing OCMs, thereby advancing them from proof-of-concept molecules toward viable cathode candidates.

1.3. Thesis outline

This dissertation is organized into six chapters:

- i) **Chapter 1** introduces the background and motivation for developing OCMs, outlines the intrinsic challenges that hinder their practical deployment, and specifies the objectives and scope of this research.
- ii) **Chapter 2** provides a comprehensive literature review of OCMs. It begins with a general overview of LIB principles including electrode chemistry and electrolyte development, followed by a detailed survey of functional groups investigated in OCMs, including carbonyls, nitro, azo, imines, and organosulfur systems. The chapter highlights key challenges, such as dissolution, conductivity, and structural reversibility, and reviews existing strategies including molecular design, carbon coupling, separator/binder engineering, and electrolyte development.

- iii) **Chapter 3** focuses on azo dye cathodes, particularly methyl orange (MO) and related derivatives. *Ex situ* characterizations confirm that the azo group serves as the redox-active center. To address dissolution and capacity fading, MO is encapsulated in porous carbon (BP2000), forming MO@BP2000 composites that show improved cycling stability and rate capability. The chapter clarifies the redox role of azo groups and demonstrates the benefits of carbon confinement.
- iv) **Chapter 4** focuses on nitroso-based organic compounds as cathode materials, including nitrosobenzene (NSB), nitrosotoluene (NST), nitrosobenzoic acid (NSBA), and polymeric dinitrosobenzene (DNSB). Spectroscopic studies reveal a common nitroso-to-azo transformation pathway. Compared with small molecules, polymeric DNSB evolves gradually through azoxy intermediates. Encapsulation of DNSB in porous carbons (BP2000, Ketjenblack) enhances stability and long-term cycling performance, as confirmed by electrochemical testing and impedance analysis. The study establishes the mechanistic basis of nitroso redox chemistry and demonstrates encapsulation as a stabilization strategy.
- v) **Chapter 5** presents experimental work on improving the cycling stability of *p*-dinitrobenzene (*p*-DNB) cathodes. Two stabilization strategies are studied: poly(ethylene oxide) (PEO)-based solid polymer electrolytes and poly(vinyl alcohol) (PVA) electrode coatings. Electrochemical tests demonstrate that PEO restricts diffusion but suffers from thermal instability, while optimized PVA coatings effectively improve room-temperature cycling stability. These results highlight the importance of polymer confinement for nitroaromatic electrodes.
- vi) **Chapter 6** concludes the thesis by summarizing the main findings on azo-, nitroso-, and nitro-based cathodes and the stabilization strategies developed to improve their performance. It also reflects on their significance for sustainable battery technology and highlights future directions in expanding chemical diversity and enhancing electrode stability.

Chapter 2. Literature Review

2.1. Overview of lithium-ion batteries

Batteries are electrochemical energy storage systems characterized by low cost, high energy conversion efficiency, convenient storage and transportation, and excellent operational stability.^[39,40] Over the past decades, extensive research has been devoted to alkali metal (Li, Na, K) ion batteries,^[41] among which lithium-ion batteries (LIBs) have achieved the highest level of commercialization and technological maturity, owing to their superior energy density, long cycle life, and reliability.

2.1.1. Working principles

A LIB generally comprises an anode, a cathode, a separator, and an ion-conducting electrolyte. During discharge, the cathode undergoes reduction accompanied by the intercalation of metal ions migrating through the electrolyte, while the anode is oxidized to release metal ions. Simultaneously, electrons flow from the anode to the cathode through an external circuit, maintaining charge neutrality. This redox process decreases the cell's chemical potential, enabling the conversion of stored chemical energy into electrical energy for external devices. During charging, the reactions and ion/electron transport proceed in the reverse direction.^[42]

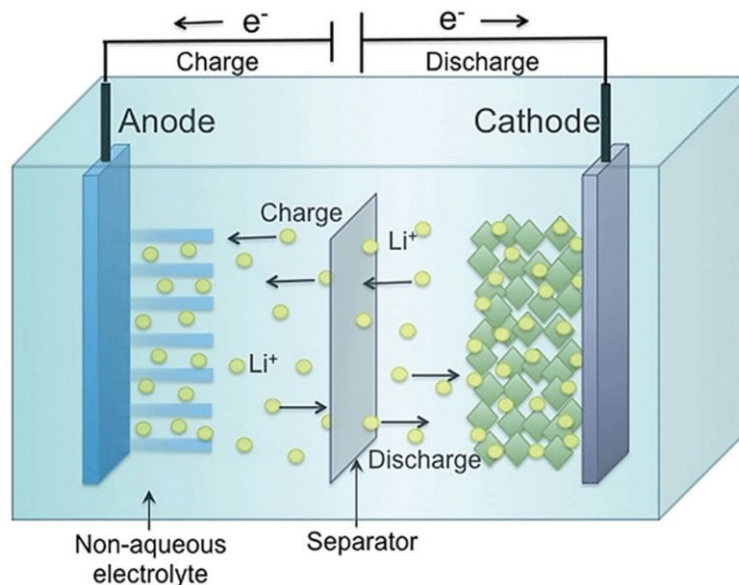
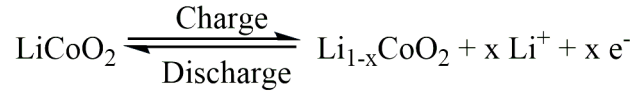


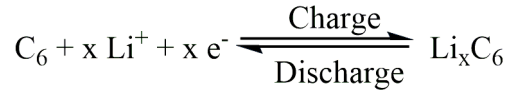
Figure 2.1. Working principle of a typical LIB.^[42]

The overall working principle is illustrated in [Figure 2.1](#) and can be represented, for example, by the following electrochemical reactions in a $\text{LiCoO}_2/\text{graphite}$ cell:

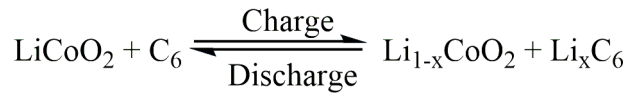
Cathode (positive electrode):



Anode (negative electrode):



Total:



2.1.2. Parameters

In general, five key parameters are commonly employed to evaluate the performance of rechargeable batteries.^[43,44]

i) Output voltage: The output voltage is determined by the difference in redox potentials between the cathode and anode materials, expressed as:

$$E = E_+ - E_-$$

where E is the output voltage, and E_+ and E_- are the operating potentials of the cathode and anode, respectively. Cathode materials with higher redox potentials and anode materials with lower redox potentials are preferred for achieving high cell voltage. The operating voltage not only dictates the energy density of the cell but also affects power output and overall device performance.

ii) Specific capacity: A specific capacity (Q) in batteries refers to the amount of electric charge a material can store per unit of mass or volume, typically measured in mAh g^{-1} for mass. The theoretical specific capacity of an electrode material can be calculated using Faraday's law:

$$Q = \frac{nF}{3600 \times Mw} \text{mAh} \cdot \text{g}^{-1}$$

where n is the number of electrons transferred per formula unit, F is the Faraday constant (96485 C mol^{-1}), and Mw is the molecular weight of the active material.

iii) Energy density: The energy density (W) reflects the total amount of energy stored per unit

mass or volume, and is given by the product of the cell voltage and specific capacity:

$$W = E \times Q$$

where E is the output voltage and Q is the specific capacity. Volumetric energy density considers the electrode density and is critical for space-limited applications such as portable electronics and electric vehicles.

iv) Cyclability: The capacity retention during repeated charge–discharge cycles reflects the long-term stability of the battery. Capacity fading can arise from structural degradation of the electrode, irreversible side reactions, or dissolution of the active material into the electrolyte. Cyclability is typically expressed as the percentage of the initial capacity retained after a given number of cycles.

v) Rate capability: The ability of a battery to deliver or accept charge efficiently at various current densities. It is primarily governed by the electron-transfer kinetics of the redox-active centers and the ion transport properties within the electrode and electrolyte, both of which are strongly influenced by the morphology and conductivity of the electrode composite.^[45,46]

Collectively, these parameters determine the applicability of LIBs across diverse application contexts. For example, electric vehicles demand high energy density, good rate performance for acceleration, and excellent cyclability over thousands of cycles, whereas grid storage systems may prioritize cost, safety, and lifetime over gravimetric energy density.

2.1.3. Development of electrode materials

Since their commercialization in the early 1990s,^[47] LIBs have revolutionized energy storage for portable electronics, electric vehicles, and stationary applications. The remarkable success of LIBs lies in the reversible intercalation of lithium ions into electrode hosts, enabling high energy density, long cycle life, and good rate performance. In contrast, earlier rechargeable battery systems such as lead–acid and nickel–cadmium batteries were limited by low energy density, shorter cycle life, and environmental concerns ([Figure 2.2](#)). Lead-acid batteries, first commercialized in the late 19th century, are inexpensive and capable of delivering high surge currents, which make them suitable for automotive starting, lighting, and ignition applications, but their low specific energy of about 30–40 Wh kg^{−1} and heavy weight limit their use in portable devices.^[48,49] Nickel-cadmium batteries, introduced in the early 20th century, offer a higher energy density of about 45–60 Wh kg^{−1} and better cycle life than lead-acid systems, as

well as superior performance at low temperatures.^[50] However, they suffer from relatively high self-discharge and environmental toxicity due to cadmium content.^[51]

These limitations drove intensive research in the 1970s and 1980s toward lightweight, high-voltage rechargeable batteries based on lithium metal anodes (lithium-metal batteries), as shown in [Figure 2.3](#). Early lithium primary batteries, such as lithium-poly(carbon monofluoride) and lithium-sulfur dioxide systems, demonstrated the high-energy-density potential of lithium chemistry but were nonrechargeable.^[52–55] The development of rechargeable lithium metal batteries began with transition metal chalcogenides such as titanium disulfide (TiS_2), which allowed fast lithium intercalation at about 2.5 V vs. Li/Li^+ and delivered relatively high capacities of about 240 mAh g^{-1} .^[56–58] This was followed by studies on layered dichalcogenides such as molybdenum disulfide (MoS_2) and niobium triselenide (NbSe_3),^[59–62] which showed improved cycling stability but still suffered from low operating voltage. In parallel, vanadium pentoxide (V_2O_5) and related bronzes attracted attention for their higher operating voltage of about 3.0 V and multiple lithium-insertion sites, though they were hindered by structural instability during deep intercalation.^[63–66]

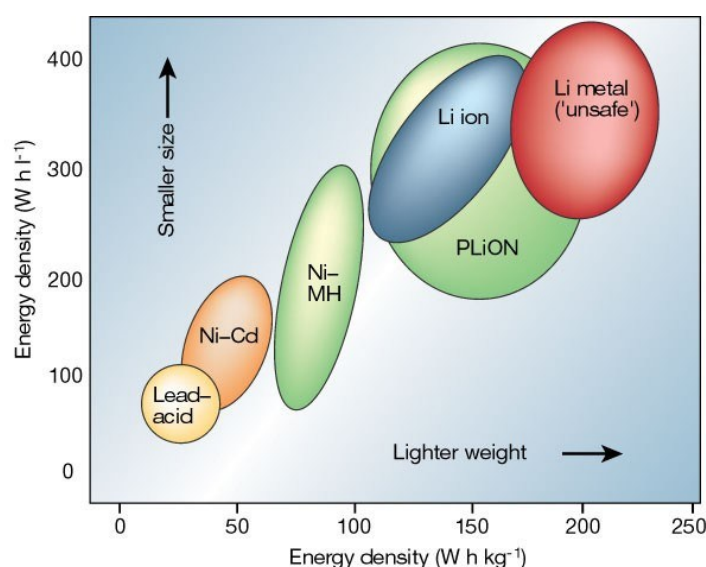


Figure 2.2. Comparison of the different battery technologies in terms of volumetric and gravimetric energy density. Adapted with permission.^[41] Copyright © 2001 Springer Nature.

While these early intercalation cathodes demonstrated the feasibility of high-energy-density rechargeable lithium batteries, the use of lithium metal anodes caused severe safety problems due to dendritic lithium growth during cycling, which could lead to internal short circuits and thermal runaway. The breakthrough came with the proposal to replace metallic lithium with

carbonaceous anodes capable of reversibly hosting lithium ions at low potentials without dendrite formation. This concept, combined with Goodenough's discovery in 1980 of layered lithium cobalt oxide (LiCoO_2) as a high-voltage cathode operating at ~ 3.9 V, enabled the first commercial LIBs introduced by Sony in 1991.^[47] LiCoO_2 offered excellent energy density and cycling stability, laying the foundation for the rapid expansion of LIB technology across consumer electronics and, later, electric vehicles.

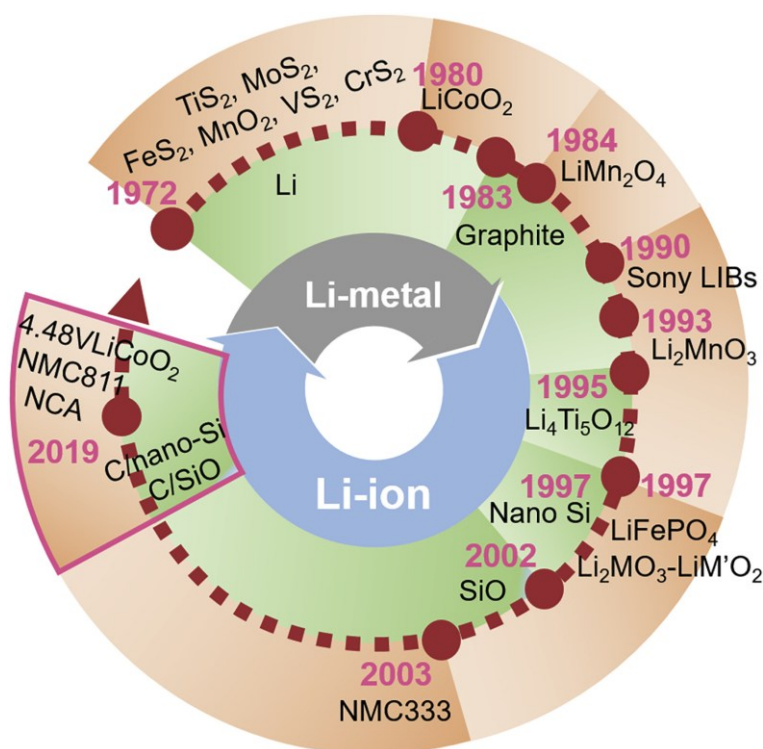


Figure 2.3. The timeline for the development of lithium-metal batteries to LIBs from 1972 to 2019.^[67]

Despite its commercial success, LiCoO_2 suffers from limited practical capacity of about 140 mAh g^{-1} , high cost, and supply risk of cobalt.^[68] In response, research shifted toward cobalt-poor alternatives. Spinel lithium manganese oxide (LiMn_2O_4 , LMO) emerged as a low-cost, low toxicity cathode with a three-dimensional lithium diffusion network, providing improved rate performance and safety.^[69] However, its capacity of about 148 mAh g^{-1} and poor cycling stability at high temperatures, attributed to Jahn-Teller distortion and manganese dissolution, limited its widespread use. The olivine lithium iron phosphate (LiFePO_4 , LFP) cathode, introduced in the late 1990s, offers high thermal stability, long cycle life, and low cost, although its low intrinsic electronic conductivity and one-dimensional lithium diffusion limit high-rate performance.^[70] These drawbacks have been mitigated by strategies such as particle downsizing,

carbon coating, and doping.^[71,72]

In pursuit of higher energy density, high-nickel layered oxides such as $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) and $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA) were developed, delivering capacities of $180\text{--}220\text{ mAh g}^{-1}$.^[73–75] Their compositions can be tuned to balance energy density, safety, and cycle life, though they remain dependent on critical metals and exhibit thermal instability at high states of charge. A comparison of these different types of LIBs is presented in [Figure 2.4](#). Parallel efforts focus on high voltage spinels,^[76,77] lithium rich layered oxides,^[78,79] and conversion type cathodes,^[80,81] aiming to break through the intrinsic capacity limits of intercalation chemistry.

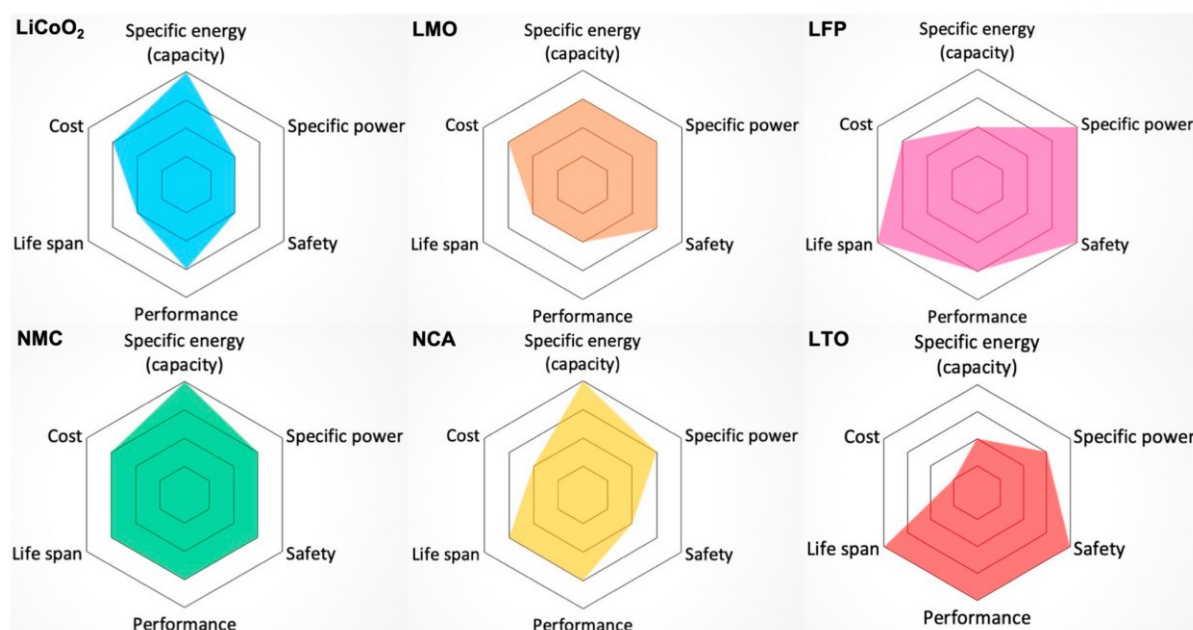


Figure 2.4. Comparisons of different types of Li-ion batteries used in EVs from the following perspectives: specific energy (capacity), specific power, safety, performance, life span, and cost.^[82]

More recently, the search for alternatives to conventional layered and olivine cathodes has expanded to encompass organic cathode materials (OCMs),^[12] polyanionic compounds,^[83,84] and metal fluorides,^[85,86] each offering distinct advantages including structural tunability, high operating voltage, or exceptionally high theoretical energy density. Despite their diversity in composition and electrochemical mechanisms, these emerging systems face common challenges including voltage hysteresis, structural degradation during cycling, limited electronic and ionic conductivity, and instability of active species.^[87] Addressing these challenges has driven development of strategies including nanoscale structural engineering, integration with highly conductive matrices, and optimization of electrode–electrolyte

interfaces, reflecting the broader push toward next-generation LIBs that combine high energy density, long service life, safety, cost-effectiveness, and environmental sustainability.

Compared with the extensive development of cathodes, conventional anodes have seen relatively fewer breakthroughs, though they are equally crucial to LIB performance (Figure 2.5). Graphite remains the dominant anode, delivering a capacity of 372 mAh g^{-1} with only $\sim 10\%$ volume expansion during lithiation (LiC_6 formation) and excellent cycle life.^[88] However, its moderate capacity limits further improvements of LIBs in energy density.

An important commercial alternative is lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO), which operates via a zero-strain insertion mechanism, exhibiting negligible volume change ($\sim 0.2\%$) and exceptional cycling stability. With a flat operating potential of $\sim 1.55 \text{ V}$ vs. Li/Li^+ , LTO inherently avoids lithium plating and offers outstanding safety, making it attractive for high-power applications such as electric buses and grid storage. Nonetheless, its relatively low specific capacity ($\sim 175 \text{ mAh g}^{-1}$) and higher operating voltage reduce the overall energy density, which restricts its use in applications requiring compact, high-energy storage.

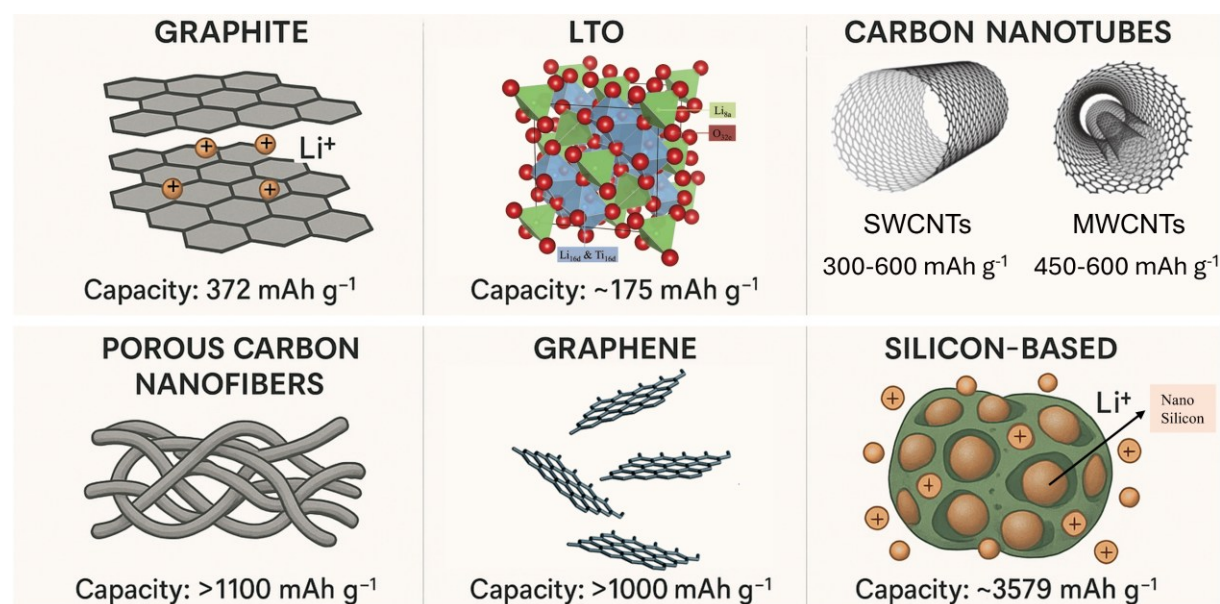


Figure 2.5. Summary of different types of anode materials in LIBs.

To further boost capacity, nanostructured carbon materials such as carbon nanotubes (CNTs), porous carbon nanofibers, and graphene have been explored.^[89–91] Single-walled CNTs (SWCNTs) can deliver $300\text{--}600 \text{ mAh g}^{-1}$, while multi-walled CNTs (MWCNTs) reach $450\text{--}600 \text{ mAh g}^{-1}$, and heteroatom doping (e.g., N-doping) further improves conductivity and capacity. Porous carbon nanofibers with high surface areas have demonstrated capacities over

1100 mAh g⁻¹ with excellent retention, while graphene anodes with engineered interlayer spacing have exceeded 1000 mAh g⁻¹. Silicon-based alloy anodes offer ultrahigh capacity (~3579 mAh g⁻¹) but suffer from large volume expansion and unstable solid-electrolyte interphase (SEI), leading to rapid capacity decay.^[92] Mitigation strategies including nanosizing, elastic binders, and silicon-carbon composites, help mitigate these problems. Beyond alloying and intercalation systems, conversion-type anodes based on transition metal oxides, sulfides, and nitrides offer even higher capacities through multi-electron redox reactions, yet their practical application remains limited by large voltage hysteresis, complex phase transformations, and insufficient long-term stability.^[93,94]

2.1.4. Development of electrolytes

The development of liquid electrolytes for LIBs began with carbonate-based systems, which remain the backbone of commercial LIB technology. A typical liquid electrolyte consists of three key components: a solvent, a lithium salt, and one or more functional additives. The specific combination of these components determines not only the ionic conductivity and electrochemical stability of the electrolyte but also the interfacial chemistry at both electrodes. Over the past three decades, liquid electrolytes for LIBs have undergone significant evolution, driven by the need to improve energy density, safety, and cycle life under diverse operating conditions. Typical solvents and salts are summarized in [Figure 2.6](#), and a comparison of various lithium salts is presented in [Table 2.1](#).

In the 1990s, the first commercial LIBs employed a formulation of lithium hexafluorophosphate (LiPF₆) dissolved in mixed carbonate solvents.^[95,96] Cyclic carbonates, such as ethylene carbonate (EC) and propylene carbonate (PC) possess a high dielectric constant, enabling efficient lithium-salt dissociation and the formation of a stable SEI on graphite anodes. In contrast, linear carbonates, such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC), exhibit low viscosity, thereby improving low-temperature ionic transport and rate performance. LiPF₆ remains the most widely used lithium salt due to its balance of ionic conductivity and Al current-collector passivation, but it suffers from poor stability and moisture sensitivity. Consequently, alternative salts, such as lithium tetrafluoroborate (LiBF₄),^[97] lithium bis(oxalato)borate (LiBOB),^[98,99] and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI),^[100] have been explored to improve thermal stability, inhibit Al corrosion, and optimize SEI/cathode-electrolyte interphase (CEI) chemistry. Additives also play a critical role: film-forming agents, such as fluoroethylene carbonate (FEC),

vinyl ethylene carbonate (VEC), and vinylene carbonate (VC), reduce initial irreversible capacity and enhance SEI/CEI quality;^[101–104] flame retardants, such as fluorinated phosphazenes and phosphates, improve thermal safety;^[105,106] and overcharge-protection additives (e.g., organic redox shuttles) suppress hazardous reactions during overcharging.^[107]

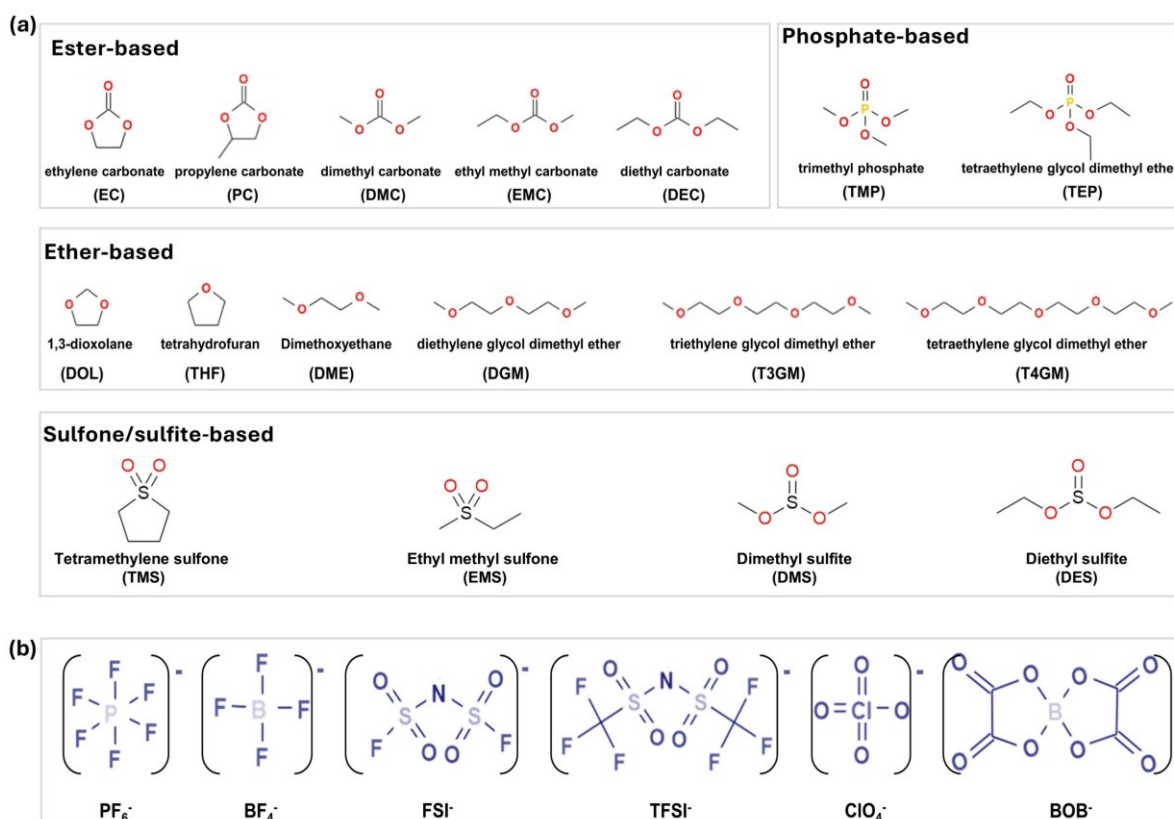


Figure 2.6. (a) Representative solvents of four electrolyte systems; (b) molecular structures of common electrolyte salt anions. Adapted with permission.^[108] Copyright © 2024 John Wiley and Sons.

In parallel, ether-based systems have been developed for lithium-metal and sulfur-based batteries.^[109,110] Ether solvents, such as 1,2-dimethoxyethane (DME), 1,3-dioxolane (DOL), and tetrahydrofuran (THF), have low viscosity and strong lithium-solvating ability, enabling high ionic conductivity at low temperatures and facilitating the formation of relatively flexible SEI layers on lithium-metal anodes to mitigate dendrite growth. In Li–S batteries, ether solvents dissolve lithium polysulfides effectively, which promotes reaction kinetics but also triggers the shuttle effect; therefore, careful salt and additive design is required.^[111,112] LiTFSI is the most common salt due to its thermal stability and compatibility with ethers, while lithium bis(fluorosulfonyl)imide (LiFSI) offers even higher ionic conductivity.^[113] Lithium nitrate (LiNO₃) is widely used as an additive to form an inorganic-rich SEI on lithium metal,

significantly improving Coulombic efficiency (CE) and cycling stability.^[114,115] To address the poor oxidative stability of ethers at high voltages, high-concentration electrolytes (HCEs) and localized high-concentration electrolytes (LHCEs) have been introduced, that alter the solvation structure and reduce free-solvent reactivity, thereby enabling application with 4 V-class cathodes.^[109,116,117]

Table 2.1. Comparison of various lithium salts. Adapted with permission.^[118] Copyright © 2022 John Wiley and Sons.

Lithium salt	Advantages	Disadvantages
LiPF ₆	With a suitable solubility and a higher ionic conductivity in the nonaqueous solvent; a stable passivation film can be formed on the surface of the aluminum foil concentration	Poor thermal stability, easy to decompose
LiBF ₄	Width of the working temperature, good high-temperature stability, excellent low-temperature performance; enhance the film formation capability of electrolyte to electrodes, inhibiting aluminum foil corrosion	Lower ion conductivity
LiBOB	High electrical conductivity, wider electrochemical window, good thermal stability, better circulating stability, passivation protection of positive, or aluminum foil fluid	Low solubility
LiAsF ₆	Have very high conductivity, stability, and battery charging discharge rate	Toxicity
LiDFOB	Good film formability, good low-temperature performance, is very well compatible with the positive pole of the battery, can form a passivation film on the surface of the aluminum foil, inhibiting electrolytic solution oxidation	Expensive
LiFSI	High electrical conductivity, low water sensitivity, and good thermal stability	Corroding aluminum foil when voltage 4.2 V
LiTFSI	Higher solubility and conductivity, thermal decomposition temperature exceeds 360 °C, not easy to hydrolyze	Corroding aluminum foil when voltage is 3.7 V
LiPF ₂ O ₂	Good low temperature performance; reduce battery interface impedance, improve the battery cycle performance	Lower solubility
LTBP	Difficult to hydrolyze, good thermal stability, and high safety	High molecular weight, high viscosity, and low conductivity
LiDFMFB	Improve cycle stability and Coulomb efficiency	High molecular weight, high viscosity, and low conductivity
LiDFEEMB	Improve cycle stability and Coulomb efficiency	High molecular weight, high viscosity, and low conductivity

Beyond these two major categories, other liquid electrolyte chemistries have been developed for specific applications. Sulfone- and sulfite-based electrolytes, such as tetramethylene sulfone (TMS), ethyl methyl sulfone (EMS), dimethyl sulfide (DMS), and diethyl sulfide (DES), are employed for high-voltage cathodes owing to their wide oxidative stability window.^[119,120] Phosphate-based electrolytes, such as trimethyl phosphate (TMP) and triethyl phosphate (TEP), are used as flame-retardant solvents to improve safety in high-power or electric-vehicle batteries.^[121–124] Ionic liquids (ILs), offering intrinsic nonflammability and wide electrochemical stability windows, have been explored for high-temperature operation and niche energy-storage applications.^[125,126]

In parallel, research into solid-state electrolytes (SSEs) has sought to address the inherent safety risks of flammable organic liquids while enabling compatibility with high-energy-density electrodes. The main research directions can be categorized into three classes, as illustrated in [Figure 2.7](#).

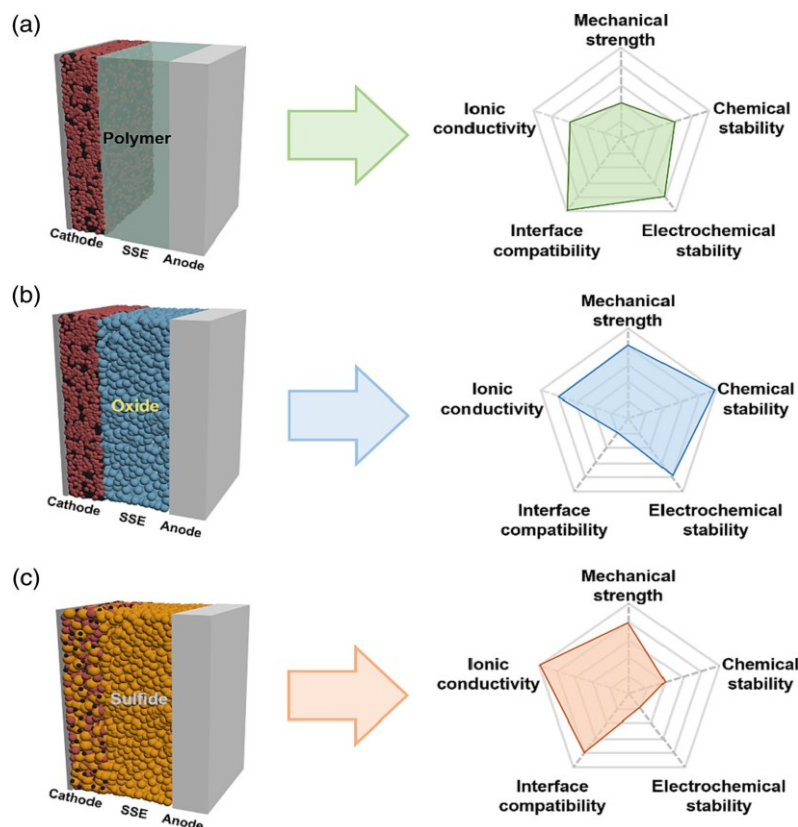


Figure 2.7. Schematic illustrations and comparison of solid-state batteries using: (a) polymer, (b) oxide, and (c) sulfide solid-state electrolytes. Adapted with permission.^[127] Copyright © 2022 Elsevier.

Solid polymer electrolytes (SPEs), composed of lithium salts dissolved in a polymer matrix, offer nonflammability, mechanical flexibility, and the potential for thin-film processing, but their ionic conductivity at ambient temperature is generally limited by sluggish ion transport in the crystalline polymer domains. Gel polymer electrolytes (GPEs) bridge the gap between liquids and solids by immobilizing liquid electrolyte within a polymer network, combining high ionic conductivity ($>10^{-3} \text{ S cm}^{-1}$ at room temperature) with improved mechanical integrity and leakage resistance.^[128,129] Poly(ethylene oxide) (PEO) is one of the most widely investigated polymer hosts due to its strong Li^+ -solvating ether oxygens; however, its semicrystalline nature limits room-temperature ion transport (Figure 2.8a).^[130,131] To overcome this, high concentrations of lithium salts such as LiTFSI or LiFSI are incorporated to promote amorphous domain formation (Figure 2.8b),^[132] while copolymerization and/or blending with low-glass-transition-temperature polymers, such as poly(vinylidene fluoride) (PVDF), and polystyrene (PS; Figure 2.8c),^[133,134] and the use of plasticizers or ILs (Figure 2.8d) have been employed to enhance segmental motion and conductivity at ambient conditions.^[135–138] *In situ* polymerization approaches (Figure 2.8e) further improve electrode–electrolyte interfacial

contact, suppress growth of interfacial resistance, and extend cycle life in lithium-metal, Li-S, and high-voltage LIB systems.^[139,140]

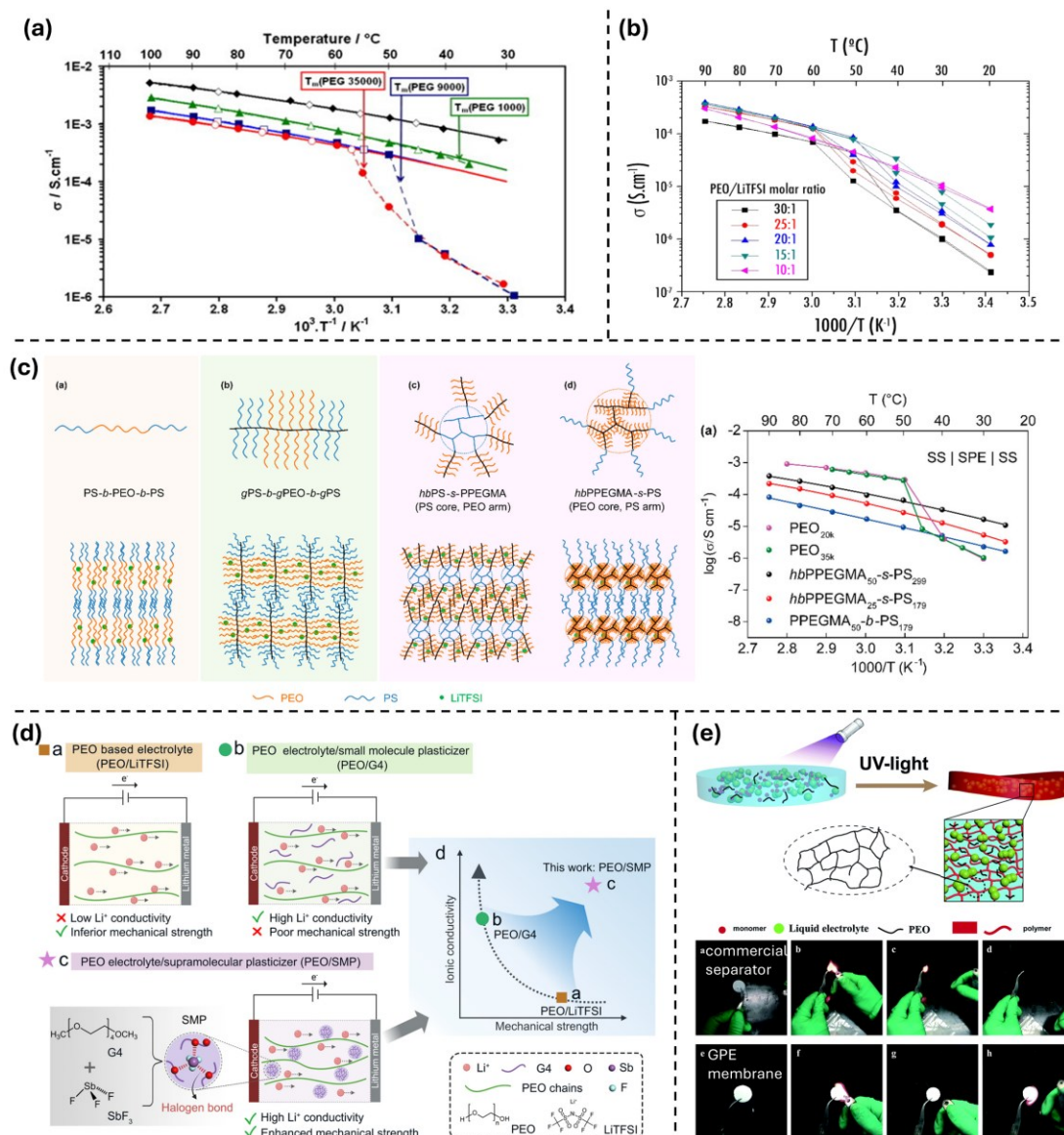


Figure 2.8. (a) Ionic conductivities of PEO/LiTFSI (EO:Li = 25) complexes as function of the inverse of temperature. Adapted with permission.^[131] Copyright © 2012 Elsevier. (b) Arrhenius plots of the ionic conductivity for PEO/LiTFSI polymer electrolyte complexes.^[132] (c) Illustration of the correlation between the topological structures and phase separation of PEO-PS copolymers blended with LiTFSI, along with the temperature-dependent ionic conductivity of representative PEO-PS copolymers. Adapted with permission.^[133] Copyright © 2019 American Chemical Society. (d) Schematic comparison of PEO-based electrolytes with and without plasticizer. Adapted with permission.^[138] Copyright © 2024 American Chemical Society. (e) The preparation and schematic illustration of the GPE membrane by *in situ* polymerization of trimethylolpropane ethoxylate triacrylate, and combustion tests of the commercial separator and the GPE membrane.^[130]

To address the limitations of purely polymeric matrices, such as low modulus and limited oxidative stability, polymer-ceramic composite electrolytes have been developed (Figure 2.9).^[141,142] Inorganic ceramics can be either Li^+ -insulative (such as TiO_2 , Al_2O_3 , SiO_2) or Li^+ -conductive (such as $\text{Li}_x\text{PO}_y\text{N}_z$ (LiPON), $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP), $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS), $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), LiTa_2PO_8 (LTPO)).^[143] Dispersing inert or ion-conductive ceramic fillers suppresses polymer crystallinity, enhances Li^+ transference number, and increases Young's modulus, thereby resisting dendrite penetration. When ion-conductive ceramics are used, they also provide fast Li^+ transport pathways, enabling synergistic conduction through both polymer and filler phases.

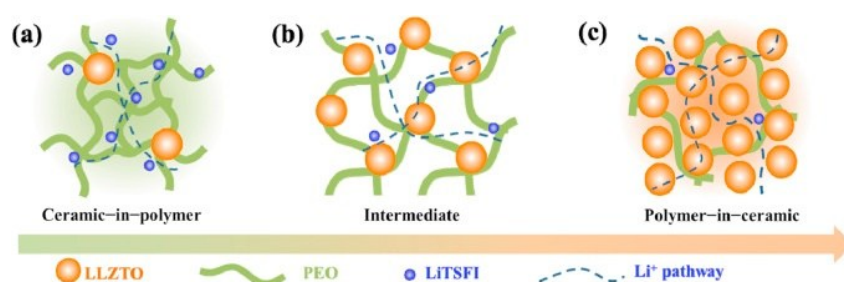


Figure 2.9. Schematic illustration for PEO-ceramic composite solid electrolyte. Adapted with permission.^[144] Copyright © 2018 Elsevier.

Inorganic solid electrolytes have followed two primary development routes. Oxide-based systems such as garnet-type LLZO and NASICON-type LATP offer outstanding electrochemical stability (>5 V vs. Li^+/Li) and air/moisture tolerance, making them more compatible with high-voltage cathodes (Figure 2.10). However, their high grain-boundary resistance and mechanical rigidity require high-temperature sintering and precise densification to achieve adequate conductivity (typically 10^{-4} – 10^{-3} S cm^{-1} at room temperature). Compositional tuning via aliovalent doping, defect engineering, and microstructural optimization is routinely applied to enhance Li^+ mobility and reduce interfacial impedance.^[145–149] In contrast, sulfide-based systems, exemplified by Li_3PS_4 (LPS),^[150,151] LGPS,^[152,153] and argyrodite-type $\text{Li}_6\text{PS}_5\text{X}$ (LPSX, X = Cl, Br, I),^[145,154] are attractive for their exceptionally high room-temperature ionic conductivities (often $>10^{-2}$ S cm^{-1}) and low grain-boundary resistance (Figure 2.11).^[155–158] Their mechanical softness allows intimate electrode contact under moderate pressure, but they suffer from poor chemical stability against lithium metal and high-voltage oxides, requiring protective interlayers or interface engineering.^[159,160]

Overall, the trajectory of electrolyte development in LIBs reflects a continuous adaptation to

evolving electrode chemistries, increasing voltage demands, and ever-stricter safety requirements. Across liquid, gel, and solid systems, the interplay between lithium salt selection, solvent or host matrix architecture, filler/additive engineering, and interfacial design remains central to achieving the delicate balance of ionic conductivity, electrochemical stability, thermal robustness, and mechanical strength required for next-generation high-energy-density LIB technologies.

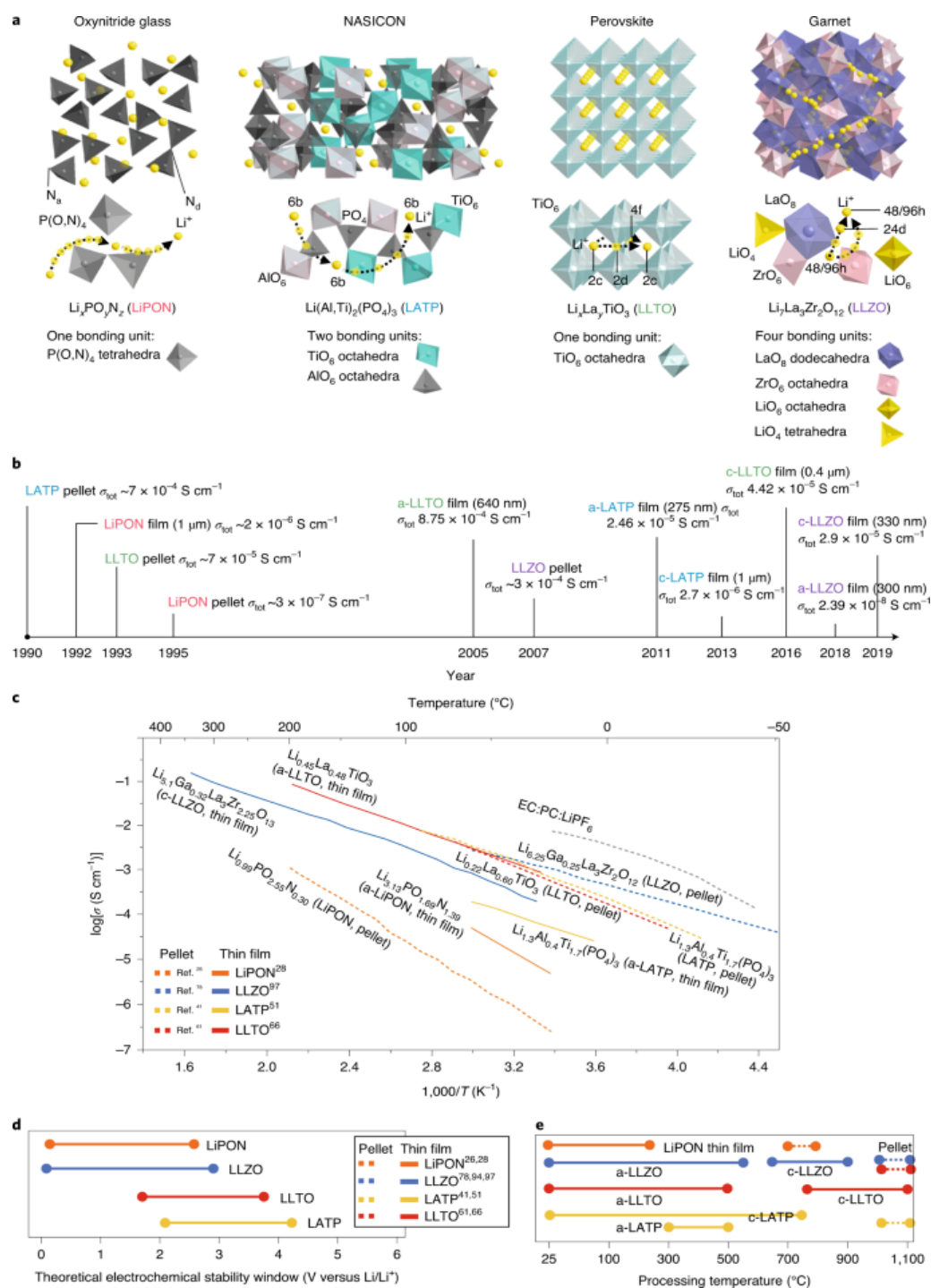


Figure 2.10. Properties of diverse oxide solid electrolytes: (a) structures, local bonding units

and network for convenient Li-ion migration paths of oxide-based Li-ion conductors; (b) the processed year of oxide solid electrolytes and the associated Li-ion conductivities; (c) Li-ion conductivities of Li-oxide-based solid-state electrolytes in pellet and thin-film form compared with that of the state-of-the-art liquid electrolyte EC:PC:LiPF₆ (d) theoretical electrochemical stability windows (V) based on first-principles thermodynamic calculations; (e) processing temperatures (°C) for reported pellets and thin films. Adapted with permission.^[149] Copyright © 2021 Springer Nature.

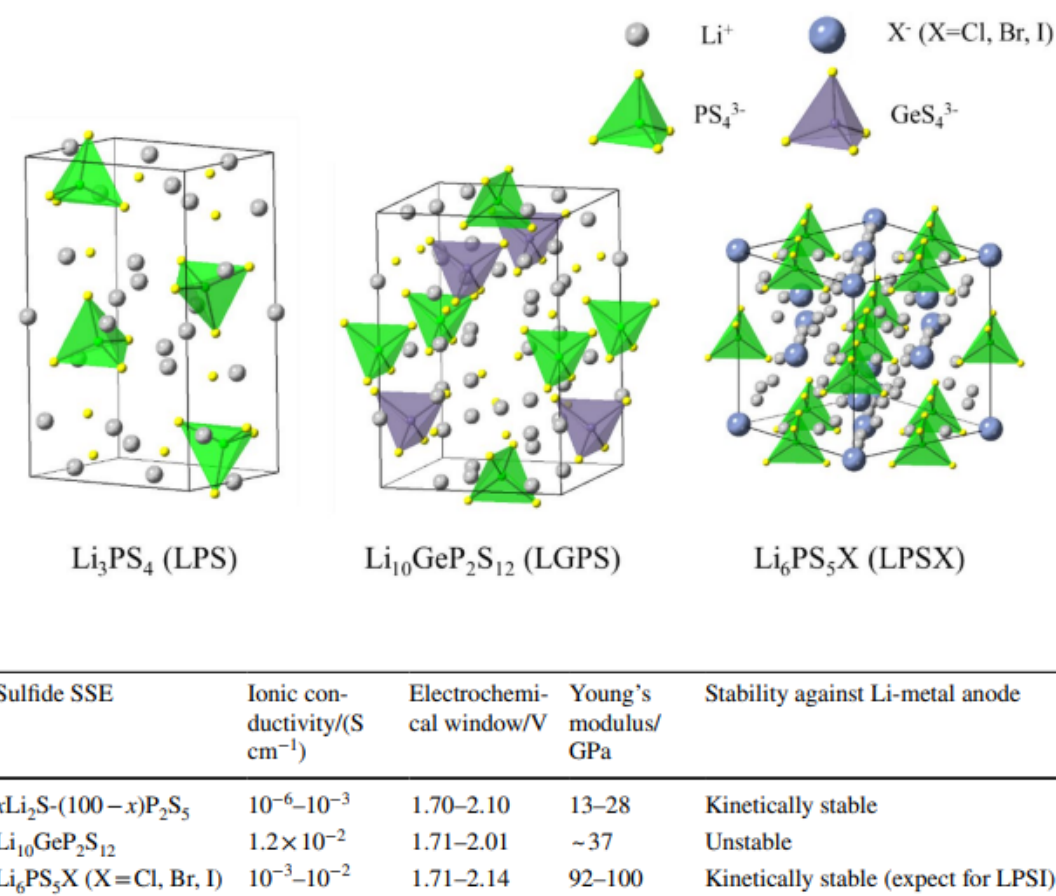


Figure 2.11. Crystal structures and comparison of properties of three typical sulfide SSEs: LPS, LGPS, and LPSX. Adapted with permission.^[161] Copyright © 2023 Springer Nature.

2.2. Development of OCMs

In rechargeable batteries, the cathode material is widely recognized as the primary factor determining the overall energy density, operating voltage, and cycling stability. While inorganic electrodes have dominated the development of rechargeable batteries, the increased expectation for low-cost, versatile, resource-abundant, and environmentally friendly electrode materials has boosted studies on organic materials since the first report of an OCM, dichloroisocyanuric acid (DCA), in 1969.^[162] OCMs have since attracted significant attention as alternatives to

conventional inorganic electrodes due to their structural diversity, tunable redox properties, and potential environmental advantages.^[12,14] Composed primarily of abundant elements such as C, H, N, O, and S, these materials avoid reliance on critical transition metals and allow molecular-level engineering to optimize redox potential, capacity, solubility, and conductivity. Their electrochemical activity originates from specific redox-active functional groups, including carbonyl (C=O), imine (C=N), azo (–N=N–), nitro (–NO₂), sulfur-containing moieties (S–S, C–S), and heteroaromatic or radical units.

2.2.1. Classification of OCMs

To better understand their electrochemical behavior and guide molecular design, organic cathode materials can be classified according to the nature of the redox center and the dominant ion–electron coupling process into n-type, p-type, and bipolar systems, as shown in [Figure 2.12](#). In n-type materials, the active sites are reduced upon discharge by accepting electrons and cations (Li⁺, Na⁺), typically involving electron-deficient groups such as C=O, C=N, N=N, or –NO₂. P-Type materials are oxidized during discharge, releasing electrons and accommodating anions from the electrolyte, with redox-active centers such as amines, thioethers, and conjugated heterocycles. Bipolar materials can operate in both oxidation and reduction modes, enabling multi-electron processes and higher capacities. Representative compounds for each class are summarized in [Figure 2.13](#) by redox group.

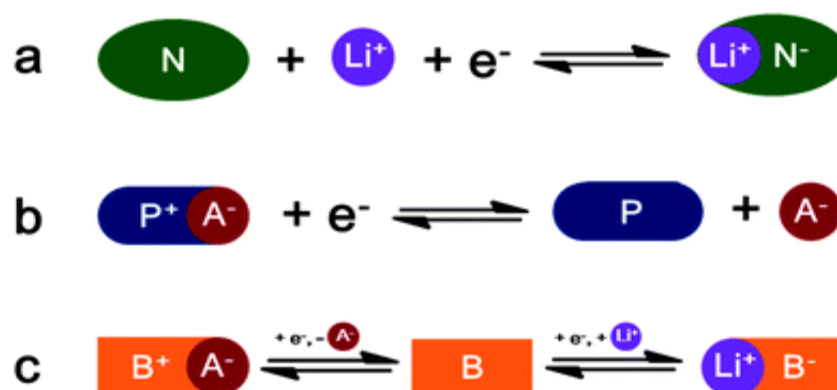


Figure 2.12. The redox reaction of three types of electroactive organics: (a) n-type; (b) p-type; (c) bipolar. A⁻ means anion of the electrolyte. Adapted with permission.^[163] Copyright © 2008 Royal Society of Chemistry.

2.2.1.1. N-type materials

Carbonyl-based compounds are the most extensively studied organic cathodes due to their high theoretical capacities, fast redox kinetics, and structural tunability. Each C=O group typically

undergoes one-electron reversible redox process via enolization. A representative example is 1,4-benzoquinone (1,4-BQ), which has a theoretical capacity of 496 mAh g^{-1} at $\sim 2.7 \text{ V}$ vs. Li/Li^+ . A notable subclass is polyanionic aromatic systems such as perylene tetracarboxylates, which can accommodate more Li^+ than predicted by stoichiometric redox counts (overlithiation), enabling exceptionally high capacities.

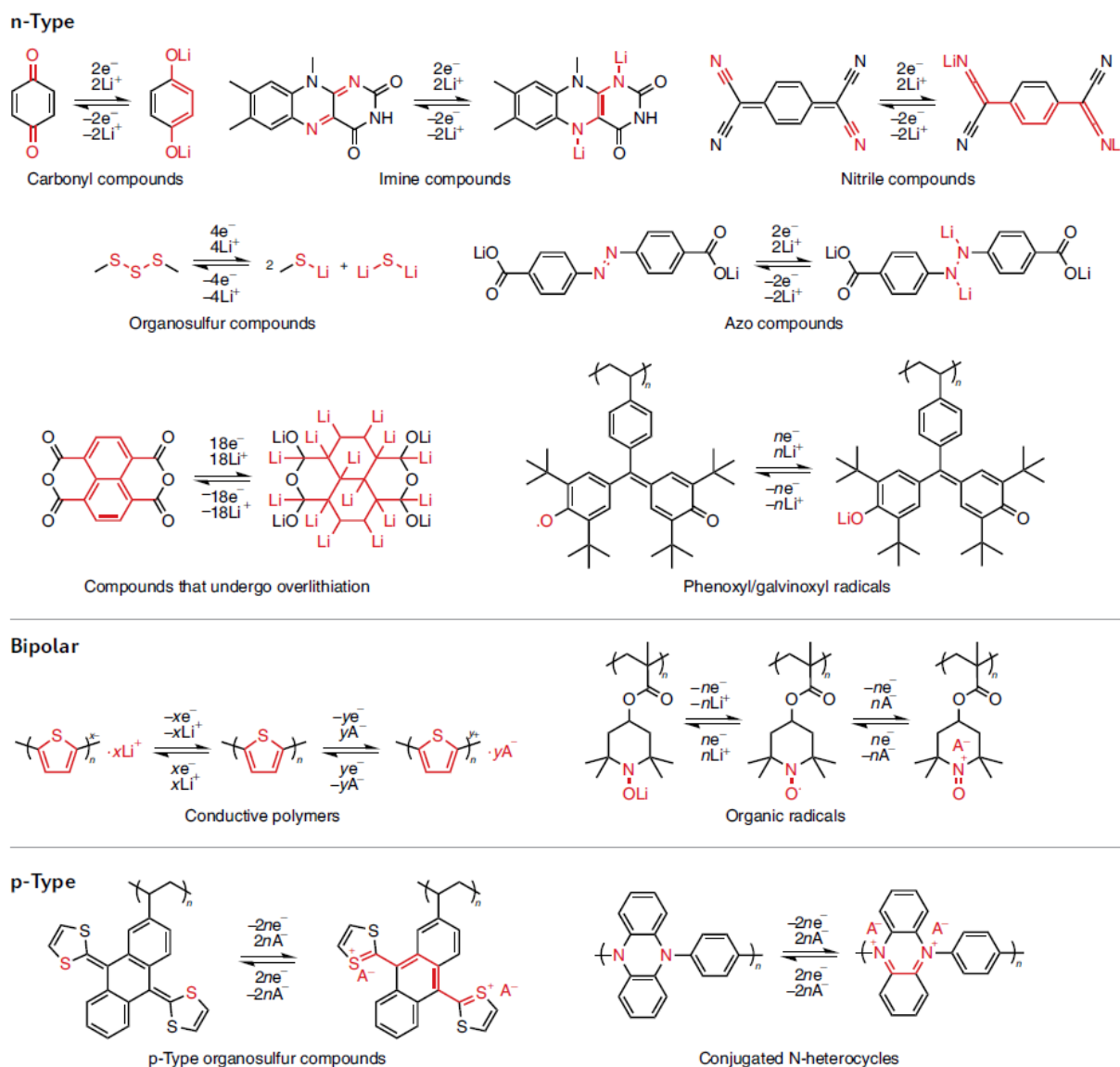


Figure 2.13. Categories of organic battery-electrode materials and their redox chemistry. Adapted with permission.^[18] Copyright © 2020 Springer Nature.

Imine- and nitrile-containing n-type systems also display high capacities. For example, tailored pteridine derivatives with alloxazinic redox centers exhibit reversible tautomerism during cycling and deliver outstanding performance, achieving up to 533 Wh kg^{-1} within 1 h and excellent cyclability with 96% capacity retention after 500 cycles at 10 A g^{-1} .^[164] Another

representative is triquinoxalinylene (3Q), composed of three pyrazine units, which undergoes a six-electron redox process to deliver 395 mAh g⁻¹ at 1 C with excellent cycling stability.^[165] Incorporation of conjugated linkers, such as cyanovinylene, further improves electrochemical stability, although the higher molecular weight can reduce specific capacity.^[166] In addition, nitrile-based systems have been explored, where the C=C-C≡N conjugation acts as the active redox motif in certain structures such as poly(etracyano-9,10-anthraquinonedimethane) (PTCAQ).^[167] A highly reversible two-electron process enables PTCAQ-Li cells to deliver 156 mAh g⁻¹ with excellent retention of 88% after 500 cycles, high material utilization of 97%, and superior CE of 99%.

Organosulfur compounds with n-type behavior store charge through reversible cleavage and reformation of S-S bonds. Early examples, such as tetraethylthiuram disulfide (TETD),^[168] exhibits low utilization due to sluggish kinetics, while polymeric structures such as poly(2,5-dimercapto-1,3,4-thiadiazole) (PDMcT) and the side-chain disulfide polymer, poly(5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracene) (PDTTA), achieve higher practical capacities of up to 422 mAh g⁻¹.^[169,170]

Azo compounds can store two Li⁺ ions per N=N bond, enabling multi-electron transfer. A modified azobenzene (AB), azobenzene-4,4'-dicarboxylic acid lithium salt (ADALS), delivers an initial capacity of 190 mAh g⁻¹ at 0.5 C (corresponding to current density of 95 mA g⁻¹).^[38] However, their operating voltages (1.25–1.47 V) are relatively low compared to conventional inorganic cathodes.

Nitroaromatic compounds, such as dinitrobenzene (DNB) isomers, undergo multi-electron reductions at high voltages and deliver capacities of 450–535 mA g⁻¹ within 1.5–3.8 V. Confinement of *p*-DNB within carbon nanospheres further increases the capacity to 620 mA g⁻¹ in LIBs and enhances both rate performance and cycling stability.^[35]

Radical polymers containing nitroxide or galvinoxyl side groups also classified as n-type systems. For instance, polygalvinoxylstyrene (PGVS) displays a discharge plateau at 3.15V versus Li/Li⁺, originating from the fast and reversible redox of the galvinoxyl/galvinolate couple.^[171] However, the specific capacity of PGVS remains relatively low (~40–50 mA g⁻¹), as the redox is limited to single-electron processes on pendant radical sites, which constrains its practical energy density despite the excellent cycling stability.

2.2.1.2. Bipolar materials

Bipolar organic cathodes undergo both oxidation and reduction, allowing wider voltage ranges and multi-electron redox reactions. Conducting polymers, such as polythiophene (PTh),^[172] polyacetylene (PAC),^[173] and poly(p-phenylene) (PPP),^[174] store charge through doping/de-doping of both anions and cations, depending on the potential. Their intrinsic π -conjugated structures provide electronic conductivity, but practical capacities are often lower than theoretical predictions due to limited doping levels and sloping charge–discharge profiles.

A nitroxide radical can be reversibly n-doped to an aminoxy anion or p-doped to an oxoammonium cation in cathodic or anodic reactions, respectively. The most prominent example is 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), which has a low molecular weight of 156.2 g mol⁻¹ and fully localized unpaired electrons. Poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA) is the most studied TEMPO-functionalized polymer due to its theoretical specific capacity of 111 mAh g⁻¹, corresponding to a one-electron transfer per unit, and an attractive discharge potential of 3.5 V vs. Li/Li⁺ at low rates.^[175] About 70% of the theoretical capacity is obtained and remains nearly unchanged even at a high current density of 12 C. However, low intrinsic conductivity, slow reaction kinetics, high solubility in electrolyte, and practical capacity limitations imposed by high molecular weight and single-electron redox still need to be addressed through structural design and synthetic optimization.

2.2.1.3. P-type materials

P-type cathodes operate via oxidation during discharge, accepting anions from the electrolyte. P-type organosulfur polymers, such as poly(2-phenyl-1,3-dithiolane), combine high doping levels with stable cycling performance, retaining over 95% of the theoretical capacity during the first 20 cycles.^[176] Conjugated N-heterocycles such as triphenylamine derivatives, poly(N-vinylcarbazole) (PVK), phenothiazine, and phenazine derivatives exhibit high redox potentials (3.4–3.8 V vs. Li/Li⁺) and excellent cycling stability. PVK delivers 125 mAh g⁻¹ at 3.7 V with 93.6% retention after 50 cycles, while phenothiazine polymer (P1a) retains 97% of its initial capacity after 30000 cycles at 100C. A phenazine derivative, 5-phenyl-10-(4-(phenylthio)phenyl)-5,10-dihydrophenazine oligomer (p-DPPZS), enables two-electron transfer per repeat unit, leading to increased specific capacities.^[177–182]

2.2.2. Challenges of OCMs

Organic electrode materials, despite their tunable structures and sustainability advantages, face

intrinsic limitations that hinder their practical deployment in LIBs. One of the most fundamental challenges is their inherently low mass density compared to conventional inorganic cathodes. While inorganic layered oxides such as LiCoO_2 possess densities around 5.0 g cm^{-3} , typical organic materials often exhibit densities below 2.0 g cm^{-3} .^[28] This large disparity directly limits the achievable volumetric energy density, even when gravimetric capacity is competitive. For example, conjugated microporous polymers (CMPs) and covalent organic frameworks (COFs) benefit from high surface areas and tailored redox-active sites, but their highly porous, low-density frameworks result in volumetric energy densities far below those of commercial inorganic systems, making electrode-level energy optimization more challenging.^[183,184]

Another critical limitation is the intrinsically low electronic conductivity of most organic redox systems, typically several orders of magnitude lower than those of transition-metal-based cathodes. As a result, sluggish electron transport within the active phase not only restricts power capability and utilization of theoretical capacity but also causes pronounced polarization and poor rate performance.^[185]

A major obstacle for OCMs is their high solubility in conventional electrolytes, which leads to continuous loss of active species and rapid capacity fading. Quinones, for example 1,4-BQ, possess a high theoretical capacity of 496 mAh g^{-1} but dissolve readily in carbonate electrolytes, causing a sharp decline in performance after only a few cycles.^[186] Nitroaromatic compounds such as DNB isomers can initially deliver capacities above 500 mAh g^{-1} , yet both the reactants and discharge products dissolve progressively, disrupting the electrode structure and accelerating capacity decay.^[35] This dissolution is particularly problematic for small molecules, which lack the structural confinement and intermolecular interactions required for stability. Once dissolved, active species migrate from the cathode into the electrolyte and eventually to the anode, where they participate in side reactions that degrade the electrode interface. In addition, a shuttle effect may occur, wherein oxidized species diffuse to the anode, undergo reduction, and subsequently return to the cathode for reoxidation. This repeated process decreases CE, accelerates capacity fading, and undermines anode stability.^[187] Addressing this issue is therefore essential for enabling the commercial application of organic cathode materials in LIBs.

2.3. Strategies to address the issues of OCMs

To overcome the intrinsic limitations of OCMs, including their high solubility in conventional electrolytes, intrinsically low electronic conductivity, and pronounced structural changes during

cycling, intensive efforts have been devoted to rational design at the molecular, electrode, and electrolyte levels. Broadly, these approaches can be categorized into three major strategies: (i) molecular design, aiming to stabilize redox centers through functional-group engineering, polymerization, or structural confinement; (ii) electrode and separator modifications, focusing on conductive frameworks, protective coatings, and interfacial engineering to suppress dissolution and enhance charge transport; and (iii) electrolyte engineering, where optimized liquid electrolytes, GPEs, and SSEs are developed to stabilize interfaces and eliminate dissolution pathways. Together, these strategies provide complementary routes toward enabling stable, high-energy-density organic rechargeable batteries.

2.3.1. Molecular design of OCMs

2.3.1.1. Oligomerization and polymerization

A straightforward strategy to address the dissolution of small organic molecules is to enlarge them into oligomers, polymers, or ordered frameworks. This molecular enlargement lowers their solubility in electrolytes, and as a result, the redox-active sites are retained within the cathode, preserving active mass and electrode integrity during long-term cycling. Representative examples are summarized in [Table 2.2](#).

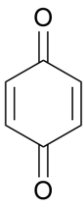
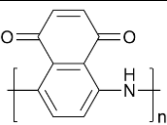
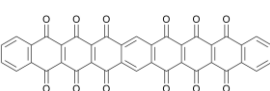
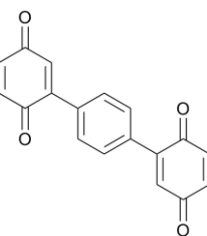
Carbonyl compounds provide a representative case for illustrating the dissolution issue and corresponding design strategies. Small quinones such as 1,4-BQ deliver a high theoretical capacity of 496 mAh g^{-1} with an average discharge voltage of $\sim 2.7 \text{ V}$ versus Li/Li^+ , but suffer from rapid dissolution in carbonate electrolytes.^[186] In contrast, polymeric quinones such as poly(5-amino-1,4-naphthoquinone) (PANQ) exhibit relatively stable cycling and high capacities.^[188] Molecular enlargement has also been pursued by designing extended quinone structures. For instance, nonylbenzo-hexaquinone (NBHQ) adopts a larger fused-quinone structure to improve cyclability, but its practical capacity of 162 mAh g^{-1} remains far below the theoretical value of 489 mAh g^{-1} , indicating incomplete utilization of carbonyl groups.^[189,190] In contrast, 1,4-bis(*p*-benzoquinonyl)benzene (BBQB) demonstrates nearly full carbonyl utilization with an initial capacity of 367 mAh g^{-1} , and its enhanced molecular planarity significantly improves stability, enabling 306 mAh g^{-1} to be retained after 100 cycles.^[191]

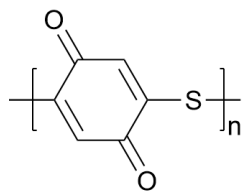
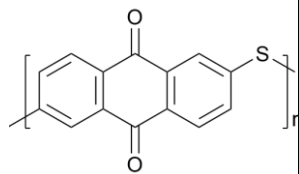
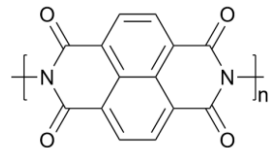
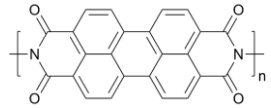
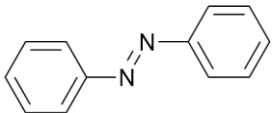
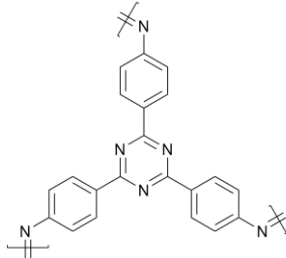
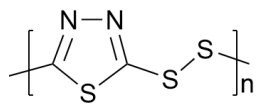
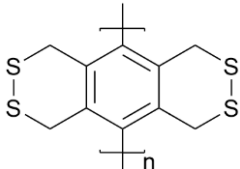
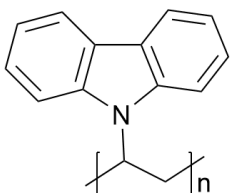
Beyond simple polymerization to curb solubility, thioether-bridged poly(benzoquinonyl sulfide) (PBQS) and poly(2,6-anthraquinonyl sulfide) (PAQS) connect carbonyl units through C–S linkages.^[192,193] These backbones sustain practical capacities while keeping voltage hysteresis

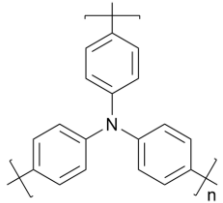
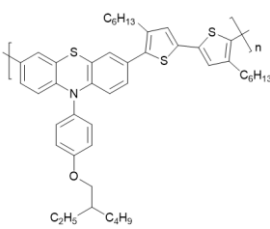
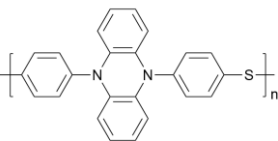
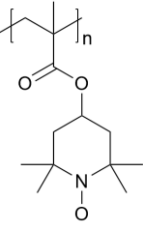
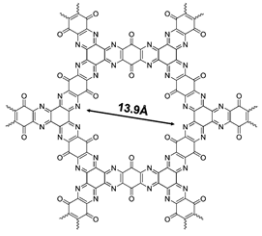
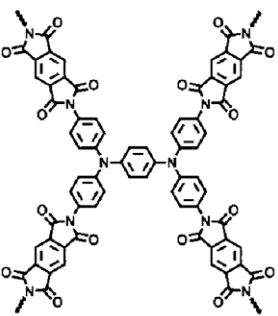
modest. Imide linkages provide another complementary backbone solution. Polyimides derived from and naphthalene- or perylene-tetracarboxylic dianhydrides (PI-1, PI-2) place two carbonyls per repeat unit and enforce planarity through the imide ring.^[29,30] The imide bond fixes the geometry and improves intrachain electronic coupling, which helps maintain stable cyclic capacities and output voltages.

In addition to carbonyl-based compounds, small azo molecules such as AB also dissolve easily during cycling, resulting in poor stability.^[36] By contrast, constructing an azo-linked covalent triazine framework (Azo-CTF) immobilizes the azo units within a rigid π -conjugated porous backbone, greatly suppressing dissolution and enabling stable long-term cycling with improved rate performance.^[194]

Table 2.2. Electrochemical performance of representative OCMs improved by oligomerization and polymerization.

OCM	Structure	Theoretical and practical capacities (mAh g ⁻¹)	Output voltage (V)	Cycling stability: retention, cycles, rate or current density	Ref.
1,4-BQ		496, 440@50 mA g ⁻¹	2.7	11%, 50 th , 50 mA g ⁻¹	[186]
PANQ		290, 256@20 mA g ⁻¹	2.6	78%, 17 th , 20 mA g ⁻¹	154
NBHQ		489, 162@7 mA g ⁻¹	2.7	74%, 300 th , 0.25 C	[189]
BBQB		370, 367@0.1 C	2.61	83%, 100 th , 0.1 C	[191]

PBQS		388, 275@50 mA g ⁻¹	2.67	86%, 1000 th , 500 mA g ⁻¹	[192]
PAQS		225, 146@100 mA g ⁻¹	2.11	99%, 100 th , 100 mA g ⁻¹	[193]
PI-1		203, 202@0.2 C	2.35	91%, 50 th , 0.2 C	[29]
PI-2		128, 130@0.4 C	2.35	85%, 50 th , 25 mA g ⁻¹	[195]
AB		294, 185@0.5 C	2.2	40%, 20 th , 0.5 C	[36]
Azo-CTF		231, 206@100mA g ⁻¹	1.9	87.6%, 2000 th , 300 mA g ⁻¹	[194]
PDMcT		362, 130@20 mA g ⁻¹	2.7	31%, 3 rd , 20 mA g ⁻¹	[196]
PDTTA		471, 422@30 mA g ⁻¹	2.6	40%, 44 th , 30 mA g ⁻¹	[170]
PVK		139, 125@20 mA g ⁻¹	3.7	94%, 50 th , 20 mA g ⁻¹	[180]

PTPAn		109, 103@0.5 C	3.8	92%, 1000 th , 20C	[177]
P1a		36, 34@1 C	3.68	100%, 2200 th , 10C	[182]
p-DPPZS		147, 133@1 C	3.6	90%, 1000 th , 5C	[197]
PTMA		111, 77@10 mA g ⁻¹	3.5	91%, 500 th , 100 mA g ⁻¹	[175]
BQ1-COF		773, 502@0.05C	2.06	81%, 1000 th , 1.54 A g ⁻¹	[184]
TPDA-PMDA		192, 178@0.5 A g ⁻¹	3.76	76%, 1800 th , 5 A g ⁻¹	[198]

Moreover, in organosulfur electrodes, in addition to stabilization achieved by polymerization, the durability of the polymer critically depends on the placement of the S–S bonds. When embedded in the main chain (e.g., PDMcT), bond cleavage breaks the backbone and compromises cycling stability, whereas side-chain configurations (e.g., PDTTA) preserve the polymer framework during redox and thus maintain structural integrity and long-term

performance.^[170,196]

P-type and radical systems follow the same principle that polymerization suppresses dissolution while backbone chemistry governs redox behavior. Representative examples include PVK,^[180] polytriphenylamine (PTPAn),^[177–179] and P1a,^[182] which benefit from rigid conjugated backbones that stabilize oxidized states and enable long-term cycling; phenazine-based short oligomers such as p-DPPZS,^[197] which combine oligomerization with dense packing to enhance volumetric capacity; and radical polymers such as PTMA,^[175] where backbone design determines the spacing and coupling of fast redox centers. Extending this concept to the lattice level, COFs (e.g., BQ1-COF, TPDA-PMDA) embed redox units into ordered porous backbones, tuning band structures and ion pathways.^[199] Altogether, these systems demonstrate that molecular enlargement and backbone engineering act in synergy to achieve stable, high-rate, and high-density organic cathodes.

2.3.1.2. Salt formation

Salt formation represents an effective molecular strategy to improve the electrochemical stability of ionizable organic cathode materials. Many redox-active organic compounds contain acidic functional groups such as carboxylic acids, phenolic hydroxyls, or other ionizable moieties that can be deprotonated and converted into alkali metal salts, most commonly lithium salts. The advantages of this approach can be summarized as follows:

Environmental and thermal stability. The thermal stability of lithiated organic cathode materials is of critical importance, since thermal instability often triggers severe side reactions and even gas release, directly compromising battery safety in practical applications. Benefiting from the strong ionic interactions of Li–O bonds, lithiated materials generally exhibit much higher decomposition temperatures than their protonated counterparts. In inert atmospheres, the thermal decomposition temperatures of lithiated organic cathodes are usually above 300 °C.^[200–203] For instance, thermogravimetric analysis (TGA) measurements demonstrate that H₂-Mn-*p*-DHT-MOF decomposes around 250 °C, whereas its lithiated analogue Li₂-Mn-*p*-DHT-MOF remains stable up to 500 °C.^[203] Similarly, lithium tetracyanoquinodimethane (Li-TCNQ) decomposes at 380 °C under N₂, much higher than the 200 °C decomposition of neutral TCNQ.^[201]

Operating voltage. The redox potential of lithiated OCMs can be effectively tuned by introducing electron-withdrawing substituents, high-ionic-potential spectator cations, or

positional substitution. Using dilithium (2,5-dilithium-oxy)-terephthalate ($\text{Li}_4\text{-}p\text{-DHT}$) as an example, which exhibits an average discharge voltage of ~ 2.6 V vs. Li^+Li .^[204,205] Replacing the two $-\text{COOLi}$ groups with stronger electron-withdrawing $-\text{SO}_3\text{Li}$ substituents yields tetralithium 2,5-dihydroxy-1,4-benzenedisulfonate ($\text{Li}_4\text{-}p\text{-DHBDS}$), which displays an increased operating voltage of 3.1 V.^[206] Substituting Li^+ at the carboxylate sites with cations of higher ionic potential, such as Mn^{2+} ($\text{Mn}(\text{Li}_2)\text{-}p\text{-DHT}$) and Mg^{2+} ($\text{Mg}(\text{Li}_2)\text{-}p\text{-DHT}$), further elevates the discharge plateau to 3.2 V and 3.4 V, respectively.^[200,203] Moreover, positional modification also influences the redox potential: switching $-\text{OLi}$ from the para to the ortho position ($\text{Li}_4\text{-}o\text{-DHT}$) leads to a ~ 300 mV voltage gain relative to $\text{Li}_4\text{-}p\text{-DHT}$, which is attributed to spatial modulation of the electronic charge distribution.^[207]

Cycling stability. The cycling stability of lithiated OCMs improves because salt formation enhances lattice energy, thereby lowering solubility in aprotic electrolytes and suppresses active-material loss. In addition, the prelithiated state mitigates initial irreversible capacity loss by avoiding *in situ* deprotonation and lithiation of functional groups during the first discharge, thereby reducing lithium consumption in side reactions and improving initial CE. Representative examples from carbonyl-based systems that have been intensively studied are highlighted and summarized in [Figure 2.14](#).^[200,204,206–213]

One of the clearest demonstrations comes from lithium-carboxylated quinones. Shimizu et al. introduced $-\text{COOLi}$ groups into anthraquinone (AQ), phenanthrenequinone (PQ), and pyrene-4,5,9,10-tetraone (PYT), rendering LCAQ, LCPQ and LCPYT, respectively. This modification significantly improves capacity retention compared to the neutral molecules, while leaving redox potentials nearly unchanged. After 20 cycles, the lithiated derivatives retain 82–105% of their initial capacities, whereas the protonated analogues decay to only 25–28%, with LCPYT delivering the most balanced performance in terms of capacity and stability ([Figure 2.14a](#)).^[209]

Another representative system is lithium rhodizonate ($\text{Li}_x\text{C}_6\text{O}_6$). In the intermediate range of $2 \leq x \leq 4$, severe microstructural changes lead to particle dissolution and detachment, accelerating fading. To circumvent this, the pre-synthesized $\text{Li}_4\text{C}_6\text{O}_6$ salt was employed as the active cathode, showing highly reversible cycling with $200\text{--}300$ mAh g^{-1} maintained over extended operation at ~ 1.8 V ([Figure 2.14b](#)).^[211,212]

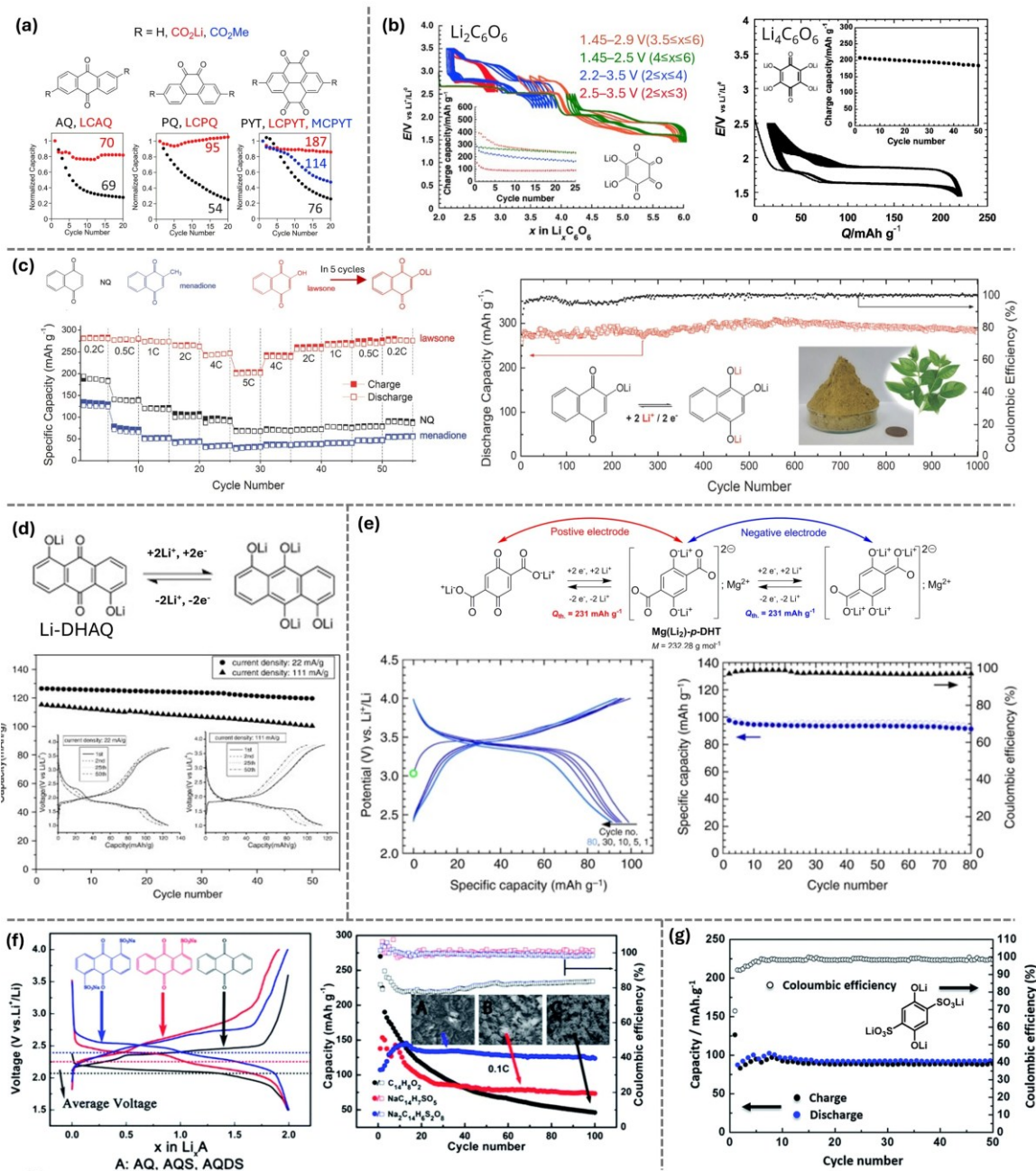


Figure 2.14. Electrochemical performance of representative modified by salt formation. (a) Normalized cycling performance of quinone derivatives at 0.2 C-rate, with the specific capacity values at the 20th cycle indicated in mAh g⁻¹. Adapted with permission.^[209] Copyright © 2014 Elsevier. (b) Potential versus composition profile, GCD curves and cycle performance of Li_xC₆O₆ at a rate of 1 Li⁺/10 h. Adapted with permission.^[211,212] Copyright © 2009 American Chemical Society. (c) Rate performance of lawsone compared with NQ and menadione, along with its long cycle performance at 0.5 C-rate. Adapted with permission.^[213] Copyright © 2017 John Wiley and Sons. (d) The discharge capacity retention and GCD curves of Li-DHAQ. Adapted with permission.^[208] Copyright © 2010 Elsevier. (e) GCD curves and cycling performance of Mg(Li₂)-p-DHT electrode material in a Li half-cell at a rate of 1 Li⁺/5 h (I = 23 mA g⁻¹) in 1 M LiPF₆ in EC/DMC as the electrolyte.^[200] (f) Typical charge/discharge curves

and cycle performance of AQ, AQS, and AQDS electrodes cycled at 0.1 C-rate. Adapted with permission.^[210] Copyright © 2014 Royal Society of Chemistry. (g) The capacity retention and the CE plots of a Li half-cell using Li₄-*p*-DHBDS·2DMF as the positive electrode material galvanostatically cycled in EC–DMC/LiPF₆ 1 M at a rate of 1 Li⁺/10 h (C/20, *I* = 6.08 mA g⁻¹). Adapted with permission.^[206] Copyright © 2018 Royal Society of Chemistry.

Natural quinones also benefit from salt formation. Lithiated lawsone delivers nearly its full theoretical capacity of 280 mAh g⁻¹ with 99% retention after 1000 cycles at 0.5 C, outperforming 1,4-naphthoquinone (NQ) and menadione derivatives (Figure 2.14c).^[213] Likewise, lithiated 1,5-dihydroxyanthraquinone (Li-DHAQ) stabilized by –OLi groups exhibits improved cycle life compared to its neutral analogue (Figure 2.14d).^[208] In more complex architectures, Mg(Li₂)-*p*-DHT combines voltage enhancement with long-term cycling stability (Figure 2.14e).^[200] Finally, sulfonated salts such as anthraquinone-1,5-disulfonic acid (AQDS) and Li₄-*p*-DHBDS also demonstrate excellent stability by coupling ionic anchoring with dissolution suppression (Figure 2.14f,g).^[206,210]

Overall, salt formation provides a general and effective route to stabilize ionizable organic cathode materials. By converting functional groups such as –COOH or –OH into lithium salts, thermal stability is enhanced, redox potentials can be tuned through substituents or spectator cations, and dissolution is effectively suppressed. These combined effects minimize irreversible lithium consumption and lead to markedly improved cycling stability, as demonstrated across diverse carbonyl, rhodizonate, natural quinone, and sulfonated systems.

2.3.2. Electrode/separator modification

2.3.2.1. Carbon coupling strategies on electrode materials

As mentioned in Section 2.2.2, the intrinsically low electronic conductivity and high solubility of most small organic molecules in liquid electrolytes result in poor rate capability and rapid capacity fading. To simultaneously address these two critical issues, coupling organic electrodes with conductive carbon substrates such as carbon fibers, CNTs, graphene, and porous carbon has proved to be an effective strategy, as the carbon framework both enhances electron transport and suppresses dissolution through physical confinement or chemical immobilization. The integration of organics with carbon can generally be divided into three categories: i) noncovalent physical composites, where interactions such as van der Waals forces, π – π stacking, and pore confinement dominate; ii) covalent grafting, where chemical bonds tether the redox-active molecules directly to the carbon surface; and iii) carbonous coating on electrodes,

wherein a thin carbon layer is applied to the organic electrode particles to improve conductivity and suppress dissolution.

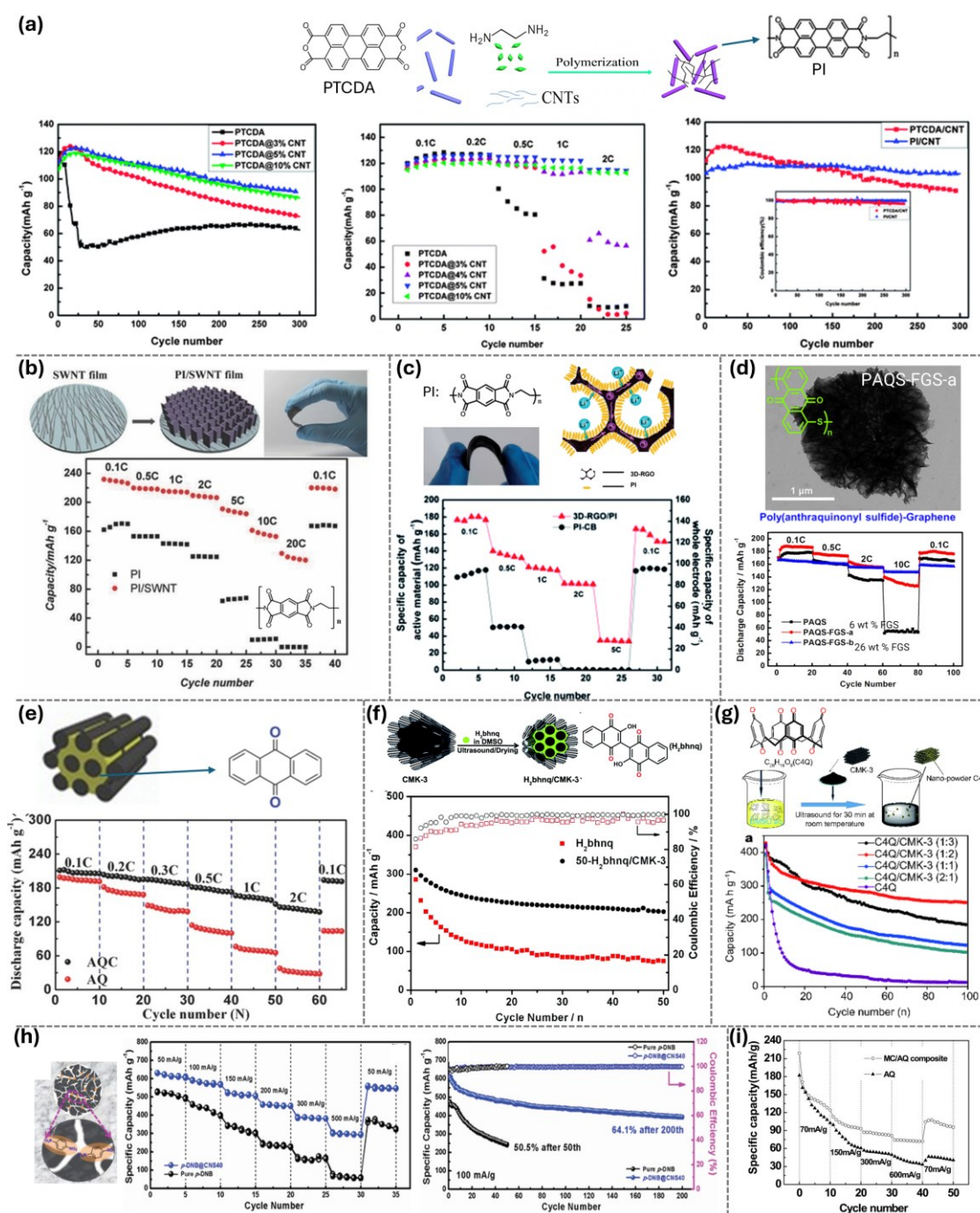


Figure 2.15. Electrochemical performance of representative non-covalent carbon-organic composites. (a) Cycling and rate performance of PTCDA and PTCDA/CNT at 100 mA g⁻¹ (1.5–4.3 V, inset: CE). Adapted with permission.^[214] Copyright © 2013 Royal Society of Chemistry. (b) Rate performance of PI and PI/SWNT. Adapted with permission.^[215] Copyright © 2014 John Wiley and Sons. (c) Rate capability of 3D-RGO/PI vs. PI-CB. Adapted with permission.^[216] Copyright © 2014 Royal Society of Chemistry. (d) Rate performance of PAQS and PAQS/FGS composites (1.5–3.5 V, 1 C = 225 mA g⁻¹). Adapted with permission.^[217] Copyright © 2012

American Chemical Society. (e) Rate performance of AQ/CMK-3 vs. AQ.^[218] (f) Cycling and CE of H₂bhnq/CMK-3 vs. H₂bhnq at a rate of 0.1 C. Adapted with permission.^[219] Copyright © 2014 Royal Society of Chemistry. (g) Cycling performance of C4Q/CMK-3 vs. C4Q at 0.1 C. Adapted with permission.^[220] Copyright © 2018 Springer Nature. (h) Rate and cycling stability of *p*-DNB@CNS40 vs. *p*-DNB. Adapted with permission.^[35] Copyright © 2020 John Wiley and Sons. (i) Rate performance of MC/AQ vs. AQ at varied current densities. Adapted with permission.^[221] Copyright © 2011 IOP Publishing.

Noncovalent physical composites. In such systems, soluble small-molecule organics are stabilized by physical confinement within conductive carbon frameworks without forming covalent bonds, thereby simultaneously providing two key functions: a continuous electron pathway and steric/adsorptive confinement that mitigates molecular leaching. CNT networks supply both conductive highways and mechanical integrity. For instance, 3,4,9,10-perylenetetracarboxylic dianhydride/CNT (PTCDA/CNT) nanocomposites prepared by mixing in ethanol shows markedly improved electrochemical performance compared with pristine PTCDA ([Figure 2.15a](#)).^[214] The composite delivers a much higher rate capability, with the discharge capacity at 2 C increasing from only 10 mAh g⁻¹ for pure PTCDA to 115 mAh g⁻¹ for PTCDA/CNT. When the composite was further subjected to *in situ* polymerization with ethylenediamine, the resulting poly(3,4,9,10-perylenetetracarboxylic dianhydride ethylene diamine)/CNT (PI/CNT) demonstrates superior long-term stability, retaining 93% of its initial capacity after 300 cycles at 100 mA g⁻¹, in contrast to 74% for PTCDA/CNT. Another notable system involves the growth of polyimide nanoflakes on SWCNT films, yielding flexible PI/SWNT electrodes ([Figure 2.15b](#)).^[215] This freestanding design exhibited both high specific capacity and outstanding rate capability in liquid electrolytes, while maintaining mechanical flexibility.

Graphene-based composites constitute another important class of noncovalent carbon hybrids, where the two-dimensional conductive network and strong π - π interactions with conjugated organics contribute to enhanced performance. A representative case is the three-dimensional reduced graphene oxide/polyimide (3D-RGO/PI) film electrode, in which polyimide was polymerized *in situ* within a porous graphene framework ([Figure 2.15c](#)).^[216] The resulting binder-free electrode contains up to 80 wt% active material and shows excellent electrochemical properties, delivering 175 mAh g⁻¹ at 0.1 C and retaining 101 mAh g⁻¹ even at 2 C, compared with a conventional PI-carbon black electrode that loses most of its capacity under high rates. Furthermore, the 3D-RGO/PI film maintains 82% of its initial capacity after

150 cycles at 0.5 C, demonstrating the critical role of graphene networks in facilitating electron transport and ensuring intimate contact with the active phase. Another example is the PAQS/functionalized graphene sheet (PAQS-FGS) composite, which exhibits enhanced utilization and ultrafast rate capability (Figure 2.15d).^[217] The composite delivers reversible capacities of 187 and 165 mAh g⁻¹ at 0.1 C for 6 and 26 wt% graphene content, respectively, corresponding to utilization ratios of 88–95% relative to the theoretical capacity of PAQS. Importantly, the 26 wt% PAQS-FGS composite retains 90% of its low-rate capacity even at 10 C and could still deliver 100 mAh g⁻¹ within only 16 s (≈ 200 C). These results highlight that graphene frameworks not only suppress dissolution but also provide highly efficient electron pathways, enabling organic cathodes to achieve both high energy and high power densities.

Porous carbons, including ordered mesoporous carbons (e.g., CMK-3) and spherical carbons (e.g., hollow carbon spheres and carbon nanospheres), provide interconnected conductive frameworks and well-defined pore structures that are highly effective for stabilizing small organic molecules in liquid electrolytes. The uniform channels and large surface area of CMK-3 enable efficient nanoconfinement of quinones and related molecules. For instance, as shown in Figure 2.15e, an AQ/CMK-3 (AQC) nanocomposite delivers an initial capacity of 205 mAh g⁻¹ at 0.2 C and still maintains 146 mAh g⁻¹ at 2 C, far exceeding the bare AQ electrode (38 mAh g⁻¹).^[218] Another representative case is the encapsulation of 2,2'-bis(3-hydroxy-1,4-naphthoquinone) (H₂bhnq) into CMK-3 pores, which exhibits an initial capacity of 309 mAh g⁻¹ at 0.1 C and maintains 203 mAh g⁻¹ after 50 cycles, while the neat molecule suffers rapid fading; even at 10 C, the composite delivers 124 mAh g⁻¹ (Figure 2.15f).^[219] In a third study, calix[4]quinone (C4Q) confined in CMK-3 at an optimized 1:2 ratio shows the best performance, with an initial discharge capacity of 427 mAh g⁻¹, 59% retention after 100 cycles, and a rate capacity of 170 mAh g⁻¹ at 1 C (Figure 2.15g).^[220] Spherical porous carbons are also effective. For instance, *p*-DNB encapsulated in microporous carbon nanospheres (CNS40), denoted as *p*-DNB@CNS40, delivers 570 mAh g⁻¹ at 100 mA g⁻¹ compared to only 56 mAh g⁻¹ for bare *p*-DNB, and retains 64% of its capacity after 200 cycles versus 50% retention for *p*-DNB after only 50 cycles (Figure 2.15h).^[35] Similarly, AQ confined in mesoporous carbons (MC) maintains 96 mAh g⁻¹ after 50 cycles at 68 mA g⁻¹, far exceeding the 40 mAh g⁻¹ of bare AQ, and shows less capacity loss when the current density was doubled, reflecting the strong confinement effect of MC (Figure 2.15i).^[221]

Covalent grafting. Covalent grafting is an effective strategy to anchor small organic molecules

onto conductive carbons, forming robust chemical bonds that suppress dissolution and enhance cycling stability. Unlike simple physical mixtures relying on weak van der Waals or π - π interactions, covalent linkages provide durable immobilization and mitigate the rapid capacity fading common in soluble quinones. A representative case is calix[4]arene quinone (CQ) covalently grafted onto activated carbon black (CBA) (Figure 2.16a). While physical mixtures of CQ with carbon black (CB+CQ) or activated carbon (CBA+CQ) shows rapid capacity fading, the covalently grafted composite (CBACQ) delivers markedly improved cycling stability, with the quinone redox plateau near 3 V remaining stable over repeated cycles.^[222] Another example is 9,10-phenanthrenequinone (PAQ) grafted onto Ketjenblack (KB) (Figure 2.16b). The resulting PAQ-KB composite achieves 75 mAh g⁻¹ at 30 mA g⁻¹, maintains 58 mAh g⁻¹ even at 1500 mA g⁻¹, and retains 71% of its initial capacity after 500 cycles, far outperforming unattached PAQ. Its high CE of 99.8% further demonstrates the durability imparted by covalent immobilization.^[223]

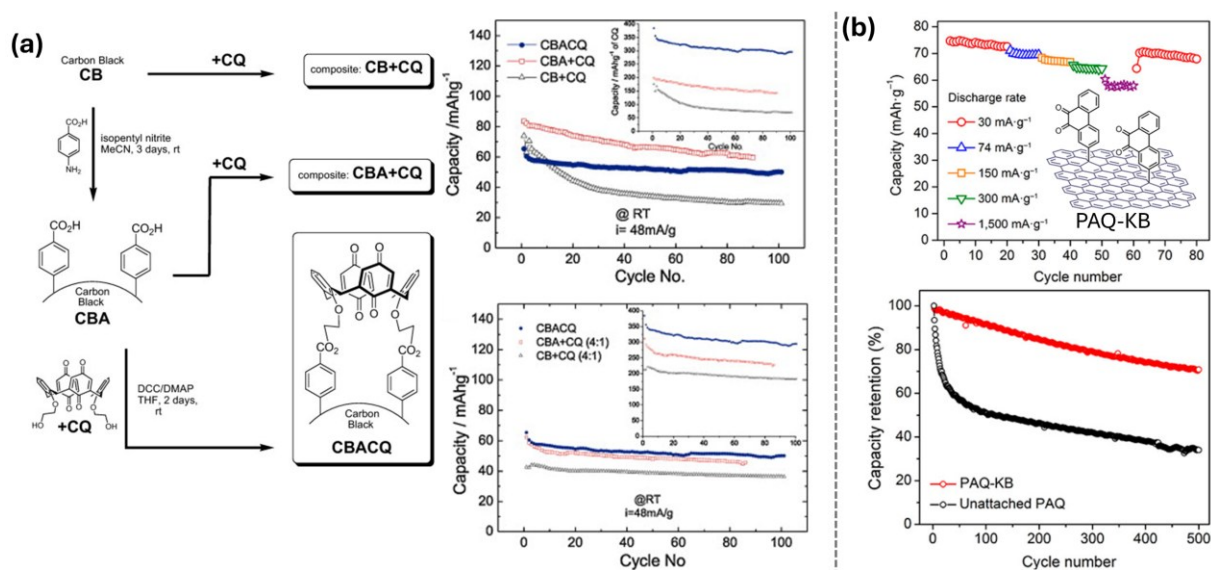


Figure 2.16. Electrochemical performance of representative covalent grafting composites. (a) Cycling performance of CQ in physical mixtures (CB+CQ, CBA+CQ) and covalently grafted on activated carbon black (CBACQ) between 2–4 V vs. Li/Li⁺ at 48 mA g⁻¹ (inset: capacities normalized to CQ content). Adapted with permission.^[222] Copyright © 2011 Elsevier. (b) Rate capability of PAQ-KB and cycling performance at 74 mA g⁻¹ compared with unattached PAQ. Adapted with permission.^[223] Copyright © 2015 American Chemical Society.

Carbonous coating on electrodes. Carbon coating represents another effective route to stabilize organic electrodes, in which a conformal conductive layer uniformly covers the particle surface, serving both as an electron-conducting medium and as a physical barrier that

suppresses dissolution in liquid electrolytes. A notable example is the use of graphdiyne (GDY) as a coating layer, synthesized through *in situ* growth on the surface of organic active particles via bottom-up polymerization of hexaethynylbenzene precursors. The GDY coating forms a porous and conductive network, which preserves fast Li^+ transport while strongly anchoring soluble molecules through π - π interactions. Benefiting from this structure, the GDY-coated PTCDA electrode (PTCDA@GDY) delivers higher reversible capacities at various current densities and greatly improved cycling stability compared to its uncoated counterpart, as shown in Figure 2.17a.^[224] Another representative case is porous lithium terephthalate ($\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$, PTAL) coated with N-doped carbon via chemical vapor deposition (CVD), as shown in Figure 2.17b. In this work, hollow PTAL microspheres prepared by spray drying were subjected to CVD treatment with urea as the nitrogen and carbon source, forming a uniform amorphous N-doped carbon layer of ~ 3 nm on the surface of each nanoparticle. The coating improves both cycling and rate performance. The optimized sample (PTALS6) maintains a reversible capacity of 150 mAh g^{-1} after 50 cycles at 0.5 C , far surpassing the 85 mAh g^{-1} retained by bulk PTAL at a much lower rate of 0.05 C . Electrochemical impedance spectroscopy further confirms that the coating reduced charge-transfer resistance and facilitated Li^+ diffusion, accounting for the superior rate capability.^[225]

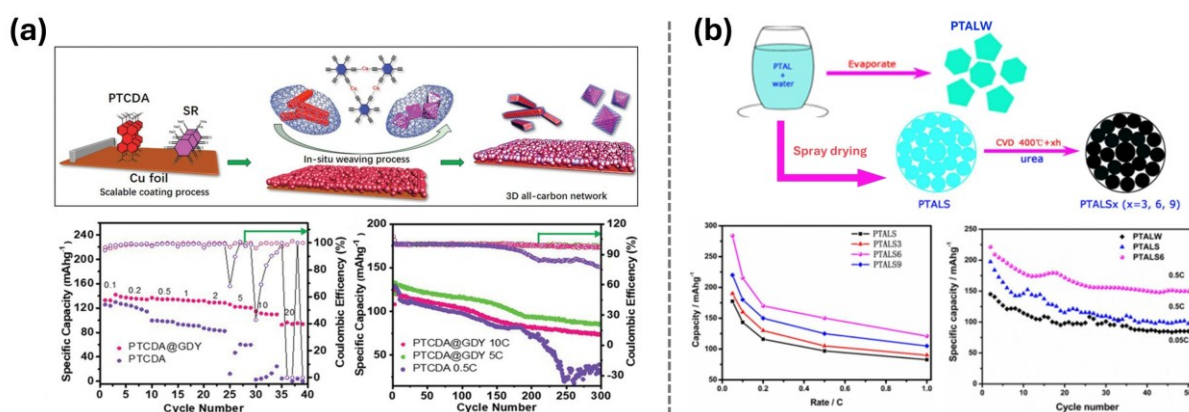


Figure 2.17. Electrochemical performance of representative carbonous coating strategies. (a) Schematic illustration of the *in situ* weaving of a GDY nanocoating to enhance the electrochemical performance of organic electrodes, together with the rate and cycling performance of PTCDA@GDY compared with bare PTCDA. Adapted with permission.^[224] Copyright © 2020 John Wiley and Sons. (b) Comparison of specific capacities of pristine PTALS and PTALSx ($x = 3, 6, 9$) with uniform N-doped carbon layers at various current rates, and the cycling performance of bulk PTALW, porous PTALS, and optimized PTALS6. Adapted with permission.^[225] Copyright © 2014 Royal Society of Chemistry.

In summary, integrating organics with carbon through physical composites, covalent grafting, or carbonous coatings effectively addresses the intrinsic conductivity and solubility issues of organic electrodes. These strategies suppress dissolution, enhance electron transport, and improve cycling stability and rate performance, thereby advancing the practical use of organic cathodes in LIBs.

2.3.2.2. Separator coatings and binder engineering

In addition to carbon compositing or surface modification of the electrodes themselves, engineering of separators and binders can also effectively enhance the cycling stability and rate capability of organic electrodes. Separator coatings mitigate shuttle effects by adsorbing and intercepting dissolved active species, while functional binders immobilize small molecules within the electrode and maintain structural integrity, thereby synergistically improving electrochemical performance.^[226–229]

Functional coatings on polymer separators have been shown to effectively suppress active-material crossover and enhance electrochemical stability with measurable improvements. For example, in Li–PTCDA cells using 1 M LiPF₆ in EC/DEC electrolyte, Kang et al. demonstrates that a CNT-coated Celgard separator retains 80% of its initial capacity after 100 cycles at 0.1 C, whereas the uncoated Celgard fails rapidly, with only 27% retention after 17 cycles ([Figure 2.18a](#)). Moreover, the coating thickness plays a decisive role: a 340 nm CNT layer (G-separator A) yields much better rate performance than both the bare separator and the thicker 640 nm layer (G-separator B).^[230] Similarly, a polypropylene (PP) separator coated with KB (C@PP) provides a physical barrier and strong adsorption capability against soluble quinones, enabling stable cycling of otherwise highly soluble cathodes ([Figure 2.18b](#)).^[231] Direct H-cell visualization confirms the suppression effect: while a PP separator allows quinone molecules to diffuse across the membrane within 12 h, turning the opposite chamber from colorless to yellow, the C@PP separator maintains only slight color change over the same period, indicating effective interception of shuttling species. With the C@PP separator, several quinone-based cathodes, including pentacene-5,7,12,14-tetrone (PT), C4Q, and AQ, achieve both high reversible capacity and durable cycling. Notably, PT delivers >300 mAh g⁻¹ with minimal fading (~0.06% per cycle over 400 cycles at 0.5 C) and excellent rate capability (retaining capacity even at 5 C), while C4Q provides high energy density of 782 Wh kg⁻¹ and retained ~60% of its capacity after 500 cycles.

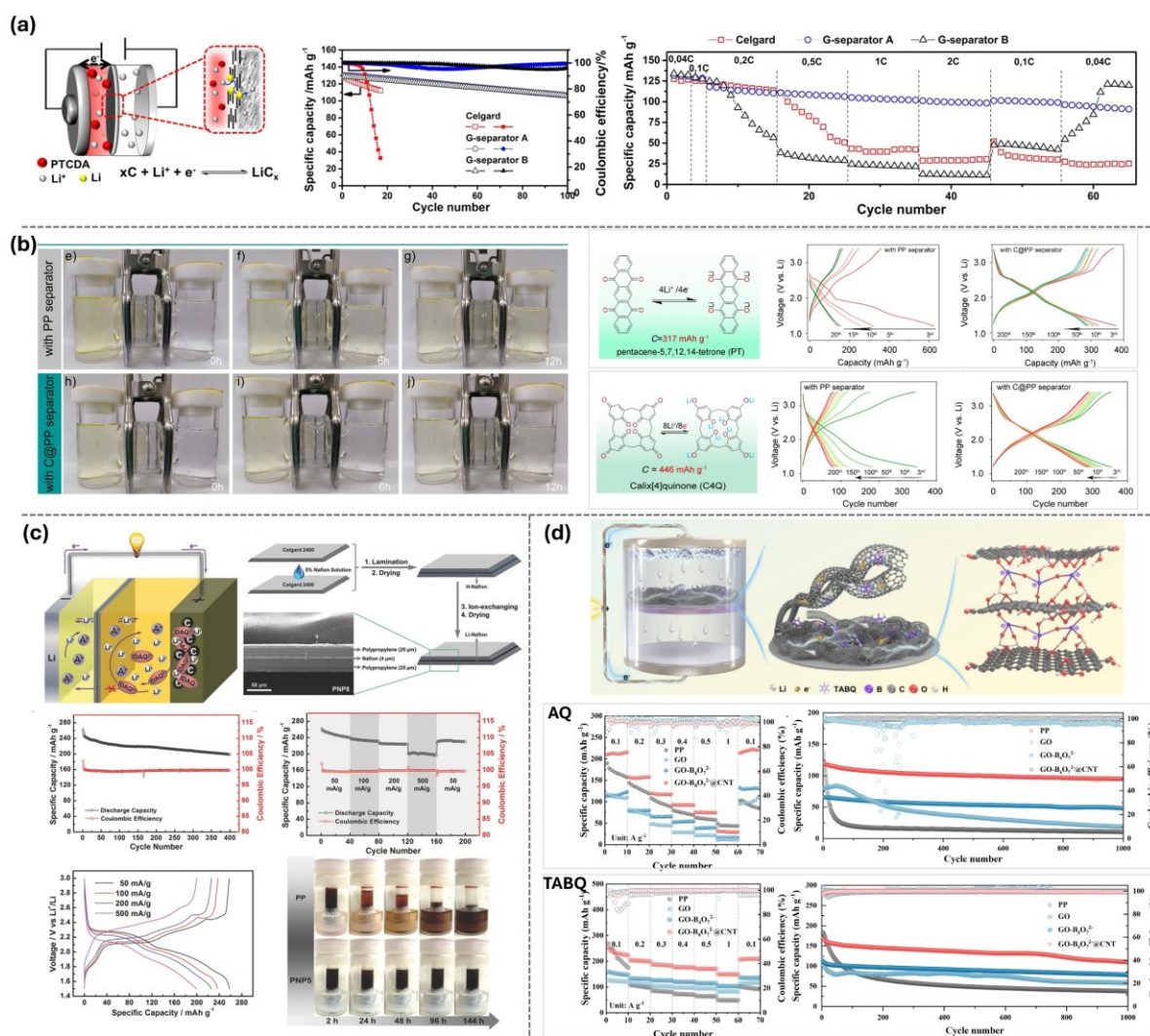


Figure 2.18. Separator modification strategies for stabilizing soluble organic cathodes. (a) Schematic illustration, cycling (at 0.1 C), and rate performance of Li-PTCDA cells with Celgard and graphene-coated separators.^[230] (b) Visual suppression test of PT diffusion and cycling performance of PT (at 0.5 C) and C4Q (at 0.2 C) batteries with PP and C@PP. Adapted with permission.^[231] Copyright © 2021 Elsevier. (c) Fabrication process of PNP separators, diffusion test, and electrochemical performance in Li-IDAQ cells, including cycling and GCD at 50 mA g⁻¹ and rate capability, compared with PP. Adapted with permission.^[232] Copyright © 2016 John Wiley and Sons. (d) Schematic illustration, rate and cycling performance (at 1 A g⁻¹) of GO-B₄O₇@CNT modified separators with AQ and TABQ cathodes compared with counterparts. Adapted with permission.^[233] Copyright © 2025 Elsevier.

Nafion-based sandwich separators represent another effective strategy to suppress active-material crossover (Figure 2.18c). A PP/Nafion/PP (PNP) trilayer structure was designed, where the Nafion layer was only 0.5–4.0 μm thick (0.3–2.2% of a typical 183 μm Nafion 117 membrane). This configuration improves Li⁺ conductivity by two orders of magnitude compared with swollen bulk Nafion, while the PP layers preserve mechanical strength and

prevent direct electrode contact. Using 1,1'-iminodianthraquinone (IDAQ) as a model cathode, the Li-IDAQ cell with PNP separators retains 199 mAh g^{-1} (76% of the initial 262 mAh g^{-1}) after 400 cycles at 50 mA g^{-1} with an average CE above 99.6%, whereas conventional PP separators allow rapid fading. Visual diffusion tests confirm that IDAQⁿ⁻ anions readily permeate through PP within 144 h, while PNP completely blocks their crossover, explaining the dramatic improvement in long-term stability.^[232] In a different design, a double-carbon layer separator was fabricated by first crosslinking graphene oxide (GO) with $\text{B}_4\text{O}_7^{2-}$ to form a dense GO- $\text{B}_4\text{O}_7^{2-}$ layer, followed by deposition of a CNT film (Figure 2.18d).^[233] The GO- $\text{B}_4\text{O}_7^{2-}$ layer provides physical blocking and charge-repulsion effects, while the CNT overlayer supplies hierarchical porosity, abundant carboxyl groups, and strong adsorption for soluble organics. This synergistic structure effectively suppresses the shuttle of diverse small-molecule cathodes, including 2,3,5,6-tetraamino-benzoquinone (TABQ), AQ, and perylenetetracarboxylic diimide (PTCDI). With the modified separator, Li-TABQ retains 78.0% of its initial capacity after 500 cycles at 0.1 A g^{-1} , Li-AQ maintains 94.6 mAh g^{-1} after 1000 cycles at 0.3 A g^{-1} (79.8% retention), and Li-PTCDI retains 93.9% of its capacity after 5000 cycles at 1 A g^{-1} . By contrast, the same cathodes with bare PP separators retains only 14.4%, 11.8%, and 52.3% under the same conditions, respectively.

While separator coatings effectively suppress shuttle effects, binder engineering provides an internal strategy to stabilize organic electrodes by anchoring active molecules within the electrode matrix and preserving structural integrity. A representative example is the dual-conductive ladder-type block copolymer PEDOT-*b*-PEG (Figure 2.19a), which combines electronic conductivity from poly(3,4-ethylenedioxythiophene) (PEDOT) with ionic conductivity from poly(ethylene glycol) (PEG).^[234] Compared with conventional PVDF, PEDOT-*b*-PEG markedly enhances the rate performance of PDI cathodes. At 60 wt% active loading, (60)PEDOT-*b*-PEG electrodes deliver 124, 122, 119, and 115 mAh g^{-1} at 0.25, 0.5, 1, and 2 C, respectively, with 93% retention at 2 C, while PVDF electrodes drop from 109 mAh g^{-1} at 0.25 C to only 52 mAh g^{-1} at 2 C (48% retention). Even at 80 wt% loading, (80)PEDOT-*b*-PEG electrodes maintain 40–69 mAh g^{-1} , whereas PVDF-based electrodes are nearly inactive, underscoring the critical role of mixed ionic-electronic conduction in enabling high active-material loadings. Another strategy employs catechol-rich binders, where the backbone chemistry strongly influences electrode performance (Figure 2.19b).^[235] Among four studied polymers, poly(dopamine acrylamide) (PDA) binder exhibits the best rate capability,

delivering 124, 116, 109, and 100 mAh g⁻¹ at 25–200 mA g⁻¹ with 81% retention at the highest current, far superior to PVDF (31% retention).

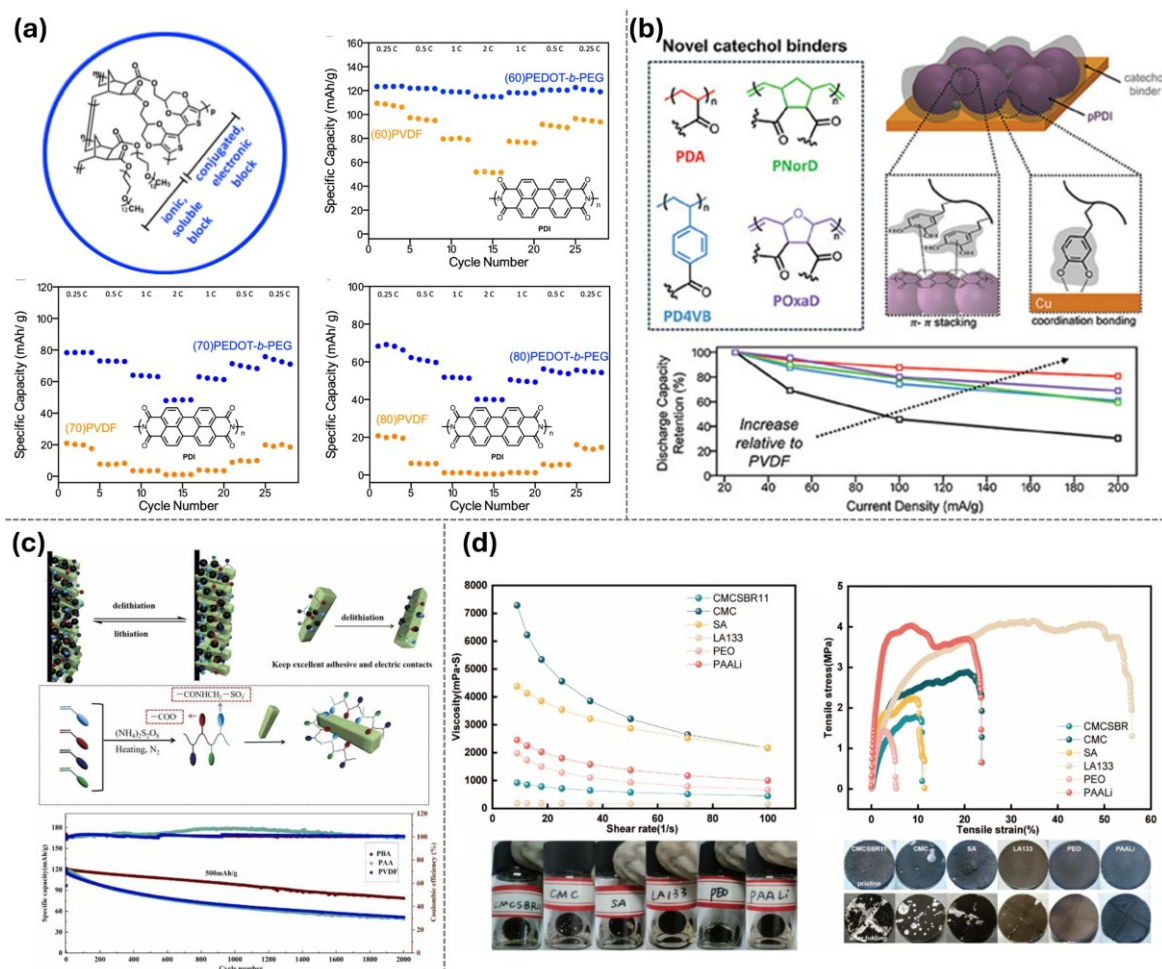


Figure 2.19. Binder engineering strategies for OCMs. (a) Molecular structure of PEDOT-*b*-PEG and rate performance of PDI-based electrodes with varying active material loadings (60–80 wt%), compared with PVDF binder. Adapted with permission.^[234] Copyright © 2022 American Chemical Society. (b) Electrochemical performance of electrodes using different catechol-rich binders versus PVDF, showing discharge capacity retention across current densities.^[235] (c) Long-term cycling test of PTCDA electrodes (500 mA g⁻¹) with different binders. Adapted with permission.^[236] Copyright © 2025 Elsevier. (d) Comparative rheology of binder solutions, peel strength, immersion test, and folding test of VY electrodes with CMC-SBR, CMC, SA, LA133, PEO, and PAALi binders. Adapted with permission.^[237] Copyright © 2025 Elsevier.

Multifunctional water-based binders have also shown promise. For instance, a poly(acrylic acid-butyl acrylate-AMPS-acrylonitrile) (PBA) binder containing –SO₃⁻, –COO⁻, –CN, and –NHCO– groups enables strong intermolecular interactions and high ionic conductivity (Figure 2.19c).^[236] When paired with PTCDA cathodes, PBA binders deliver 126 mAh g⁻¹ at 0.1 A g⁻¹

and remarkable stability of 78.5 mAh g^{-1} after 2000 cycles at 0.5 A g^{-1} (64.5% retention, 0.017% decay per cycle), compared with only 51.3 mAh g^{-1} (43.6% retention) for PVDF. The PBA system also supported extreme rates, maintaining 71 mAh g^{-1} at 30 C , far exceeding PVDF or PAA binders. In another study, practical binder selection for thick organic electrodes of Vat Yellow 3RT (VY) was systematically evaluated, comparing sodium carboxymethyl cellulose (CMC), CMC-styrene butadiene rubber (CMC-SBR), sodium alginate (SA), polyacrylic latex (LA133), PEO, and lithium polyacrylate (PAALi) in terms of slurry rheology, adhesion strength, and mechanical flexibility to identify optimal candidates for high-loading configurations (Figure 2.19d).^[237] Peel-strength tests reveal LA133 and PAALi to provide the strongest adhesion, while PEO suffers severe delamination after electrolyte immersion. High-loading electrodes (10 mg cm^{-2}) prepared with PAALi binder deliver stable capacities, while those with PEO release only $\sim 50 \text{ mAh g}^{-1}$ due to poor adhesion. Flexibility tests further confirm that PAALi and PEO binders allow electrodes to withstand folding without cracking, unlike CMC or CMC-SBR. Overall, PAALi was identified as the optimal binder for thick electrodes, balancing viscosity, adhesion, and mechanical resilience.

2.3.3. Electrolyte engineering

Electrolyte engineering is a powerful strategy for organic cathodes because it directly governs solvation, ion transport, and interfacial chemistry. Without altering the molecular structure of the active species, an appropriate electrolyte medium can suppress dissolution, minimize parasitic side reactions, and stabilize the CEI, while maintaining high Li^+ conductivity. In this context, strategies such as increasing the electrolyte concentration, employing ILs or mixed solvents, and developing quasi-solid-state or all-solid-state electrolytes have all shown promise in mitigating dissolution and improving long-term performance of organic electrodes. As the broader development of electrolytes has been systematically reviewed in [Section 2.1.4](#), this section specifically focuses on their application to OCMs in LIBs.

2.3.3.1. Liquid electrolytes

Electrolyte properties, including solvent composition,^[218,238,239] salt concentration,^[240–244] and the use of additives or ILs,^[218,245] play a decisive role in governing the dissolution behavior, ionic conductivity, and interfacial chemistry at the electrodes. Careful optimization along these parameters has been shown to markedly improve the cycling stability and rate capability of otherwise soluble organic electrodes.

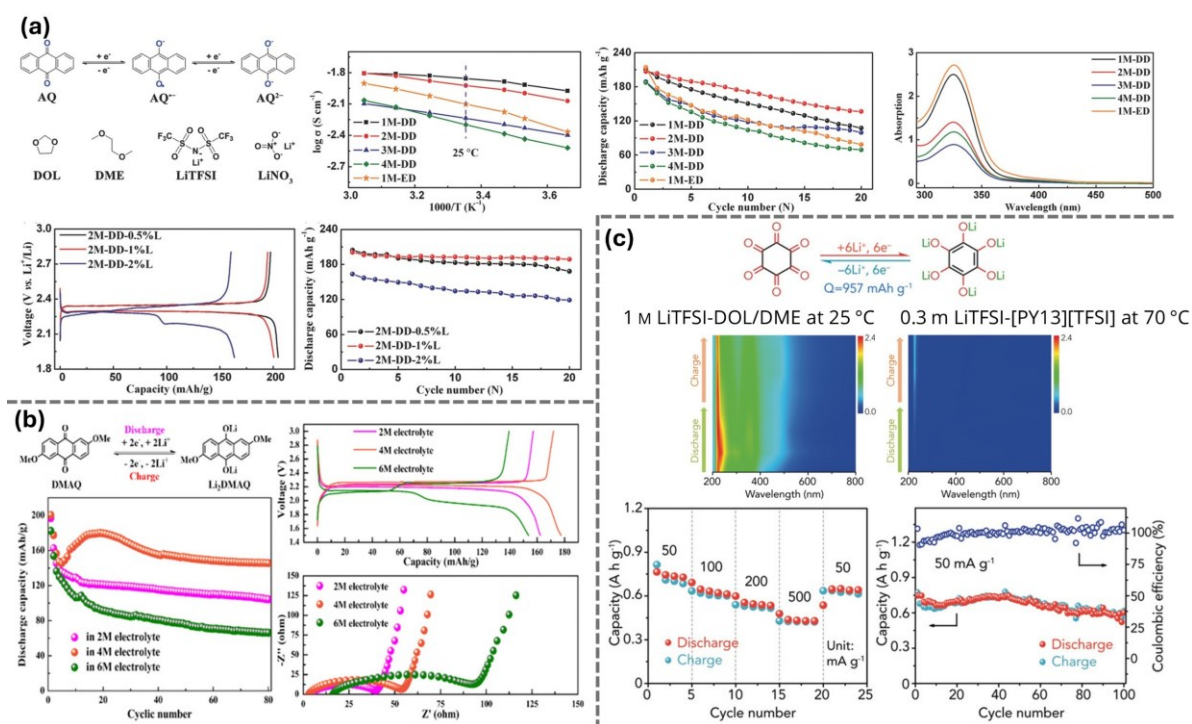


Figure 2.20. (a) Electrochemical performance of AQ in different electrolytes (1M-DD, 1–4M-DD): ionic conductivity, cycling stability (at 0.1 C), UV-vis solubility tests, and effects of LiNO₃ additives.^[218] (b) GCD and cycling (at 0.2 C) results of DMAQ in electrolytes with varied concentrations in a voltage window of 1.5–3.0 V. Adapted with permission.^[244] Copyright © 2020 American Chemical Society. (c) *Ex situ* UV/Vis of C₆O₆ in LiTFSI-DOL/DME and LiTFSI-[PY13][TFSI] electrolytes, and rate and cycling performance in 0.3 M LiTFSI-[PY13][TFSI] electrolyte at 70 °C. Adapted with permission.^[245] Copyright © 2019 John Wiley and Sons.

For instance, AQ was investigated in conventional carbonate electrolyte (1 m LiPF₆ in EC/DEC, 1M-ED) and in ether-based LiTFSI electrolytes (1–4 M in DOL/DME, denoted 1M-DD to 4M-DD). In 1M-ED, AQ delivers 214 mAh g⁻¹ but suffers from severe dissolution, with the electrolyte turning brown after 30 days. By contrast, ether-based electrolytes reduce solubility, and 2M-DD provides the best balance: it delivers 207 mAh g⁻¹ with high ionic conductivity (11.9 mS cm⁻¹) and, with 1% LiNO₃ additive, achieves 94% capacity retention after 20 cycles at 0.1 C (Figure 2.20a).^[218] SEM and Raman confirms that LiNO₃ promotes the formation of a protective film on the Li anode, preventing parasitic reactions.^[246–248] A similar concentration-dependent effect was observed for 2,6-dimethoxy-9,10-anthraquinone (DMAQ), which reaches 200 mAh g⁻¹ in 4 M LiTFSI-DOL/DME and maintains 146 mAh g⁻¹ after 80 cycles, compared with only 53% retention in 2 M and 36% in 6 M electrolytes (Figure 2.20b).^[244] These results demonstrate that electrolyte concentration not only tunes ionic conductivity but also dictates

dissolution and cycling stability. Mechanistic studies in related systems, such as glyme-based,^[238,249] localized high-concentrated,^[242,250–252] and fluorinated electrolytes,^[243,253] have confirmed that the electrolyte environment critically governs interphase formation, shuttle suppression, and long-term redox reversibility; however, systematic investigations in combination with organic cathode materials remain limited. Beyond conventional liquid electrolytes, IL systems have also shown promise for stabilizing soluble quinones.^[240,241] For example, calix[6]quinone (C6Q) in Li[TFSI]/[PY13][TFSI] exhibits exceptional long-term cycling, retaining 70% and 72% capacity after 1000 cycles at 0.2 C and 0.5 C, respectively, and still maintaining 155 mAh g⁻¹ after 10000 cycles at 5 C.^[241] Similarly, cyclohexanhexone (C₆O₆) in ILs delivers an ultrahigh capacity of 902 mAh g⁻¹ with 82% retention after 100 cycles at 50 mA g⁻¹ (Figure 2.20c).^[245]

In summary, increasing salt concentration reduces free solvent molecules and thereby suppresses active-material dissolution, while IL electrolytes further offer low volatility, wide electrochemical windows, and weak interactions with organics, collectively demonstrating that electrolyte design is a powerful route to stabilize organic cathodes and extend their practical application.

2.3.3.2. Polymer-based GPEs and SPEs

Polymer-based electrolytes have attracted wide attention in organic lithium-ion batteries because they combine the safety and mechanical robustness of solid electrolytes with the processability and ion transport of liquids. As a representative demonstration with organic cathodes, C4Q was paired with a poly(methyl acrylate)/PEG (PMA/PEG)-based GPE containing LiClO₄ in DMSO (Figure 2.21a).^[254] The quasi-solid-state Li–C4Q cell delivers a high initial discharge capacity of 422 mAh g⁻¹ (close to its theoretical value of 446 mAh g⁻¹) and retains 379 mAh g⁻¹ after 100 cycles at 0.2 C, corresponding to 90% capacity retention. The stable cycling behavior and nearly constant cyclic-voltammetry peak currents indicate that the PMA/PEG gel effectively suppresses C4Q dissolution compared with conventional liquid electrolytes. The design is further validated with another soluble molecule, 2,2'-bi(1,4-naphthoquinone) (BNQ), where the quasi-solid system maintains 322 mAh g⁻¹ after 30 cycles, nearly double that of the liquid system (163 mAh g⁻¹).

Another notable example with organic electrodes involves poly(4-vinyl catechol) (P4VC) combined with single-ion conducting polymer nanoparticle (NP) electrolytes, in comparison

with a 1 M LiTFSI in succinonitrile (SN) electrolyte (Figure 2.21b). The solid-state Li–P4VC cell exhibits an initial capacity of 352 mAh g⁻¹, excellent electrochemical stability up to 5.5 V, and high ionic conductivity of 0.2×10^{-3} S cm⁻¹ at room temperature (10^{-3} S cm⁻¹ at 90 °C) with a lithium transference number of 0.99. These features enable outstanding rate performance (>100 mAh g⁻¹ at 794 mA g⁻¹) and long cycle life (500 cycles) while maintaining mechanical robustness (20 MPa) and thermal stability (90 °C). The high performance is attributed to dense packing of single-ion conducting NPs, which provides stable ion pathways and avoids anion depletion at the electrode–electrolyte interface.^[255]

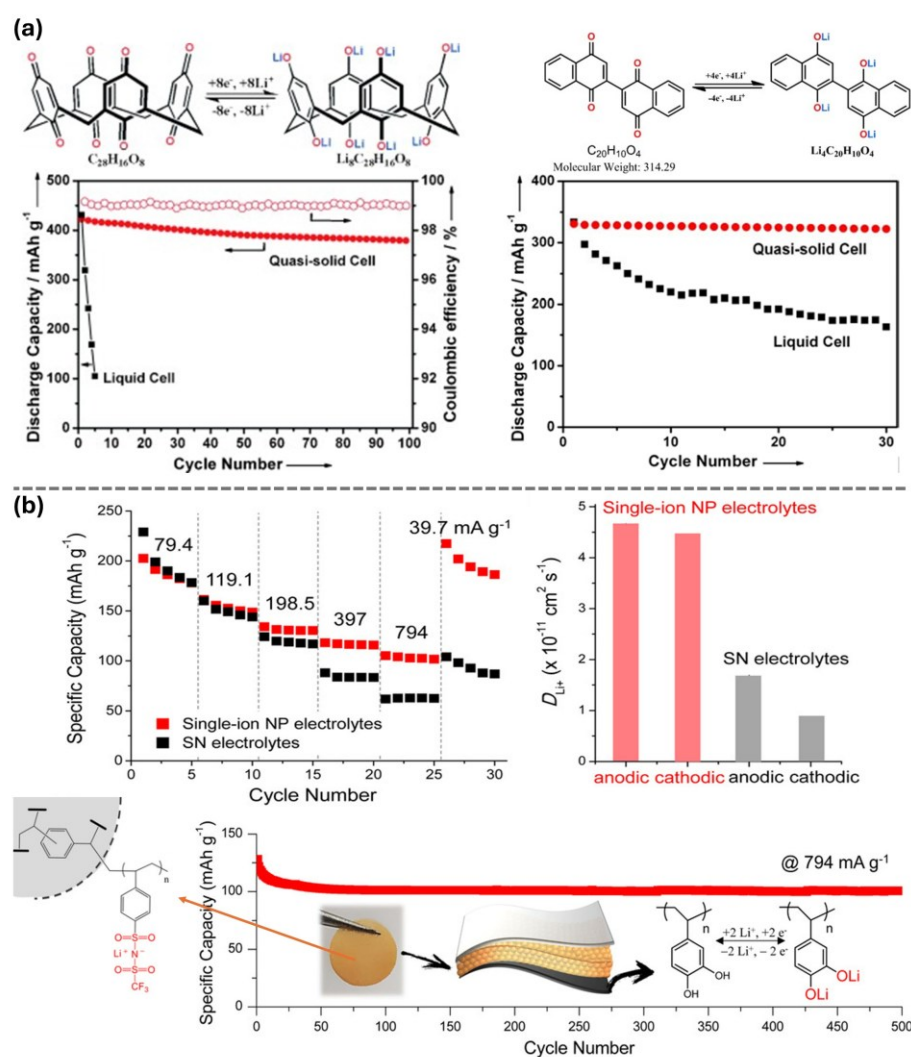


Figure 2.21. (a) Cycling performance of C4Q and BNQ cathodes with PMA/PEG-based gel polymer electrolyte (LiClO₄ in DMSO) compared with liquid cells at 0.2 C. Adapted with permission.^[254] Copyright © 2013 John Wiley and Sons. (b) Electrochemical performance of LIBs using single-ion NP electrolytes, including rate capability, Li⁺ diffusion coefficients, and long-term cycling with P4VC cathodes at 25 °C. Adapted with permission.^[255] Copyright © 2020 John Wiley and Sons.

Overall, polymer-based GPEs and SPEs provide a unique balance of safety, flexibility, and tunable ion transport that liquid systems and inorganic SSEs alone cannot fully achieve. Their non-volatility and mechanical compliance make them well suited to suppress dissolution and buffer the volume changes of organic electrodes, thereby enhancing interfacial stability and long-term cycling. Although their relatively low ionic conductivity at room temperature and high interfacial resistance remain bottlenecks, advances in polymer design, such as single-ion conducting architectures, tailored side-chain functionalities, and composite formulations with inorganic fillers, are steadily addressing these challenges. With these developments, polymer electrolytes are increasingly positioned as a practical and scalable platform for integrating organic cathode materials into solid-state LIBs.^[256–260]

2.3.3.3. Inorganic SSEs (sulfides and oxide ceramics)

While polymer-based electrolytes provide flexibility and safety, their low ionic conductivity and tendency to partially dissolve organic molecules remain major limitations. In contrast, inorganic SSEs offer intrinsically higher ionic conductivity and superior electrochemical stability, making them promising for integrating with OCMs. Among them, sulfide-, oxide-, and halide-based systems have been explored in the context of lithium-organic batteries.

Sulfide electrolytes such as LGPS and $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) deliver high room-temperature ionic conductivities (10^{-3} – 10^{-2} S cm^{-1}), comparable to liquid electrolytes, and their mechanical softness allows intimate contact with organic cathodes under moderate pressure. The redox potentials of many OCMs (1.5–3.5 V vs. Li^+/Li) also fall within the practical window of sulfide SSEs.^[261] Representative studies include Luo et al., who demonstrate that functionalized azo cathodes such as 4-(phenylazo) benzoic acid lithium salt (PBALS) can form ionic bonding with LPS, stabilizing interfacial contact and yielding reversible capacities around 83 mAh g^{-1} over 120 cycles (Figure 2.22a).^[262] Yao's group further employed pyrene-4,5,9,10-tetraone (PTO) with LPSCl, where solvent-assisted mixing and cryomilling produce a PTO-interphase-LPSCl “core-shell” structure, enhancing utilization from 78% to 99.5% and delivering material-level specific energy up to 828 Wh kg^{-1} (Figure 2.22b).^[263,264] Organodisulfide cathodes such as poly(trithiocyanuric acid) (PTTCA) paired with $\text{Li}_7\text{P}_3\text{S}_{11}$ also shows promising performance when composited with CNTs (410 mAh g^{-1} , 83% retention after 100 cycles, Figure 2.22c).^[265] Despite these advances, sulfide SSEs suffer from intrinsic drawbacks including narrow electrochemical stability windows (~ 2 –2.2 V), interfacial side reactions, and poor compatibility with lithium metal, which limit their broader application in LIBs.^[266]

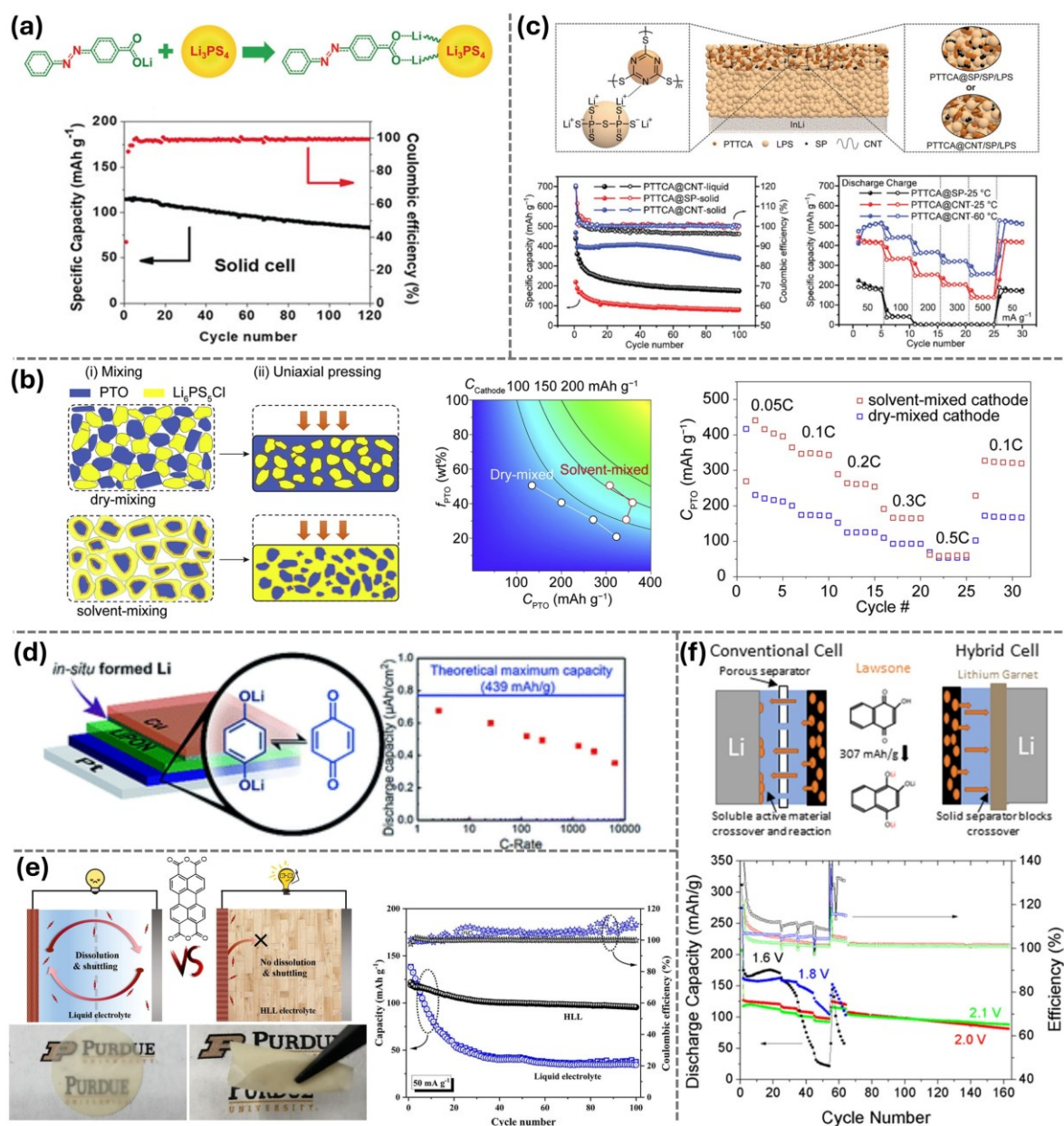


Figure 2.22. (a) Interaction between PBALS and LPS SSE, and cycling performance of PBALS in all-solid-state cells at 20 mA g⁻¹. Adapted with permission.^[262] Copyright © 2018 John Wiley and Sons. (b) Preparation of dry- and solvent-mixed PTO/LPSCl cathodes and comparison of their cathode-level capacities at different PTO fractions and rate performances at $f_{\text{PTO}} = 40$ wt%.^[263] (c) Electrode architectures with PTTCA@SP and PTTCA@CNT composites, and the corresponding cycling and rate performances at various current densities and temperatures. Adapted with permission.^[265] Copyright © 2021 John Wiley and Sons. (d) Discharge capacity of Li₂Q thin-film batteries with ALD-grown LiPON electrolyte at different C rates. Adapted with permission.^[267] Copyright © 2018 Royal Society of Chemistry. (e) Photographs of the HLL composite membrane in flat and bent states, and cycling performance of PTCDA/Li cells using liquid electrolyte and HLL. Adapted with permission.^[268] Copyright © 2021 Elsevier. (f) Effect of lower cutoff voltage on the cycling performance of LS|LLZO cells with

LiTFSI:Pyr₁₃FSI catholyte, operated with an upper cutoff of 2.8 V and lower cutoffs between 1.6–2.1 V.^[269]

Compared with sulfide systems, oxide-based solid electrolytes such as LiPON, garnet-type LLZO, and NASICON-type LATP offer wide electrochemical stability windows (>4 V vs. Li⁺/Li) and excellent oxidative resistance, making them attractive for higher-voltage organic cathodes. However, their high rigidity, grain-boundary resistance, and relatively low room-temperature conductivities ($\sim 10^{-4}$ – 10^{-3} S cm⁻¹) often require careful interface engineering.^[147] One representative example is the use of atomic/molecular layer deposition (ALD/MLD) to fabricate ultrathin organic–oxide solid-state batteries. He and co-workers demonstrate an *in situ* lithiated quinone (Li₂Q) cathode paired with ALD-grown LiPON electrolyte, achieving fast kinetics (40% of theoretical capacity in <0.25 s at 6500 C) and power densities exceeding 500 W cm⁻³, highlighting the feasibility of nanoscale organic–oxide integration in thin-film devices (Figure 2.22d).^[267]

In another approach, Pol et al. designed all-solid-state Li–organic batteries using PTCDA cathodes, lithium metal anodes, and hybrid polymer–LLZTO composite electrolytes (HLL). The system delivers long lifespan (79% retention after 100 cycles at 50 mA g⁻¹ and 91% retention after 1000 cycles at 500 mA g⁻¹) and superior thermal/mechanical stability, underscoring the benefit of combining oxide ceramics with flexible polymer phases to enhance conductivity and interfacial contact (Figure 2.22e).^[268] In addition, Tucker and co-workers employed LLZO separators in hybrid organic–inorganic cells with small-molecule quinones such as lawsone. The LLZO membrane effectively prevents cathode dissolution and enabled stable cycling at various rates, though capacity is limited by low-voltage side reactions and incomplete utilization of carbonyl groups (Figure 2.22f).^[269] It is worth noting that oxide-based SSEs are frequently combined with polymer matrices to offset their brittleness and improve electrode–electrolyte contact. Polymer–oxide composites leverage the wide electrochemical stability of oxides while benefiting from the flexibility and processability of polymers, offering a more practical route for organic solid-state batteries.^[270–272]

2.3.4. Summary

OCMs combine molecular tunability, structural diversity, and sustainability, but their practical use is still restricted by three intrinsic challenges: i) high solubility in conventional electrolytes, leading to active-material loss and shuttle effects; ii) intrinsically low electronic conductivity,

which limits utilization efficiency and rate performance; and iii) pronounced structural transformations during cycling, which undermine stability and reversibility. Current research therefore focuses on three major strategies: molecular design, electrode/separator modification, and electrolyte engineering.

Molecular design provides a primary route to suppress dissolution and stabilize redox centers. Oligomerization and polymerization reduce solubility and retain active mass while enabling charge delocalization along conjugated backbones. Salt formation transforms ionizable groups into alkali salts, improving thermal stability, adjusting redox potentials, and avoiding irreversible lithiation during initial cycles. Incorporating rigid linkages or extended π -conjugation, as in imide- or azo-based frameworks and COFs, further enhances stability and rate capability. These strategies, however, may sacrifice theoretical capacity or increase synthesis complexity, requiring careful trade-offs in molecular engineering.

Electrode and separator modification offers external stabilization. Conductive carbon frameworks such as CNTs, graphene, and mesoporous carbon provide electronic pathways while physically confining soluble species. More durable immobilization is achieved through covalent grafting or conformal carbon coatings. Separator coatings using conductive carbons, Nafion, or layered hybrids block dissolved molecules and alleviate shuttle effects, while functional binders improve adhesion, supply mixed ionic/electronic conductivity, and stabilize thick electrodes. Although these approaches markedly extend cycle life and rate performance, they inevitably introduce inactive components and require precise optimization to minimize impedance.

Electrolyte engineering tackles dissolution and interfacial degradation from the electrolyte side. HCEs and localized high-concentration electrolytes LHCEs reduce free solvent activity, suppress dissolution, and promote stable interphase formation. ILs expand electrochemical windows and offer low volatility, enabling extended cycling. GPEs and SPEs combine processability, flexibility, and dissolution suppression, though their limited conductivity at room temperature remains a challenge. Inorganic SSE, particularly sulfides and oxides, provide higher ionic conductivities and broader stability windows. Sulfides allow close electrode contact and fast ion transport but suffer from narrow stability ranges and reactivity with lithium, whereas oxides are chemically robust yet brittle and resistive at interfaces. Hybrid polymer-ceramic electrolytes are emerging as promising compromises, pairing the chemical stability of oxides with the flexibility of polymers.

Taken together, these approaches are complementary rather than isolated. Integrated designs, such as polymerized frameworks confined within conductive carbons and coupled with hybrid solid electrolytes, can simultaneously suppress dissolution, enhance conductivity, and stabilize interfaces. However, unresolved issues remain: molecular enlargement reduces capacity density, electrode modifications add inactive weight, and solid electrolytes still require breakthroughs in conductivity and interface engineering.

Looking ahead, progress is expected to hinge on multi-level, integrated strategies that unite molecular engineering, electrode architecture, and electrolyte innovation. Scalable syntheses of high-capacity frameworks, multifunctional binders and separators for high-loading electrodes, and SSEs with both high conductivity and interfacial stability will be central. The convergence of these efforts is expected to unlock the full potential of OCMs as sustainable, high-performance alternatives to transition-metal-based cathodes for both conventional and solid-state LIBs.

Chapter 3. Electrochemical Performances of Azo Dyes as Organic Cathodes for Lithium-Ion Batteries

This chapter is adapted from the article *Electrochemical Performances of Azo Dyes as Organic Cathodes for Lithium-Ion Batteries* published in *Journal of Power Sources* (Volume 657, 30 November 2025, 23814) by Ximeng Zhang, Liuqing Yang, Xudong Liu, Jay Nejad, and Zhibin Ye. In this article, Ximeng Zhang contributed to conceptualization (with Professor Ye), experimental work, methodology design, computation, data analysis, curation, drafting, and visualization. Professor Zhibin Ye oversaw supervision, conceptualization, project management, methodology, validation, manuscript revision, and funding. Liuqing Yang, Xudong Liu, and Jay Nejad participated in data interpretation and provided critical feedback to refine the study's framework and conclusions.

Abstract

Organic electrode materials present a promising pathway toward green and sustainable lithium-ion batteries (LIBs) due to their abundant resources, high theoretical capacities, molecular diversity, and environmental sustainability. In this study, we systematically investigate a set of commercially available azo dyes to explore their electrochemical performances as organic cathode materials, with a particular focus on methyl orange (MO), which shows the best performance and lowest cost within the set. *Ex situ* structural characterizations during discharge-charge tests, including X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) characterization, confirm that MO undergoes reversible lithiation/delithiation at the azo group. Furthermore, to address issues of dissolution and capacity fading during cycling, MO has been encapsulated within BP2000 conductive porous carbon. The resulting MO@BP2000 composite shows significantly improved cycling stability and rate capability, achieving an initial reversible capacity of 150 mAh g⁻¹ and retaining 121 mAh g⁻¹ after 50 cycles at 30 mA g⁻¹. These findings clarify the redox behavior of azo dyes in LIBs and provide mechanistic insights that can potentially guide the molecular design of high-performance azo-based cathode materials.

3.1. Introduction

In recent years, the demand for secondary batteries has been rising significantly to meet the

rapid growth of consumer electronics, electric vehicles, and grid integration of renewable energy markets. However, the supply chain of conventional inorganic electrode batteries poses considerable environmental challenges. The mining and refining of raw materials (such as nickel, cobalt, and manganese ores) and battery production processes can lead to severe environmental impacts, including land degradation, biodiversity loss, hazardous waste generation, and pollution of water, soil, and air. Improper or even illegal disposal of batteries aggravates toxic contamination. Simultaneously, the scarcity of these non-renewable minerals threatens the global electrification goals.^[273–276]

Consequently, there has been significant interest in identifying suitable alternative electrode materials. Compared to conventional transition-metal-based inorganic electrodes, organic electrodes offer several advantages, including resource sustainability, low cost, high flexibility, and a reduced carbon footprint. In the last decades, a large family of organic electrode materials has been explored for lithium-ion batteries (LIBs). Such materials store energy through the reversible reaction of lithium ions with their redox-active functional groups,^[277,278] such as carbonyl (C=O),^[27,211,279–281] imine (C=N),^[164,165,282] organosulfur (S–S),^[168,283,284] free radical,^[171,175,285] azo (N=N), and nitro (–NO₂) groups.^[35,37] In particular, Wang et al. reported the unique electrochemical conversion of nitro in a nitroaromatic compound to azo and subsequently revealed the reversible 2-electron electrochemical redox activity of the latter. This has inspired us to investigate in this work a common class of organic azo dyes as the organic cathode materials for LIBs. These azo-containing dyes, primarily in the form of organic salts, exhibit several advantages, including stable physical and chemical properties, low cost, simple production processes, abundant resources, and diverse structures. Furthermore, their recycling and treatment have been extensively studied, offering richer, more efficient, and cost-effective methods with lower environmental impact compared to inorganic electrode materials.^[286]

Herein, a set of four common commercially available azo dyes is screened for their electrochemical performance as cathode materials, including methyl orange (MO), methyl red (MR), Congo red (CR), and orange G (OG). A particular focus has been placed on MO, which shows the best performance among the set. Systematic *ex situ* characterizations have been performed on the MO active material during the discharge-charge process, including X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS), revealing the reversible redox electrochemistry of the azo group. To address the capacity decay as a result of its dissolution, MO has also been

encapsulated within BP2000 conductive porous carbon, forming MO@BP2000 that shows improved cycling stability. This study employs MO as a representative azo dye to reveal redox mechanisms, offering insights into the design of azo-based organic cathode materials for next-generation LIBs.

3.2. Experimental

3.2.1. Chemicals and materials

MO ($\geq 85\%$), MR (ACS reagent), OG ($\geq 80\%$), CR ($\geq 85\%$), lithium hydroxide (LiOH, 98%), toluene (ACS reagent), 2-propanol ($\geq 99.5\%$), Nafion (5 wt% in mixture of lower aliphatic alcohols and water), ethanol (ACS reagent), lithium bis(trifluoromethane)sulfonimide (LiTFSI, 99.95%), sodium *p*-toluenesulfonate (NaTs, 95%) were obtained from Aldrich and used as received. 1,3-dioxolane (DOL, 99%, Aldrich) and dimethoxyethane (DME, anhydrous, 99.5%, Aldrich) were dried and stored over a 4 Å molecular sieve before use. Super-P carbon black (IMERYS Graphite & Carbon, Belgium), BP2000 porous carbon (Cabot), and Celgard 2400 separator (Celgard LLC) were used as received. Deionized (DI) water was prepared using a Milli-Q purification system. An ethylene-olefin-copolymer (EOC) elastomer, Engage 8130, was obtained from Dow Chemical and was used as the binder for the azo dye cathodes.

3.2.2. Synthesis of MO lithium salt (MOLS)

MO (1.63 g, 5 mmol) was dissolved in hot DI water (50 mL), and LiOH (0.24 g, 10 mmol) was added to the solution under stirring. The solution was stirred for 1 h at 95 °C. The reaction solution was afterwards slowly cooled to 2 °C to obtain orange crystals. The obtained solid was filtered and washed with 10 mL of cold DI water. To ensure complete ion exchange, the solid product was redissolved in 50 mL of hot DI water and subjected to the same LiOH treatment and crystallization process as described above. This ion exchange and recrystallization procedure was repeated two additional times under identical conditions. After the third ion exchange cycle, the final solid product was collected and dried in an oven at 100 °C for 48 h to obtain the lithiated product, MOLS.

3.2.3. Synthesis of MO@BP2000

To prepare the MO encapsulated within BP2000, MO was dissolved in hot DI water (95 °C) at a concentration of 50 g/L, followed by the addition of 0.5% (v/v) of 2-propanol. The hot solution was injected into a vacuumed flask containing a desired amount of BP2000 (MO/BP2000 mass

ratio: 1/1). After stirring for 12 h, the dispersion was naturally evaporated in air for 48 h, followed by drying in an oven at 100 °C for 24 h to remove water, rendering MO@BP2000.

3.2.4. Materials characterizations

XRD patterns were collected on a Rigaku SmartLab SE X-ray diffractometer with Cu K α radiation (1200 kW). Raman spectra were recorded with a Fergie spectrometer (Princeton Instruments) upon excitation with a 532 nm laser. FTIR spectra were obtained on a Thermo Scientific Nicolet 6700 Analytical FTIR spectrometer. XPS measurements were undertaken on a Thermo Scientific Theta Probe XPS spectrometer with a monochromatic Al K α X-ray source at a spot area of 400 μ m. Thermogravimetric analysis (TGA) was performed on a Q50 TGA from TA Instruments. N₂ sorption measurements were performed on a Micromeritics ASAP2020 physisorption analyzer at 77 K. Ion chromatography (IC) was conducted on a 930 Compact IC Flex system. Microscopic images were taken using a Westover metallurgical microscope (MMT-2305) with a WF10 $\times$ eyepiece and PL 40 $\times$ objective under reflected light illumination.

Density functional theory (DFT) calculations on the molecular structures and the IR spectra of MO, MO–Li, and MO–2Li were performed by using Gaussian 09W. The molecular geometry was optimized, and the IR spectra were simulated at the B3lyp/6-31+g(d,p) level of theory, incorporating solvation effects using the Solvation Model based on Density (SMD) model with diethyl ether (DE) as solvent. For comparison, the Polarizable Continuum Model (IEFPCM) was also employed with dielectric constants (ϵ) of 7.1 and 7.2, solvent radius of 3.71 and 4.19 Å to represent DOL and DME, respectively.^[287,288]

3.2.5. Electrochemical measurements

To fabricate electrodes with each azo dye, a mixture of the grinded azo dye, Super-P conducting carbon, and EOC binder at a weight ratio of 50:50:10 was mixed in toluene to form a homogeneous slurry. Electrodes were prepared by coating the slurry onto carbon-coated Al foil disks at the azo dye loading of about 1.33 mg cm⁻² (total azo dye mass: about 2 mg per electrode), followed by drying at 70 °C for 8 h and then at 70 °C under vacuum for 24 h before use. To prepare electrodes with MO@BP2000, a mixture of grinded MO@BP2000, Super-P conducting carbon, and EOC binder at a weight ratio of 80:10:10 was mixed in toluene to form a homogeneous slurry. Electrodes were prepared in the same method as mentioned above. For all cathodes, CR2016-type coin cells were assembled with lithium metal anode, 1 M LiTFSI in

a mixture of DOL/DME (1:1 by volume) as the electrolyte, and double-layer Celgard 2400 as the separator. All electrochemical measurements were conducted at room temperature. Galvanostatic charge–discharge (GCD) tests of the cells were undertaken on a battery testing system (Land, CT2001A, China). Cyclovoltammetry (CV) curves were recorded on an Metrohm Autolab PGSTAT128N electrochemical workstation at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were performed on an Metrohm Autolab PGSTAT128N electrochemical workstation from 100 kHz to 0.01 Hz with an AC amplitude of 5 mV. EIS data analysis was performed by using Zview (Version v3.1, USA).

For *ex situ* FTIR, Raman, and XPS characterizations of MO/MOLS cathodes during charge and discharge, coin cells with MO/MOLS cathode discharged/charged to different voltages were disassembled in an argon-filled glove box. Each cathode was tested under the protection with an argon atmosphere. For *ex situ* XRD tests, materials from five electrodes at each desired voltage were collected and tested under argon atmosphere.

3.3. Results and discussion

3.3.1. Electrochemical performances of azo dyes as cathode materials

Common commercially available azo dyes, such as MO, MR, OG, and CR (see [Figure 3.1a](#) for their structures) investigated herein, are widely used in the textiles, food, and pharmaceutical industries, making them readily accessible for battery applications. The theoretical specific capacities of the four dyes have been calculated (see [Figure 3.1b](#)) with the assumption that each azo (–N=N–) group participates in a two-electron redox reaction, with MO, MR, and CR exhibiting relatively high values of 164, 199, and 154 mAh g⁻¹, respectively. Beyond electrochemical considerations, the cost-effectiveness of the four dyes has also been compared based on their market prices (per 1 kg for pack sizes of >500 g) from Thermo Scientific Chemicals (US), as shown in [Figure 3.1b](#). For reference, the typical price of commercial inorganic cathode materials is also included in [Table S3.1](#) and marked in [Figure 3.1b](#), clearly identifying MO as the most economical option. In addition, [Table S3.2](#) presents a cost comparison with other representative organic cathode materials, further highlighting the commercial availability and significant cost advantage of MO.

The electrochemical performances of the four dyes (MO, MR, OG, and CR) as cathode materials have been assessed in Li-metal half-cells. Each cathode is comprised of azo active material, Super-P conductive carbon and a polyolefin elastomer binder at a mass ratio of

50:50:10 on an aluminum foil current collector.^[36,38] The electrolyte used for all cells is 1.0 M LiTFSI in DOL/DME, with its volume controlled at 10 μL per mg of active material to mitigate dissolution-related capacity loss.

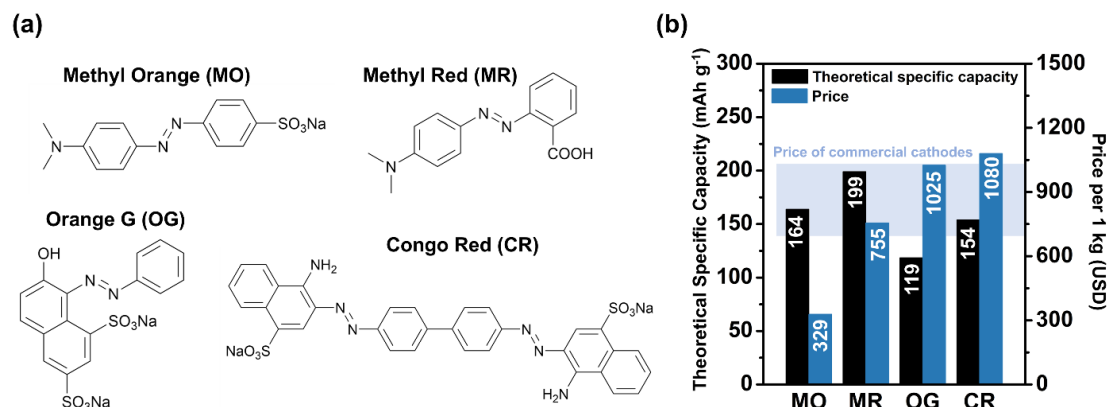


Figure 3.1. (a) Chemical structures of four azo dyes; (b) comparison of theoretical specific capacities and prices of the azo dyes.

Figure 3.2 shows the GCD and CV results of the azo dye cathodes at 30 mA g⁻¹ and 0.1 mV s⁻¹, respectively, as well as EIS measurements of the four cathodes at their fresh state and after the 1st charge (fitting results in Figure S3.1). MO exhibits a highly reversible redox process, with the voltage profile showing two short plateaus at 1.89 V and 1.65 V, respectively, followed by a long, well-defined plateau at 1.47 V in the first discharge. In the first charge, a long plateau at 1.53 V and two short plateaus at 1.71 and 2.58 V are observed. The first discharge cycle delivers 164 mAh g⁻¹, a competitive value among the four dyes, while the first charge exhibits a reversible capacity of 141 mAh g⁻¹, corresponding to an initial Coulombic efficiency (CE) of 85.5%. Consistent with previously reported behavior of azo-based compounds,^[36] this relatively low CE is possibly attributed to the formation of a solid electrolyte interphase (SEI) layer on the electrode surface, which is confirmed by the appearance of a very small semicircle at the high frequency region in the Nyquist plot after 1st cycle of discharge-charge.^[289] In the subsequent GCD cycles, a gradual capacity decay down to 87 mAh g⁻¹ is observed upon cycling up to 50 cycles due to the gradual dissolution of the organic cathode material, but with a stable CE at about 100% and well-retained discharge voltage plateaus at 1.88, 1.65, and 1.49 V, respectively. This confirms the good redox reversibility of MO. In the first cycle of the CV curve, MO exhibits four cathodic peaks at 1.80, 1.60, 1.32, and 1.0 V, respectively, and a broad anodic peak at 1.62 V. The cathodic peak at 1.0 V, associated with SEI formation, appears only in the first discharge. Notably, MO exhibits minimal peak shift over multiple cycles in the CV

test, also confirming excellent electrochemical reversibility.

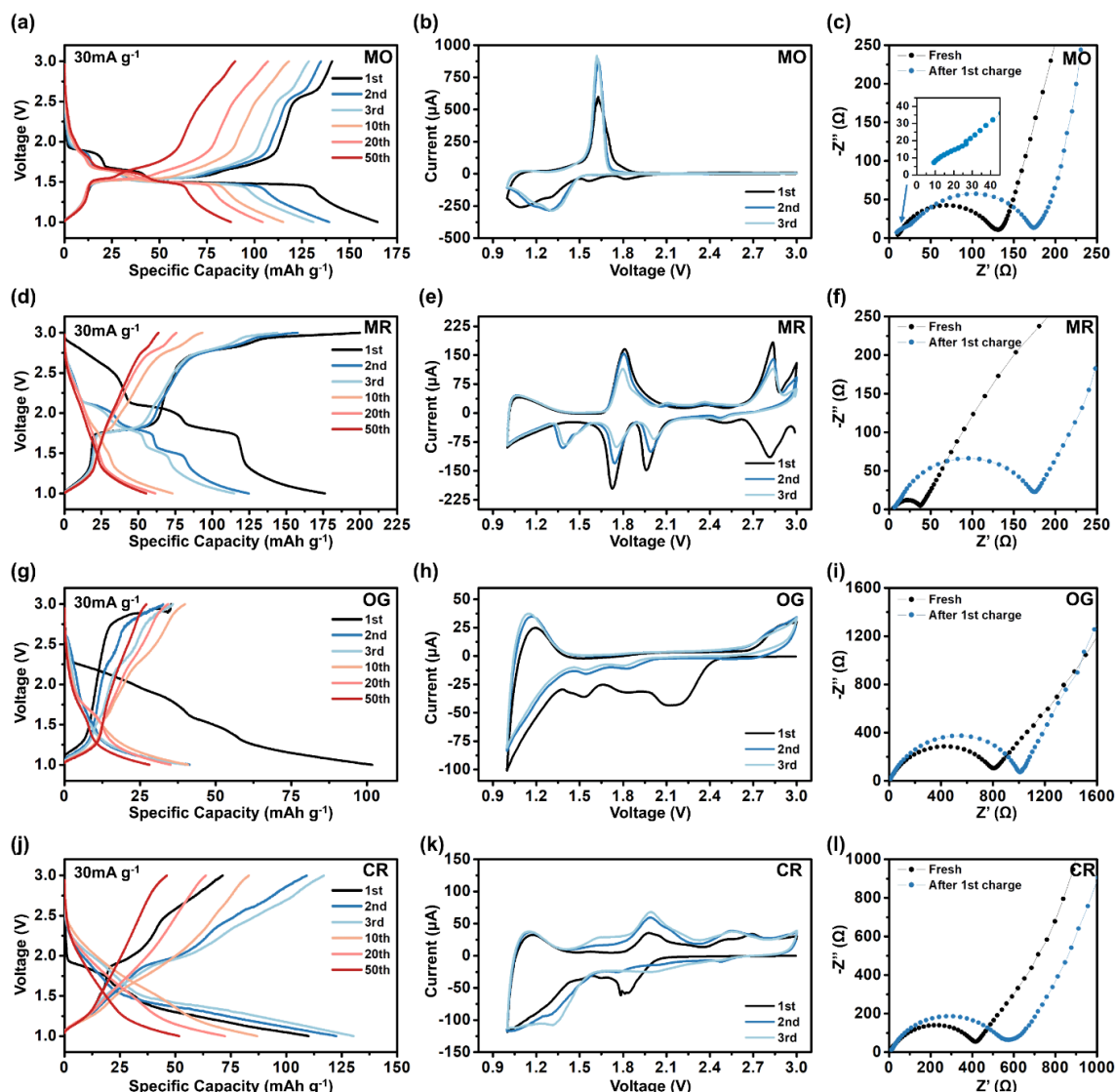


Figure 3.2. Electrochemical performances of the four azo dye cathodes in LIBs: (a,d,g,j) GCD curves at a current density of 30 mA g^{-1} ; (b,e,h,k) CV curves at a scan rate of 0.1 mV s^{-1} ; (c,f,i,l) Nyquist plots of fresh cathodes and cathodes after one cycle of galvanostatic discharge-charge at 30 mA g^{-1} .

MR, by contrast, displays a broader voltage plateau range in GCD, indicating a multi-electron redox process with more complex charge storage dynamics. Its first GCD discharge cycle shows four plateaus centered at 2.66, 2.06, 1.79, and 1.08 V, respectively, with a discharge capacity of 176 mAh g^{-1} , the highest among the four dyes. Upon subsequent cycling, the voltage profile deteriorates dramatically with no clear voltage plateau seen beyond the 10th cycle. This is also accompanied with a fast capacity decay to the discharge capacity of only 52 mAh g^{-1} in the 50th cycle, suggesting its structural instability and/or the presence of irreversible reactions. Aside

from the redox reaction with the azo group, the -COOH group in MR is also expected to participate in the electrochemical reaction, where its lithiation commonly takes place within the range of 1.0–3.0 V.^[290–292] This is verified with the GCD and CV results. The sloping plateau at 2.66 V in the first galvanostatic discharge curve is attributed to the formation of -COOLi group,^[293–295] followed by the reversible lithiation of C=O group at 1.3–1.0 V.^[279] CV curves also support this observation, with an irreversible cathodic peak at 2.81 V corresponding to the formation of -COOLi in the first discharge and a reversible cathodic peak in the voltage range of 1.30–1.55 V corresponding to lithiation of C=O group. The irreversible salinization reaction also leads to a significant increase in the charge transfer resistance of the cathode, as evidenced by the sharply enlarged semicircle in the Nyquist plot (Figure 3.2f). In addition, reversible cathodic peaks are also seen in the CV curves at 1.96 and 1.72 V with corresponding voltage plateaus at 2.09 and 1.81 V in the galvanostatic discharge curves, which should arise from the lithiation of the azo group. Moreover, gradual minor shifts of anodic peaks to lower voltages and cathodic peaks to higher voltages in the CV curves are also observed, suggesting a gradual reduction in resistance over cycling.

Unlike MO and MR, OG exhibits a sloping voltage profile in GCD curves with no distinct plateau, indicating a less defined redox transition of crystal structure. Its initial discharge capacity of 102 mAh g^{-1} is the lowest among the values of the four studied dyes with a drastic drop to 41 mAh g^{-1} in the second cycle, indicating the highly irreversible reactions. The CV curves of OG reveal a broad, irreversible cathodic peak at 2.11 V in the first cycle, suggesting the occurrence of irreversible reactions at this potential. Moreover, the decreasing peak intensities of the cathodic peaks at 1.83 V and 1.55 V and the anodic peak at 1.15 V in 2nd and 3rd cycles further confirm the fast loss of electrochemical activity. These results underscore its poor reversibility and electrochemical stability, making OG with the lowest overall performance.

CR presents dual sloping plateaus centered at 1.80 and 1.20 V in the first cycle galvanostatic discharge curve, along with a reversible sloping charge profile. The first discharge renders a capacity of 110 mAh g^{-1} . Unlike other dyes, CR exhibits an initial increase in discharge capacity from the first to third cycle, suggesting the presence of an activation process. This is also corroborated with its CV curves, where the cathodic peak observed in the first cycle at 1.80 V disappears, while other peaks gradually increase in intensity, indicating that several cycles are required to fully activate the CR cathode. Meanwhile, a broadening of the redox peaks in the CV curves is also observed upon cycling, suggesting high internal resistance and sluggish

charge transfer kinetics that lead to delayed electrochemical stabilization.

To further evaluate the long-term stability of the four azo dye cathodes, galvanostatic cycling tests were conducted at 30 mA g^{-1} (Figure 3.3a) and 150 mA g^{-1} (Figure 3.3b), respectively. At 30 mA g^{-1} , MO exhibits an initial discharge capacity of 164 mAh g^{-1} and the best cycling stability among the four cathodes, with a discharge capacity of 87 mAh g^{-1} and capacity retention of 52.7% at the 50th cycle. Its CE value is well maintained at about 100% over cycling, signifying the highly reversible redox reaction. Both MR, with the highest initial discharge capacity of 176 mAh g^{-1} , and CR, with an activated discharge capacity of 130 mAh g^{-1} , experience faster capacity fading upon cycling with the capacity retention of only 31.4% and 39.2%, respectively, at the 50th cycle, suggesting more severe dissolution of active materials and/or irreversible reactions. OG displays the lowest capacity throughout the cycling, indicating its poor charge storage capability. Meanwhile, MR exhibits overcharging behavior with CE in the range of 113–133%, while CR and OG undergo over-discharge with CE within 86.5–99.4%. These overcharging/over-discharging conditions may induce structural degradation and irreversible side reactions, which contribute to their faster capacity fading and reduced long-term stability.

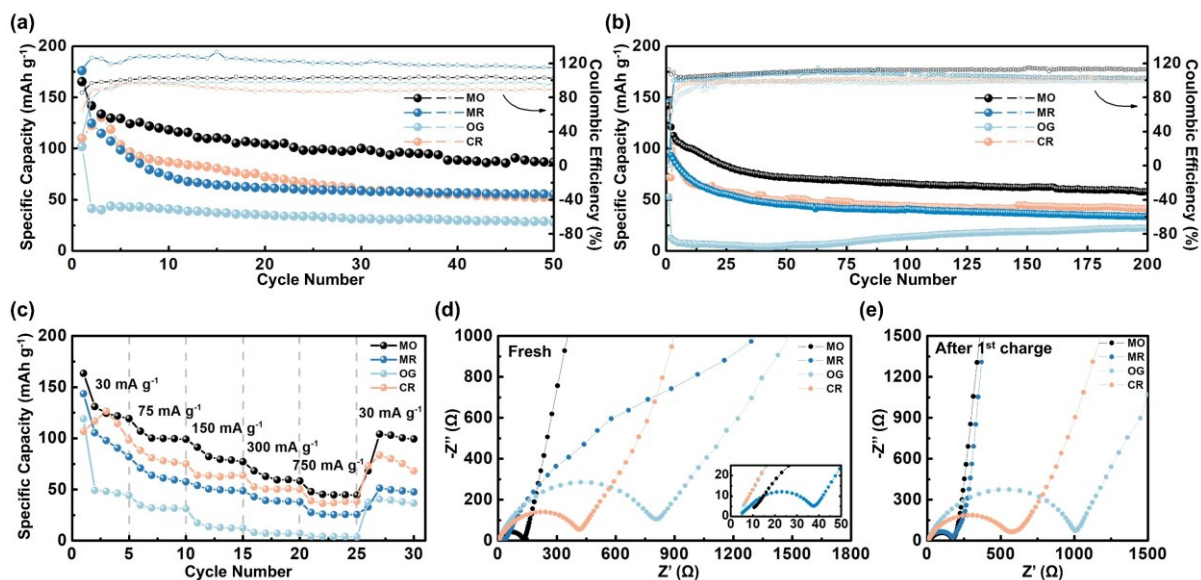


Figure 3.3. Cycling performance and impedance analysis of azo dye-based electrodes: (a,b) discharge capacity and CE versus cycle number at current density of (a) 30 mA g^{-1} and (b) 150 mA g^{-1} ; (c) discharge capacity at current densities ranging from 30 mA g^{-1} to 750 mA g^{-1} ; (d) Nyquist plots of four fresh batteries; (e) Nyquist plots of four batteries after 1st charge.

At the higher current density of 150 mA g^{-1} , MO also demonstrates the best performance among

the four dyes, with the highest capacity retention of 40.7% (58 mAh g^{-1}) after 200 cycles. However, it can also be noted that the CE of MO gradually increases to exceed 100% upon cycling, indicating the overcharging behavior that potentially affects its long-term stability. MR (33 mAh g^{-1} and 23.1% of retention at 200th cycle) and CR (41 mAh g^{-1} and 38.1% of retention at 200th cycle) show more severe capacity decay at this rate, indicating that increased charge/discharge rate leads to higher polarization and diffusion limitations. Moreover, OG fails to sustain any significant capacity at this rate, further confirming its poor electrochemical kinetics.

As shown in [Figure 3.3c](#), the rate performances of the four azo dye cathodes have been examined at current densities ranging from 30 mA g^{-1} to 750 mA g^{-1} . As the current density increases, all dyes exhibit a decline in specific capacity due to increased polarization and limited ion diffusion. However, MO consistently outperforms the other dyes across all applied current densities and demonstrates a significant capacity recovery when the current density is returned to 30 mA g^{-1} , also suggesting its high structural stability and redox reversibility.

To further elucidate the charge transfer kinetics and internal resistance of the electrodes, we compare Nyquist plots of the fresh and charged cathodes in [Figure 3.3d](#) and [e](#), respectively. The semicircle in the high-frequency region represents the charge transfer resistance (R_{ct}), while the inclined line in the low-frequency region corresponds to ion diffusion. In fresh and charged cathodes, MO exhibits a moderate semicircle, with a steep slope in the low-frequency region, suggesting good ion transport, consistent with its superior electrochemical performance. Although the fresh MR cathode displays the smallest semicircle, implying the lowest R_{ct} among four dyes, the lithiated MR after 1st charge shows similar semicircle and slope as MO. But its rapid capacity decay suggests that the irreversible reaction and/or severe dissolution into electrolyte rather than electronic resistance is the primary limitation. Relative to MO, OG and CR present significantly larger semicircles and smaller slopes of the inclined line, confirming their much higher R_{ct} and reduced ion transport. These correlate with their low capacity and poor rate performance as shown above.

Overall, a comparison of the electrochemical performances of all four dyes reveals that MO exhibits the most stable and well-defined electrochemical performance, with high reversibility, cycling stability, and efficient charge transfer kinetics. MR and CR demonstrate moderate performances but suffer from fast capacity fading. OG, with its highest resistance and poorest electrochemical stability, shows the worst performance. Therefore, these results highlight MO

as a cost-effective and promising azo dye-based cathode material, making it a strong candidate for potential organic battery applications. A subsequent study in the following sections has thus been focused exclusively on MO.

3.3.2. Reaction mechanism of MO

To better understand the electrochemical reaction mechanism of MO, the intermediate products formed during a GCD cycle have been systematically characterized.

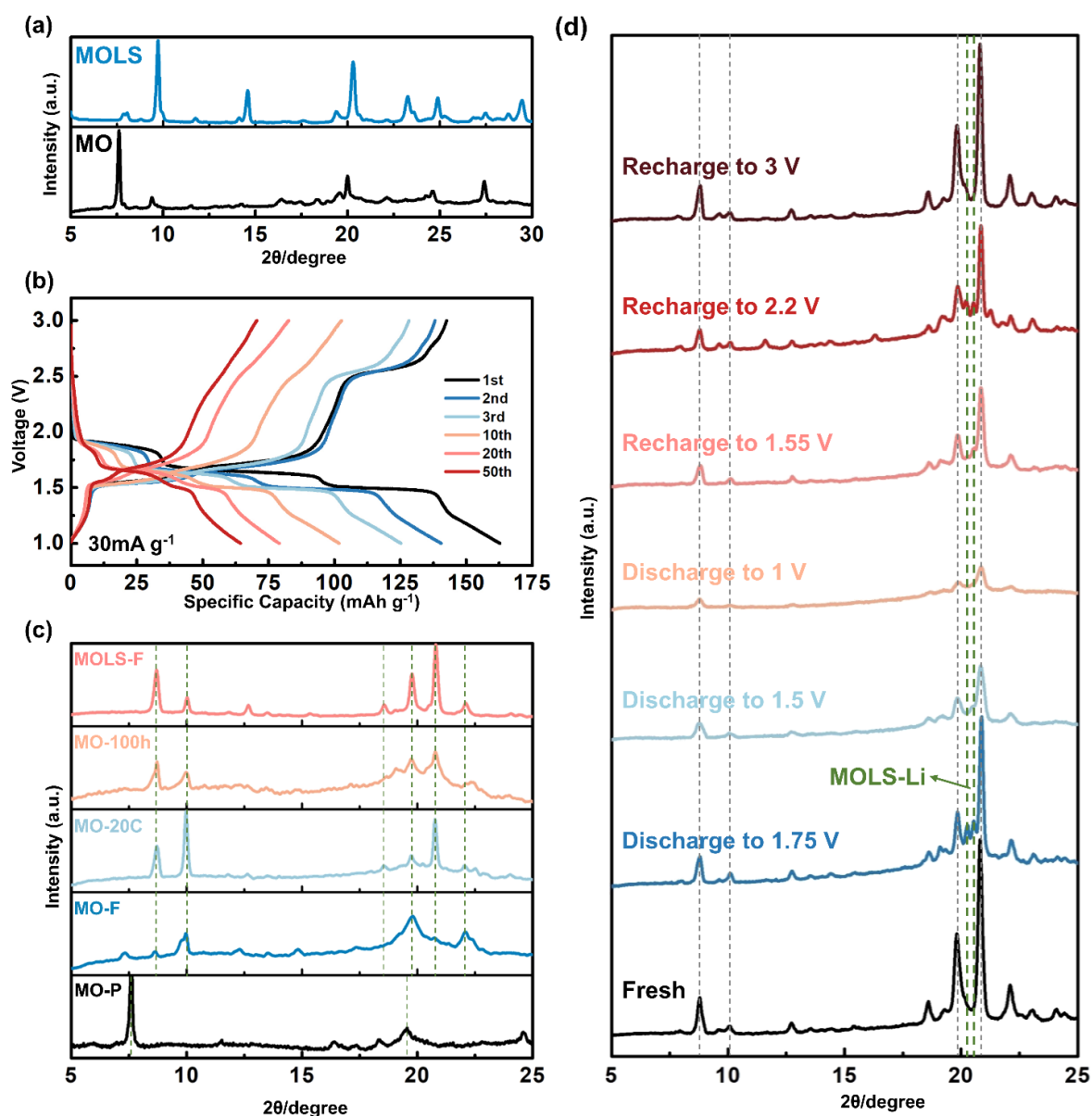


Figure 3.4. (a) XRD patterns of MO and MOLS powders; (b) GCD curves of MOLS cathode at a current density of 30 mA g^{-1} ; (c) XRD patterns of MO-F, MO-20C, MO-100h, and MOLS-F electrodes; (d) *ex situ* XRD patterns of MOLS electrode at different stages of the first GCD cycle at 30 mA g^{-1} .

In GCD curves of MO ([Figure 3.2a](#)), the persistent presence of voltage plateaus at fixed voltages upon cycling indicates that MO undergoes reversible redox reactions at the corresponding voltages, resulting in changes to its crystalline phase. Nevertheless, one can also observe changes in the length of each plateau upon cycling. For instance, during the first discharge, the two discharge regions (3–1.5 V with the two short plateaus and 1.5–1 V with the long plateau and a sloping line) contribute specific capacities of 47 and 118 mAh g⁻¹, respectively, with corresponding relative contributions of 28.6% and 71.4% towards the total discharge capacity. In subsequent cycles, the proportion of capacity contribution by the high-voltage discharge region gradually increases, while that of the low-voltage region decreases. At the 50th cycle, these corresponding proportions are 52.8% and 47.2%. A similar trend of change can also be observed in the charging curves.

We attribute this phenomenon to the gradual structural changes in the MO cathode during cycling, likely caused by the gradual ion exchange of Na⁺ ion with Li⁺ ion that leads to the formation of MOLS. To verify this hypothesis, we have synthesized MOLS through ion exchange and confirmed its purity via IC ([Figure S3.2](#)). As shown in [Figure 3.4a](#), the XRD pattern of MOLS exhibits distinct differences compared to that of MO in terms of diffraction peak positions and intensities, indicating a change in crystal phase after ion exchange.

We have assembled half-cells with MOLS as cathode and have conducted GCD tests at 30 mA g⁻¹ (see [Figure 3.4b](#)). The plateau voltages of MOLS well match those of the MO cathode. The capacity proportions of the two discharge regions (3.0–1.5 V and 1.5–1.0 V) in the first cycle are 56.7% and 43.3%, respectively. These two proportions remain similar throughout cycling, with corresponding values of 55.2% and 44.8% at the 50th cycle. These proportion values are close to the corresponding values of the MO electrode at the 50th cycle.

We further compare in [Figure 3.4c](#) the XRD patterns of MO pristine electrode (MO-P), MO fresh electrode obtained right after cell fabrication (MO-F), MO electrode after 20 cycles of GCD testing at 30 mA g⁻¹ (MO-20C), MO electrode after resting for 100 h without charge/discharge (MO-100h), and MOLS fresh electrode (MOLS-F). Except for MO-P, all other electrodes were disassembled from respective coin cells with/without testing. Compared to MO raw material, MO-P shows an evident broadening of the peak at 19.5° and significantly reduced intensity of peaks at 9.4° and 20.0°. This suggests a decrease in the crystallinity of MO after mixing with conductive carbon. After assembling into batteries, MO-F exhibits a significant reduction in the intensity of the diffraction peaks at 7.6° and 19.6°, and appearance

of new peaks at 8.6° , 10.0° , 19.8° and 22.1° compared with MO–P. This distinct difference can be attributed to the change in crystal lattice upon the adsorption of electrolyte molecules within the MO electrode.^[296] The same phenomenon can also be observed in MOLS–F, which exhibits new diffraction peaks at 8.6° , 10.0° , 19.8° , 20.8° and 22.1° , confirming the impact of electrolyte infiltration on the XRD pattern of the electrode. We also find that MO–100h electrode shows almost identical diffraction peaks as MOLS–F electrode. This indicates the occurrence of ion exchange in the absence of electrochemical discharge/charge, turning MO in the electrode to MOLS. Moreover, MO–20C electrode also exhibits almost identical diffraction peaks as MOLS–F, confirming that ion exchange occurs during electrochemical cycling. These observations collectively suggest that during cycling and resting, MO undergoes a structural transformation toward MOLS phase through ion exchange.

We have subsequently investigated the reversible transformation of the crystal structure of the MOLS electrode during the discharge-charge process through a detailed *ex situ* XRD study at different voltages during a GCD cycle at 30 mA g^{-1} (Figure 3.4d).

From the MOLS fresh electrode to the discharged states at 1.75 V, the main diffraction peaks at 8.6° , 10.0° , 19.8° , and 20.8° exhibits slight weakening, and two new peaks emerge at 20.3° and 20.6° , which may be attributed to the monolithiated MOLS (MOLS–Li) phase. Upon further discharge to 1.5 V, the characteristic peaks of MOLS–Li significantly weaken, possibly suggesting that the MOLS–Li intermediate is further reduced to form the dilithiated MOLS (MOLS–2Li) phase. After further discharging to 1.0 V, the MOLS–Li peaks fully disappear.

Subsequently, as the cathode is charged to 1.55 V and 2.2 V, the MOLS–Li peaks at 20.3° and 20.6° reappear, mirroring the changes observed during discharge. Upon a full charge back to 3.0 V, the MOLS–Li peaks disappear, and the electrode shows all the peaks seen with the fresh electrode. These *ex situ* XRD results support the reversible transformation of the MOLS crystal structure during the charge–discharge process.

To further study the redox process, we have also conducted *ex situ* Raman, FTIR, and XPS studies on the MO electrodes at different voltage states during the GCD cycle at 30 mA g^{-1} . In the Raman spectra (Figure 3.5a), the fresh MO electrode shows the characteristic peak centered at 1450 cm^{-1} for azo group. When it is gradually discharged to 1.0 V, the peak weakens and a new peak appears at 1293 cm^{-1} , which is attributable to dilithiated azo group (Li–N–N–Li).^[38] Upon the gradual recharge to 3.0 V, the new peak at 1293 cm^{-1} weakens and then disappears at

3.0 V, confirming the reversible redox reaction between the azo group and lithium ions.

In the FTIR spectra of the pristine MO electrode (Figure 3.5b), bands attributed to the sulfate group are detected in the range of 1250–1000 cm^{-1} .^[297,298] These bands are well retained throughout the discharge and charge processes, indicating that the sulfonate group in MO does not participate in the redox reaction with lithium ion. Furthermore, the low specific capacity ($< 10 \text{ mAh g}^{-1}$) of the cell employing NaTs as the active cathode material (Figure S3.3) further corroborates that sulfonate group is not electrochemically active within the voltage window of 3.0–1.0 V. The band located at 1366 cm^{-1} corresponds to the $\nu(\text{N}=\text{N})$ vibration, while bands at 1606 and 1519 cm^{-1} are attributed to $\nu(\text{C}=\text{C})$ vibrations in aromatic rings.^[298] Additionally, the bands at 1444 and 1415 cm^{-1} are assigned to $\nu(\text{CH}_3)$ vibrations.^[297] Notably, as the voltage is lowered from the pristine state to 1.0 V, the intensity of the azo band gradually decreases and nearly vanishes at 1.0 V. Simultaneously, a new peak emerges at 1337 cm^{-1} and progressively intensifies. During the subsequent delithiation process, as the voltage increases to 3.0 V, the azo band recovers while the peak at 1337 cm^{-1} diminishes. Throughout the entire cycle, the positions and intensities of peaks corresponding to other functional groups remain unchanged, demonstrating that the reversible redox reaction primarily involves the $\text{N}=\text{N}$ group, despite the appearance of more than two charge–discharge plateaus.

Theoretical investigations by DFT calculations reveal a similar trend in the IR simulation results for the molecular structures of MO, MO–Li, and MO–2Li (Figure 3.5c,d and Figure S3.4). Using the SMD model with DE as solvent, which provides the best agreement with experimental results, the simulated IR spectrum of MO shows bands at 1607 and 1515 cm^{-1} corresponding to $\nu(\text{C}=\text{C})$ vibrations in benzene ring and a band at 1360 cm^{-1} attributed to the $\nu(\text{N}=\text{N})$ vibration, and bands between 1200 and 1020 cm^{-1} arise from sulfonate groups. These findings are in excellent agreement with the experimental FTIR spectrum of the fresh and recharged electrodes. Upon lithiation to form MO–Li, DFT predicts a partial shift of the $\nu(\text{N}=\text{N})$ band to lower frequencies, reflecting the reduction of the azo group. However, due to the coexistence of multiple species at intermediate states (e.g., 1.75 V), the signature of MO–Li is not clearly resolved in the *ex situ* FTIR spectra. Further lithiation to MO–2Li leads to a more pronounced red-shift of the $\nu(\text{N}=\text{N})$ band to 1332 cm^{-1} in the simulated spectrum, corresponding to the lithiated azo motif. This is consistent with the experimental observation of a new band at 1337 cm^{-1} in the fully discharged state, alongside the diminishing 1366 cm^{-1} peak. These results confirm a gradual transformation of the azo functionality upon stepwise

lithium insertion, and the close agreement between simulated and experimental spectra supports the proposed redox mechanism.

Ex situ XPS measurements have also been performed on MO electrodes at various voltage states. Using the C 1s peak at 284.8 eV as a reference for binding energy calibration, we have focused on the N 1s spectrum to track changes in the chemical environment of the nitrogen-containing functional groups. [Figure 3.5e](#) shows the N 1s XPS spectra of MO electrodes at different voltage states during a GCD cycle at 30 mA g⁻¹. Initially, the pristine electrode exhibits two primary peaks in the N 1s spectrum. The peak at 399.8 eV is attributed to the dimethyl amino group (–N(CH₃)₂),^[299] while the peak at 400.5 eV corresponds to the azo group (N=N),^[36] which shows the electrochemical activity. Upon discharging to 1.75 V, significant changes are observed in the N 1s spectrum. Relative to the peak arising from the amino group, the intensity of the azo (N=N) peak at 400.5 eV decreases markedly, indicating a partial reduction of the azo group. Simultaneously, a new peak emerges at 399.2 eV, representing the lithiated azo group (Li–N–N–Li). The position of the new peak is consistent with those in previously reported spectra for lithium azide,^[300] supporting the hypothesis that lithiation occurs through the addition of lithium ions to the azo group. Further discharging to 1.0 V amplifies the intensity of the Li–N–N–Li peak while the azo peak almost disappears, suggesting a nearly complete reduction of the azo group to the lithiated form. This progression confirms that the nitrogen atoms in the azo group are the primary active site for the redox reaction.

During the subsequent charging steps, the reversibility of this reaction can be clearly observed. At 1.55 V, the N=N peak begins to recover as the Li–N–N–Li peak diminishes. By the end of the charge cycle at 3.0 V, the intensity of the N=N peak returns to nearly the same level as that of the pristine state and the Li–N–N–Li peak nearly completely disappears. Furthermore, the area ratio of the N=N peak to the C–N peak at 3.0 V closely matches that of the pristine electrode, confirming that the redox reaction is reversible and no significant degradation of the azo group occurs during cycling.

Furthermore, XPS analysis provides evidence for the formation of SEI during the first cycle. As shown in [Figure S3.5](#), after recharging to 3.0 V, the O 1s spectrum of the electrode exhibits distinct changes. In addition to the characteristic –SO₃⁻ signal at 532.2 eV originating from the sulfonate group,^[301,302] a new peak appears at 533.3 eV, which is assigned to C–O bonding environments of (CH₂CH₂O)_n. These poly(ethylene oxide) segments are organic-rich SEI components formed via the decomposition of ether-based electrolytes.^[303,304] This observation

supports that the low initial CE arises from SEI formation.

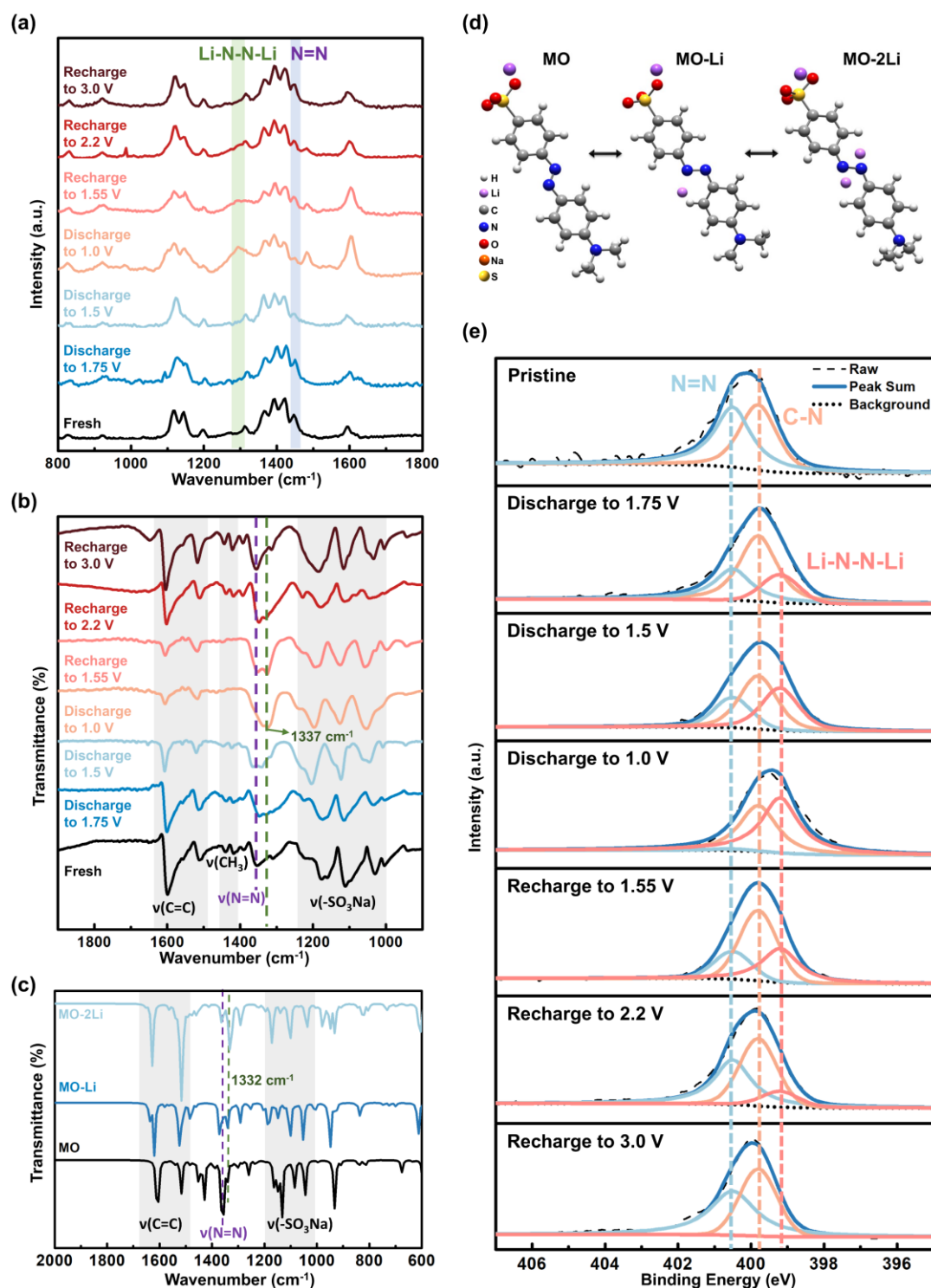


Figure 3.5. Analysis of reaction mechanism with *ex situ* spectroscopic techniques: (a) Raman; (b) FTIR; (c,d) simulated Infrared (IR) spectra and molecule structures of MO, MO–Li, and MO–2Li from b3lyp/6-31+g(d,p) DFT calculations in implicit solvent modeled using SMD (DE) solvation model; (e) N 1s XPS spectra of MO electrodes at different discharge-charge voltages.

The XPS results align with the trends observed in the *ex situ* Raman and FTIR results. However,

the observation of multiple discharge/charge plateaus in the GCD curves raises questions. Ideally, a two-electron reaction should exhibit one or two distinct voltage plateaus corresponding to the stepwise reduction of the azo group. But in the experimental GCD curves, three distinct plateaus and a sloped region have been observed during discharge. The appearance of multiple electrochemical platforms for MO can be explained by the coexistence and distinct behaviors of its *E* (trans) and *Z* (cis) isomers.^[305]

The isomerization around the azo (N=N) bond creates two forms with significantly different geometries: the planar *E* isomer, which is thermodynamically more stable, and the bent *Z* isomer, which exhibits steric strain.^[306] This structural difference translates into distinct electronic environments, influencing their electrochemical properties. For example, CV studies have shown that azobenzene *Z* isomers typically require slightly more negative potentials (a shift of 60 mV in the cathodic direction) for the first electron reduction compared to its *E* counterpart, reflecting the higher energy state and lower electron affinity of *Z* form.^[307] The difference leads to distinct redox potentials and provides a rational explanation for the multiple plateaus observed in the GCD curves of MO.

3.3.3. MO@BP2000 composite

With its reversible redox reaction, MO shows its potential as an organic cathode material. However, its electrochemical performance in terms of cycling stability and rate capability still requires significant improvement. To address these challenges, we have been inspired by the sulfur cathode design in lithium-sulfur batteries and have encapsulated MO within BP2000 porous carbon.^[308] This encapsulation approach is expected to suppress the solubilization of the organic material in electrolytes, enhance conductivity through improved contact between MO and carbon, and ultimately increase the utilization efficiency of the active material. Compared to MOLS, MO offers better cycling performance and lower cost, making it a more suitable precursor. An MO@BP2000 composite with a mass ratio of 1:1 has been synthesized via a solution infusion method.

The TGA results shown in [Figure 3.6a](#) compare the thermal behavior of MO and MO@BP2000, along with pure BP2000 and an equi-mass physical mixture of MO and BP2000, MO+BP2000. For pure MO, a total weight loss of 73.2% at 800 °C is observed, reflecting significant thermal decomposition. As an azo dye with a rigid aromatic backbone, MO undergoes degradation primarily through bond cleavage, including its azo (N=N) bond and functional groups such as

sulfonate ($-\text{SO}_3$) and methyl groups ($-\text{CH}_3$).^[309] These processes generate intermediate carbonaceous fragments that resist volatilization and instead undergo carbonization, leaving behind solid residues. This behavior is characteristic of aromatic compounds with high thermal stability. For MO+BP2000, the total weight loss is reduced to 34.5%, consistent with the 1:1 mass ratio of MO to BP2000. BP2000, as a porous carbon material known for its high thermal stability, has no significant weight loss up to 800 °C. The thermal decomposition of MO in the mixture follows a pathway similar to that of pure MO. Relative to MO+BP2000, MO@BP2000 composite exhibits a reduced weight loss of 27.4%, indicating enhanced thermal stability due to the confinement effect.

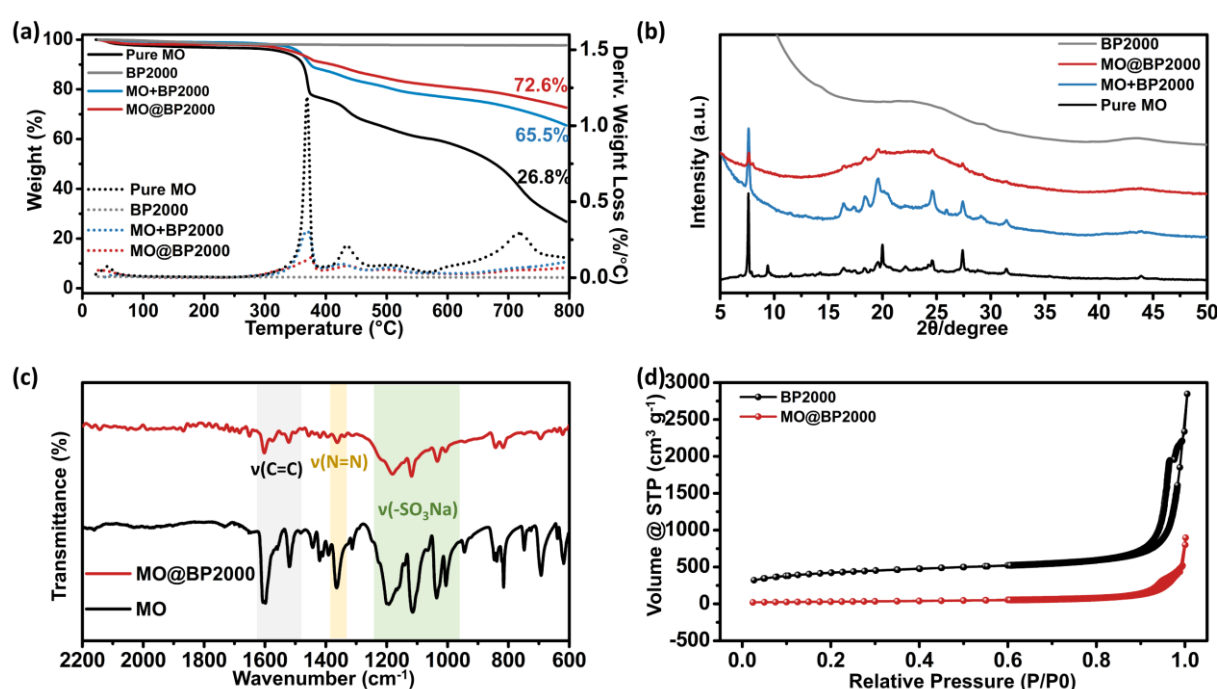


Figure 3.6. Characterizations of MO@BP2000: (a,b) TG, DTG curves, and XRD pattern in comparison with those of pure MO and MO+BP2000 mixture (w/w: 1/1); (c) FTIR spectrum in comparison with that of pure MO; (d) N₂ sorption isotherm in comparison with that of BP2000.

The XRD patterns (Figure 3.6b) provide insights into the structural integration of MO with BP2000 porous carbon. For MO@BP2000, its diffraction peaks corresponding to MO are significantly reduced in intensity and sharpness compared to those observed in the MO+BP2000. This suggests a decrease in the crystallinity of MO, which can be attributed to the dispersion and confinement of MO molecules within the pores of BP2000. The confinement disrupts the long-range periodicity of MO crystals, leading to a more amorphous-like structure. In addition to the changes with MO diffraction peaks, the broad diffraction peak centered

around 24° , which is characteristic of the amorphous carbon structure of BP2000, becomes more prominent in MO@BP2000. This also indicates the successful embedding of MO into the carbon matrix, where MO molecules are well-dispersed and integrated with the amorphous carbon framework. Such structural integration improves the interaction between MO and BP2000, which contributes to boosting conductivity and mitigating the solubilization of MO during electrochemical cycling. Notably, the positions of the diffraction peaks corresponding to MO remain unchanged after encapsulation, confirming that the encapsulation process does not alter the intrinsic crystal structure of MO.

The FTIR spectrum (Figure 3.6c) provides critical evidence for the preservation of the molecular structure of MO after encapsulation into BP2000. Although all characteristic absorption bands of MO, including the stretching vibration of the azo bond (N=N) at 1366 cm^{-1} , the symmetric and asymmetric stretching vibrations of the sulfonate group ($-\text{SO}_3\text{Na}$) near $1250\text{--}1000\text{ cm}^{-1}$, and the aromatic C=C vibrations around 1600 cm^{-1} , are still observable, their intensities are markedly reduced. This attenuation is attributed to the strong confinement effect and surface interactions with the porous carbon matrix.^[310,311]

The nitrogen sorption isotherm of MO@BP2000 (Figure 3.6d) offers further insights into the structural integration of MO within BP2000. The pristine BP2000 exhibits a Type IV isotherm, with a high specific surface area of $1525\text{ m}^2\text{ g}^{-1}$ and a pore volume of $2.87\text{ cm}^3\text{ g}^{-1}$. These values highlight its highly porous nature and suitability as a mesoporous host material for MO encapsulation. In contrast, MO@BP2000 demonstrates dramatic reductions in both specific surface area ($112\text{ m}^2\text{ g}^{-1}$) and pore volume ($0.67\text{ cm}^3\text{ g}^{-1}$), indicating that the majority of pores in BP2000 have been filled with MO molecules during the solution infusion process.

The morphology of the four samples was examined under optical microscopy at $400\times$ magnification (Figure S3.6). Pristine MO appears as distinct orange crystalline particles, consistent with its high crystallinity. In contrast, pure BP2000 shows dark, irregular aggregates, reflecting significant particle agglomeration, typical of high-surface-area carbon materials. In the physical mixture (MO+BP2000), MO crystals remain clearly visible and are distributed among the surrounding carbon clusters. However, in the MO@BP2000 composite, no obvious MO crystals can be observed. Instead, the sample exhibits a more uniform and finely dispersed morphology, accompanied by a noticeable reduction in BP2000 agglomeration. These features, consistent with TGA, XRD, BET, and FTIR analyses, indicate that the encapsulation process facilitates intimate mixing and effective confinement of MO within the porous carbon network,

resulting in a well-integrated composite structure.

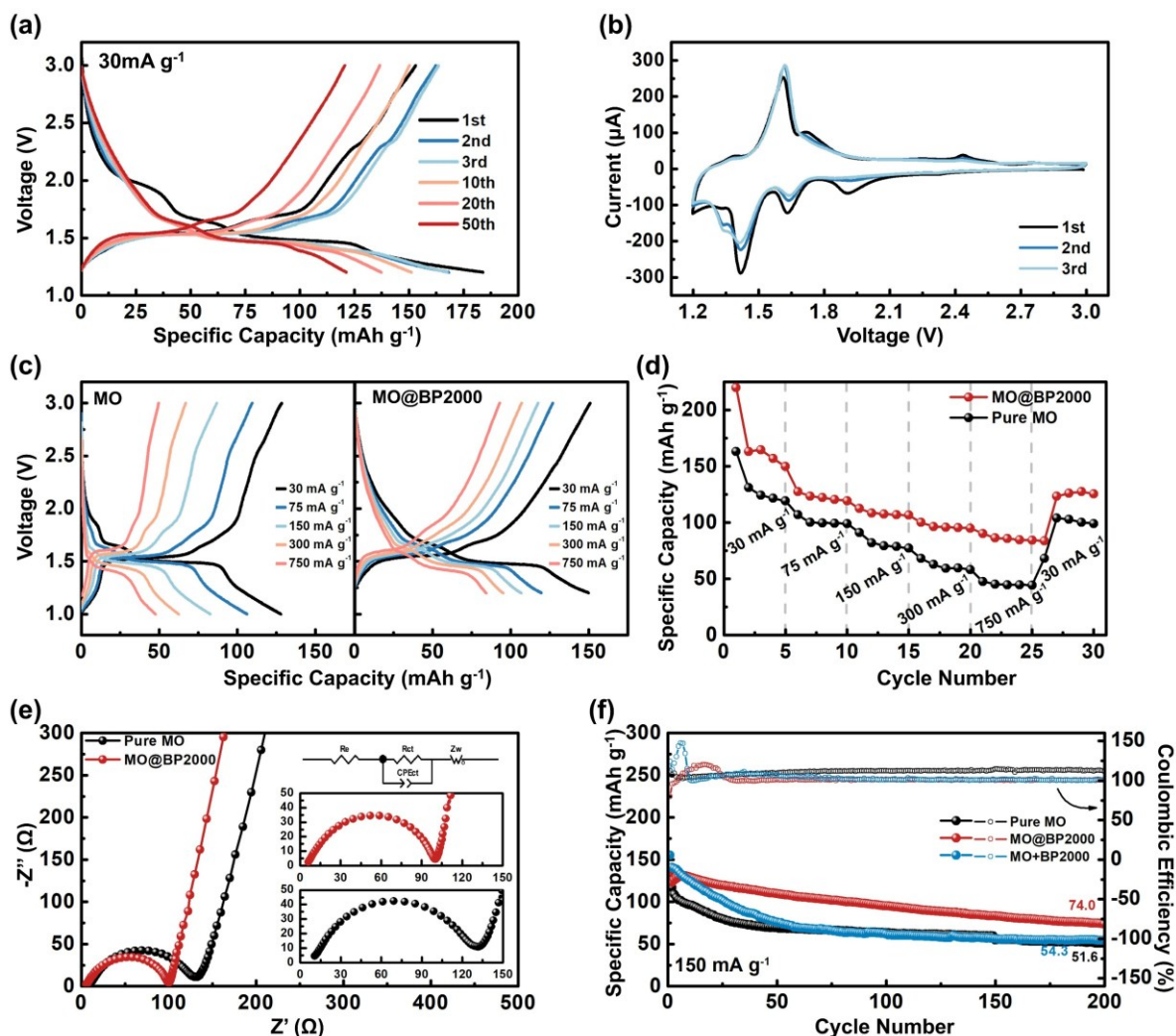


Figure 3.7. Electrochemical performance of MO@BP2000 as cathode material in LIBs : (a) GCD curves at 30 mA g⁻¹ within 1.2–3.0 V versus Li⁺/Li; (b) first three cycles of CV curves at 0.1 mV s⁻¹; (c) GCD curves and (d) rate performance at various current densities (30–750 mA g⁻¹); (e) comparative Nyquist plots of 2-electrode cells of MO@BP2000 and pure MO tested at open circuit potential after 3 GCD cycles at 30 mA g⁻¹ with the inset showing their high-frequency regions and equivalent circuit; (f) cycling performance with discharge capacity and CE versus cycle number at 150 mA g⁻¹.

The electrochemical performance of MO@BP2000 as a cathode material for LIBs has been investigated within the narrower range of 3.0–1.2 V using coin cells paired with a lithium metal anode in 1.0 M LiTFSI dissolved in DOL/DME (Figure 3.7). This voltage range was chosen to minimize side reactions and eliminate potential capacitive contributions from BP2000 at lower voltages. As shown in Figure 3.7a, at a current density of 30 mA g⁻¹, MO@BP2000 cathode exhibits two sloping plateaus at 1.99 and 1.70 V, respectively, during the first discharge,

followed by a long flat plateau at 1.48 V. These correspond to the three plateaus observed for the pure MO cathode, reflecting its multi-step redox reactions at the azo group. The sloping nature of the plateaus for MO@BP2000 indicates reduced crystallinity due to the dispersion of MO within the porous BP2000 matrix. The CV curves (Figure 3.7b) further corroborate this observation, showing a prominent cathodic peak at 1.37 V and two smaller peaks at 1.64 V and 1.80 V, while a single anodic peak at 1.61 V dominates the charge process. Compared to pure MO, the discharge voltages for MO@BP2000 are higher, while the charge voltages are lower, indicating improved electrode kinetics.

During the first discharge, MO@BP2000 delivers a high specific capacity of 183 mAh g⁻¹, exceeding that of the pure MO cathode and the theoretical value. The formation of the SEI is identified as a major contributor to the excessive discharge capacity, in addition to the higher utilization efficiency of MO and the minor charge storage contribution from BP2000. In the subsequent charge process, a reversible capacity of 153 mAh g⁻¹ is achieved, with the irreversible portion ascribed to SEI formation, as evidenced by the 83.3% initial CE. In subsequent cycles, the reversible capacity remains within the theoretical limit and gradually declines upon cycling, while the CE increases to over 96% and quickly approaches 100%. After 50 cycles, a reversible capacity of 121 mAh g⁻¹ is retained, which is significantly higher than that of pure MO (87 mAh g⁻¹).

The rate capability of MO@BP2000 was evaluated across various current densities, and the results are shown in Figure 3.7c and d. At an initial current density of 30 mA g⁻¹, MO@BP2000 still exhibits extra discharge capacity in the first cycle, while the reversible capacity stabilizes at 162 mAh g⁻¹ (Figure S3.8), indicating the formation of the SEI layer. As the current density increases, the voltage gap between the discharge and charge plateaus for MO@BP2000 grows slightly, but consistently smaller than the corresponding ones of the pure MO electrode. Even at a high current density of 750 mA g⁻¹, MO@BP2000 retains a specific discharge capacity of 84 mAh g⁻¹, far superior to 48 mAh g⁻¹ of pure MO cathode. When the current density is reverted to 30 mA g⁻¹, a capacity of 128 mAh g⁻¹ is recovered, significantly higher than 104 mAh g⁻¹ achieved with pure MO electrode, demonstrating improved rate performance and structural stability.

These improvements are attributed to the enhanced conductivity of MO@BP2000 composite. The intimate contact between the conductive carbon matrix and the smaller-sized MO crystals reduces internal resistance and facilitates efficient electron transfer. Additionally, the abundant

pores in BP2000 significantly shorten the ion diffusion pathways, enabling rapid transport of lithium ions within the electrode.

The enhanced conductivity can be easily revealed by EIS results (Figure 3.7e). The Nyquist plots show a smaller equivalent series resistance (R_e) of 5.4 Ω and R_{ct} of 96.4 Ω for MO@BP2000, compared to 9.3 Ω and 116.9 Ω , respectively, for pure MO cathode. The reduced resistances highlight the role of conductive BP2000 matrix in facilitating charge transfer within the electrode and at the electrode/electrolyte interface.

Finally, as a critical performance for organic electrodes, the long-term cycling stability of MO@BP2000 is illustrated in Figure 3.7f. At 150 mA g⁻¹, the composite retains 80.7% of its initial capacity after 50 cycles and 54.5% after 200 cycles, far surpassing those (50.7% and 37.7%, respectively) observed for the pure MO electrode. The CE of MO@BP2000 stabilizes above 99% after the 30th cycle, while pure MO electrode shows overcharging with an increasing CE, which reaches 111.5% after 200 cycles. The enhanced cycling stability of MO@BP2000 is primarily attributed to the suppression of MO dissolution in the electrolyte, achieved through its encapsulation within BP2000. The encapsulation effectively preserves the active material and minimizes capacity degradation during prolonged cycling.

We have also tested the cycling performance MO+BP2000 electrode for the purpose of comparison. Although the capacity decay is somewhat mitigated with a capacity retention of 49.0% after 50 cycles, its performance shows no significant difference relative to pure MO electrode after 100 cycles. This suggests that simple physical mixing with carbon is insufficient to resolve the core issue of MO dissolution in the electrolyte. In contrast, the successful encapsulation of MO within BP2000 proves to be an effective strategy by addressing the dissolution problem and stabilizing the active material.

3.4. Conclusions

In this study, we have employed MO as a representative, commercially available azo dye to investigate the redox chemistry and electrochemical behavior of azo-based organic cathode materials for lithium-ion batteries. Systematic electrochemical and structural analyses confirm that the azo group in MO acts as the active site for reversible lithiation/delithiation. Among the group of azo dyes (MO, MR, OG, and CR) screened herein, MO demonstrates the best electrochemical performance, including high reversibility, stable cycling performance, and efficient charge transfer kinetics. However, the dissolution of MO in the electrolyte results in

capacity fading and limited long-term stability. To overcome these challenges, MO has been encapsulated within BP2000 conductive porous carbon to form the MO@BP2000 composite. This encapsulation strategy effectively renders suppressed dissolution, enhanced conductivity, and stabilized electrode structure, leading to significant improvements in electrochemical performance. MO@BP2000 exhibits an initial discharge capacity of 183 mAh g^{-1} at 30 mA g^{-1} , with 121 mAh g^{-1} maintained after 50 cycles, far surpassing the performance of pure MO. Moreover, rate capability and cycling stability have also been significantly enhanced, confirming the effectiveness of the BP2000 encapsulation strategy. Overall, this work not only elucidates the redox mechanism of azo-based cathodes but also provides valuable guidance for the future molecular design of azo-based organic cathode materials.

Chapter 4. Revealing the electrochemical evolution of nitroso-to-azo cathodes for lithium-ion storage

This chapter is adapted from a manuscript titled *Revealing the electrochemical evolution of nitroso-to-azo cathodes for lithium-ion storage*, published in *Journal of Energy Chemistry* by Ximeng Zhang, Jay Nejad, and Zhibin Ye. Ximeng Zhang contributed to conceptualization (with Professor Ye), experimental work, methodology design, computation, data analysis, curation, drafting, and visualization. Professor Zhibin Ye oversaw supervision, conceptualization, project management, methodology, validation, manuscript revision, and funding. Jay Nejad participated in data interpretation and provided critical feedback to refine the study's framework and conclusions.

Abstract

In this paper, aromatic nitroso compounds are investigated for their electrochemical performance as organic cathodes for lithium-ion batteries, with an elucidation of their redox mechanism. For the first time, *ex situ* spectroscopic analyses of small-molecule mono-nitroso compounds (including nitrosobenzene, 2-nitrosotoluene, 4-nitrosobenzoic acid, and lithium 4-nitrosobenzoate) reveal a universal, irreversible transformation of their nitroso dimers to azo species during the first electrochemical cycle, establishing azo groups as the true redox-active centers. Unlike small-molecule analogues that convert rapidly, polymeric 1,4-dinitrosobenzene (DNSB) evolves gradually through azoxy intermediates, accompanied by increased conjugation and enhanced structural stability. To enhance utilization efficiency and cycling stability, DNSB is encapsulated in porous carbons (BP2000, Ketjenblack) via solution infusion, yielding composites with a high initial capacity of 383 mAh g⁻¹ and a stable reversible capacity of 102 mAh g⁻¹ after 800 cycles at 150 mA g⁻¹. Electrochemical impedance spectroscopy confirms reduced charge-transfer resistance and improved interfacial stability. This work uncovers the fundamental nitroso-to-azo conversion mechanism and demonstrates a scalable carbon-confinement strategy to construct durable polymeric azo-type organic electrodes from nitroso compounds for sustainable energy storage.

4.1. Introduction

The increasing demand for sustainable and high-performance lithium-ion batteries (LIBs) has spurred significant interest in organic electrode materials as alternatives to transition-metal-based inorganic cathodes. Organic materials offer advantages such as synthetic tunability, structural diversity, and the use of earth-abundant, environmentally benign elements.^[273–277] Among various redox-active functional groups, carbonyl-based compounds, including quinones, carboxylates, and anhydrides, have been most extensively studied due to their well-defined two-electron redox mechanisms and moderate stability.^[27,211,279–281,312] Other functional groups, such as imine,^[164,165,313] organosulfur,^[168,283] nitro,^[35,37,314] and azo,^[36,38] have also shown promise in delivering reversible redox activity and tunable electrochemical properties.

Despite this progress, current research remains focused on a narrow range of chemical motifs, while many potentially redox-active groups remain underexplored. Among them, aromatic nitroso compounds represent a unique and promising class that has received little attention in the context of energy storage. Their distinct $\text{N}=\text{O}$ functionality imparts strong polarity and versatile chemical reactivity, offering opportunities to access redox processes beyond those of carbonyl or azo systems. In the solid state, nitroso groups often associate with each other through reversible dimerization to form azodioxide linkages, giving rise to rigid, planar assemblies stabilized by intermolecular interactions and extended conjugation.^[315,316] This structural organization reduces molecular mobility and solubility, which are critical challenges for organic electrode materials. This tendency is further reinforced in dinitroso-derivatives, frequently leading to polymeric frameworks with enhanced mechanical robustness and lower solubility compared to small-molecule analogues.^[317,318] Moreover, a substitution on the aromatic ring provides a wide chemical space for tuning electronic structure, redox potential, and solubility.^[314,319] Taken together, these features suggest that nitroso compounds can not only serve as structurally versatile molecular platforms but also offer unexplored redox chemistry distinct from conventional nitro or carbonyl systems.

In this present work, a range of aromatic nitroso compounds has been systematically investigated for their electrochemical performance as cathode materials in LIBs, including monomeric nitroso compounds (nitrosobenzene (NSB), 2-nitrosotoluene (NST), 4-nitrosobenzoic acid (NSBA), and its lithium salt, lithium 4-nitrosobenzoate (LiNSBA)) and polymeric 1,4-dinitrosobenzene (DNSB). Through *ex situ* Fourier-transform infrared (FTIR), Raman, and X-ray photoelectron spectroscopy (XPS) techniques, the redox mechanisms of

these aromatic nitroso compounds have also been revealed. Lastly, polymeric DNSB has been encapsulated within porous conductive carbons, and the resulting composite cathode materials have been thoroughly characterized for their electrochemical performance, with significantly improved properties demonstrated. As the first study revealing the electrochemical redox chemistry of aromatic nitroso compounds as organic cathode materials, this work offers the mechanistic insight into the effective design of high-performance organic cathodes for LIBs.

4.2. Experimental

4.2.1. Chemicals and materials

NST (97%), dichloromethane (ACS reagent), oxone, 1.0 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate/dimethyl carbonate solution (EC/DMC, 50/50 (v/v), battery grade), *n*-hexane (ACS reagent), hydrogen peroxide (H₂O₂, Certified ACS, 30%), hydrochloric acid (HCl, ACS reagent, 37%), lithium hydroxide (LiOH, 98%), toluene (ACS reagent), Nafion (5 wt% in a mixture of lower aliphatic alcohols and water), ethanol (ACS reagent), lithium bis(trifluoromethane)sulfonimide (LiTFSI, 99.95%), chloroform-*d* (CDCl₃), dimethyl sulfoxide-*d*₆ (DMSO-*d*₆), and deuterium oxide (D₂O) were obtained from Aldrich and used as received. NSB (98.0%+), *p*-benzoquinone (*p*-QDO, 95%), and 4-aminobenzoic acid (4-ABA, 99.0%+) were obtained from Fisher and used as received. 1,3-Dioxolane (DOL, 99.9%, Aldrich) and dimethoxyethane (DME, 99.5%, Aldrich) were dried and stored over 4 Å molecular sieves before use. Super-P carbon black (IMERYS Graphite & Carbon, Belgium), BP2000 porous carbon (Cabot), Ketjenblack EC600JD conductive carbon black (KB, analytical grade, MSE Supplies), and Celgard 2400 separator (Celgard LLC) were used as received. Deionized (DI) water was prepared using a Milli-Q purification system. An ethylene-olefin-copolymer (EOC) elastomer, Engage 8130, was obtained from Dow Chemical and was used as the binder for cathodes.

4.2.2. Synthesis of NSBA and LiNSBA

NSBA was first prepared based on the synthetic route in the literature.^[320] An aqueous solution of oxone (8.97 g in 45 mL, 14.6 mmol) was added to a solution of 4-ABA (1.0 g, 9.3 mmol) in CH₂Cl₂ (12 mL), and the suspension was vigorously stirred at room temperature for 1 h. The precipitated product, NSBA, was isolated by filtration, washed with H₂O, and dried. Proton nuclear magnetic resonance (¹H NMR, 300 MHz, DMSO-*d*₆) analysis shows signals at δ 8.25 (d, *J* = 8.6 Hz, 1H) and 8.03 (d, *J* = 8.5 Hz, 1H). LiNSBA was prepared as follows: 200 mg of

NSBA was dispersed in 20 mL of ethanol with 33.4 mg of LiOH powder. The solution was stirred at room temperature for 48 h. Then the solution was filtered to collect the precipitate. The precipitation (LiNSBA) was washed with ethanol and dried in a vacuum oven at 100 °C overnight. All materials were characterized with ^1H NMR (see [Figure S4.1](#) for the spectrum).

4.2.3. Synthesis of DNSB

DNSB was prepared as follows. A suspension consisting of 1.38 g (10 mmol) of *p*-QDO in 10 mL of DI water was heated under stirring to 55 °C and poured into 2.17 g (22 mmol) of concentrated HCl (37%). Under these conditions, 1.25 g of H_2O_2 solution (11 mmol) was added dropwise within 30 min. The resulting precipitate was filtered and washed with cold water three times. The obtained product was washed with ethanol and dried in a vacuum oven at 60 °C for 24 h. To further purify the product, the dried solid was subjected to vacuum sublimation at 110 °C, during which the vapor was directed onto a surface maintained at 0 °C. Upon condensation, the crystalline solid, DNSB, was collected from the cold surface.

4.2.4. Synthesis of DNSB@BP2000 and DNSB@KB

To encapsulate DNSB within the porous carbon, 150 mg of ground DNSB and carbon (BP2000 or KB) at a mass ratio DNSB: carbon = 2:1 were dispersed in 15 mL of toluene and stirred at 80 °C for 24 h. Then the hot suspension was gradually evaporated under a fume hood for 48 h, followed by drying in the oven at 100 °C for 24 h, obtaining DNSB@BP2000 or DNSB@KB.

4.2.5. Materials characterizations

Raman spectra were recorded on a Fergie spectrometer (Princeton Instruments) upon excitation with a 532 nm laser. FTIR spectra were obtained on a Thermo Scientific Nicolet 6700 Analytical FTIR spectrometer. XPS measurements were undertaken on a Thermo Scientific Theta Probe XPS spectrometer with a monochromatic Al K_α X-ray source at a spot area of 400 μm . Thermogravimetric analysis (TGA) was performed on a Q50 TGA from TA Instruments. ^1H NMR spectra of the copolymers were obtained on a Bruker 300 Hz spectrometer at the ambient temperature. Deuterated solvents (CDCl_3 , $\text{DMSO-}d_6$, and D_2O) were used for NMR measurement. Optimization for each structure was performed by density functional theory (DFT) with the B3LYP functional and 6-311G+(d,p) basis sets in the Gaussian 09 program. The calculations on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) diagrams were conducted on the fixed geometries.

4.2.6. Electrochemical measurements

To fabricate electrodes with NSB, NST, NSBA, and LiNSBA, a mixture of the ground active material, Super-P conductive carbon, and EOC binder at a weight ratio of 53:37:10 was mixed in *n*-hexane to form a homogeneous slurry. For DNSB and its composites (DNSB@BP2000, DNSB@KB), the electrode slurries were prepared with the desired conductive carbon and Nafion binder dissolved in ethanol. The weight ratio of DNSB/carbon material/binder was maintained at 53/37/10. Electrodes were prepared by casting the slurry onto carbon-coated Al foil disks at an active material loading of about 1.33 mg cm^{-2} (total active material mass was $\sim 2 \text{ mg}$ per electrode). Due to the high volatility of NSB and NST at room temperature, their electrodes must be used immediately after preparation and drying for 30 min at room temperature. The other electrodes were dried in the oven at 60°C for 24 h before use. For all electrodes, CR2025-type coin cells were assembled with a lithium metal as the anode and a double-layer Celgard 2400 as the separator. Galvanostatic charge-discharge (GCD) tests of the cells were undertaken on a battery testing system (Land, CT2001A, China). Cyclic voltammetry (CV) curves were recorded on Metrohm Autolab PGSTAT128N electrochemical workstation at a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were performed on a Metrohm Autolab PGSTAT128N electrochemical workstation from 100 kHz to 0.01 Hz with an alternating current amplitude of 5 mV. EIS data analysis was performed by using Zview (Version v3.1, USA). For *ex situ* FTIR, Raman, and XPS characterizations of cathodes during charge and discharge, coin cells discharged/charged to different voltages were disassembled in an argon-filled glove box. Each cathode was tested under the protection of an argon atmosphere.

4.3. Results and discussions

4.3.1. Mono-nitroso aromatics in dimer form

NSB, the simplest aromatic nitroso compound, exists predominantly as a *cis*-dimer in air (Figure 4.1a). This structural form is confirmed by FTIR, which exhibits characteristic absorption bands at 1403 and 1392 cm^{-1} , attributed to the symmetric and asymmetric N→O stretching vibrations of the *cis*-dimer configuration, respectively (Figure 4.1b).^[320–323] The (O)N=N(O) bond length within the dimer is $1.327 \text{ \AA}$ (Figure 4.1c),^[324] an intermediate value between a typical N–N single bond ($1.447 \text{ \AA}$ in hydrazine) and N=N double bonds observed in azoxy and azo compounds ($1.265 \text{ \AA}$ in *p*-methyloxybenzene, $1.247 \text{ \AA}$ in azomethane),^[325–327]

reflecting the partial double-bond character.

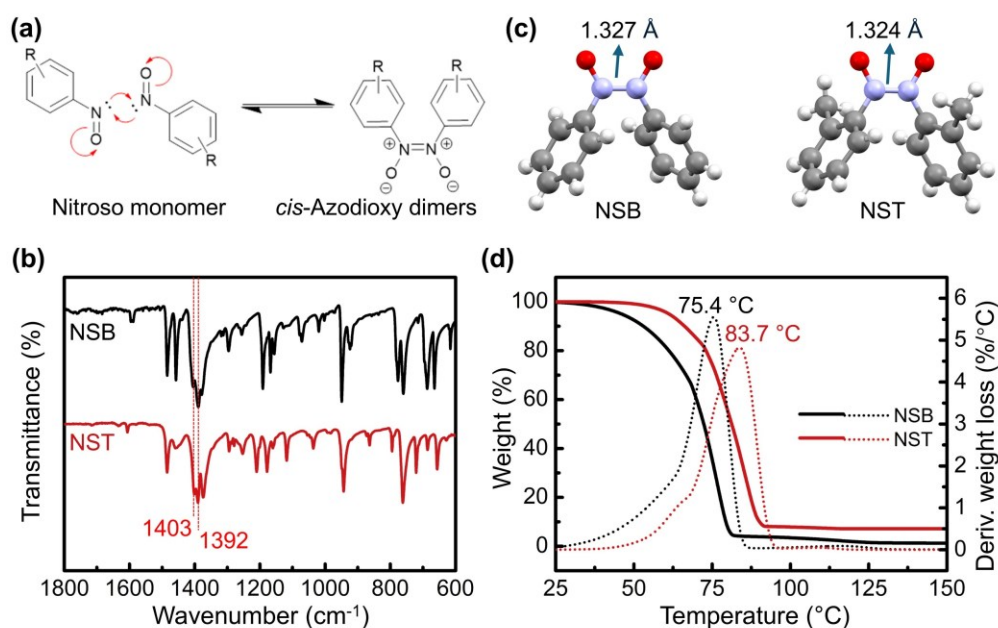


Figure 4.1. (a) Illustration of dimerization of NSB and NST (R=H, 2-CH₃); (b) FTIR spectra, (c) calculated molecular structures, and (d) comparative TGA curves of NSB and NST.

Compared to NSB, NST introduces an *ortho*-substituted methyl group. Like NSB, NST also crystallizes in the solid state as a *cis*-dimer, as evidenced by its FTIR spectrum (Figure 4.1b), which shows characteristic peaks at 1403 and 1392 cm⁻¹ corresponding to the *cis*-dimeric structure. The N–N bond length in its azodioxy group is 1.324 Å (Figure 4.1c),^[328] which is comparable to that of the NSB dimer and falls within the range between a typical N–N single bond and an N=N double bond. Moreover, the introduction of the methyl substituent enhances the thermal stability of NST relative to NSB, as evidenced by an increase in the peak weight-loss temperature from 75.4 °C for NSB to 83.7 °C for NST in the TGA results (Figure 4.1d).

The electrochemical performances of NSB and NST have been evaluated using coin-type half-cells assembled with lithium metal as the anode and either 1 M LiPF₆ in EC/DMC or 1 M LiTFSI in DOL/DME as the electrolyte. In cells with LiPF₆-EC/DMC electrolyte (Figure 4.2a), the first galvanostatic discharge of NSB at 50 mA g⁻¹ displays two flat voltage plateaus at 2.57 and 1.87 V within a voltage window of 1.6–3.8 V, indicating a two-step lithium insertion process. The initial discharge capacity reaches 185 mAh g⁻¹, falling short of the theoretical capacity of 250 mAh g⁻¹ based on a two-electron transfer per NSB dimer. The observed capacity corresponds to approximately 74% of active material utilization, primarily due to the easy dissolution of NSB in the electrolyte (see Figure S4.2). This solubility issue also leads to a low

initial Coulombic efficiency (CE) of 50.5%.

Nevertheless, two well-defined charge plateaus centered at 3.30 and 3.58 V are observed during the initial charging process, corresponding to a reversible two-electron oxidation, in agreement with the preceding discharge behavior. From the second cycle onward, the distinct two-step behavior disappears, giving way to a single lithiation plateau centered at around 1.87 V with the corresponding delithiation plateau at 2.72 V, followed by a gradual slope. Meanwhile, the CE is markedly improved to over 90%, reflecting the establishment of a more stable and reversible redox process.

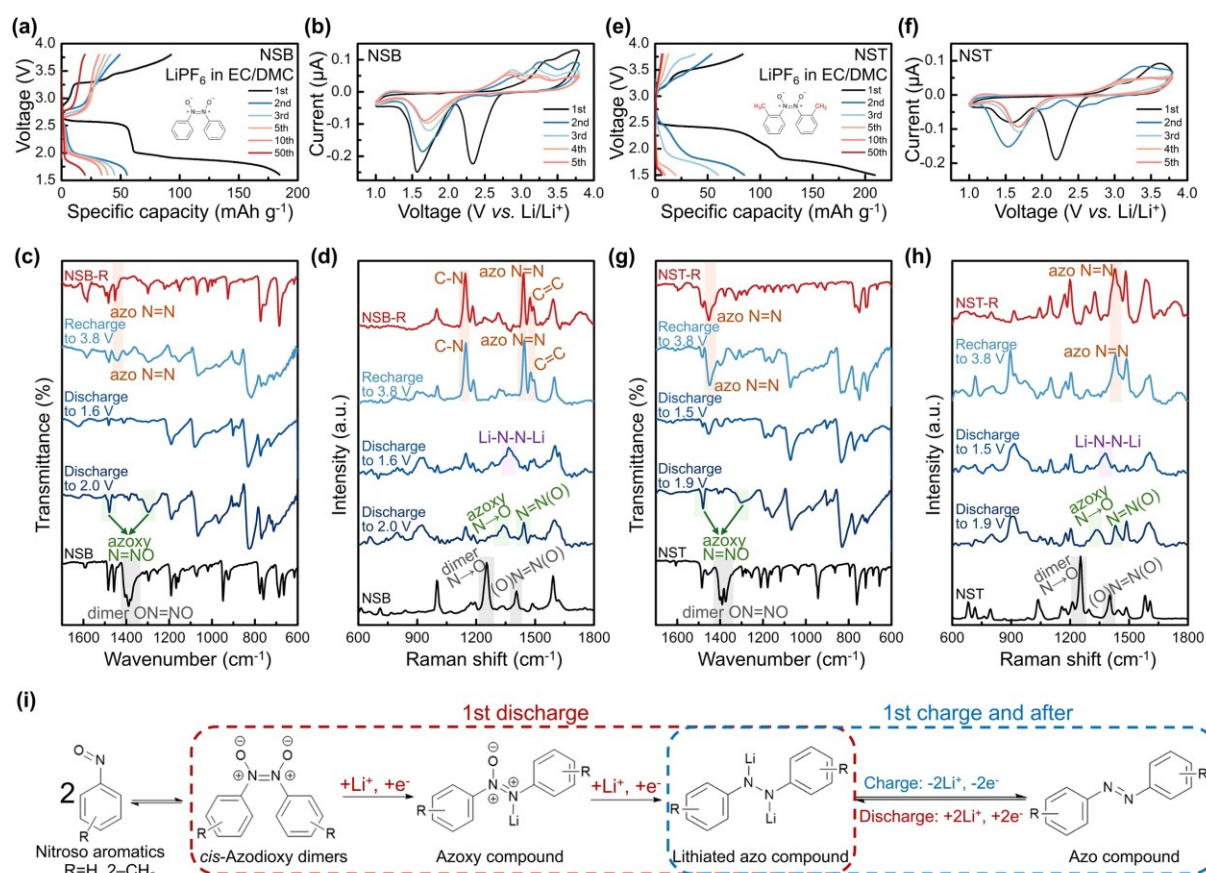


Figure 4.2. Electrochemical performance and *ex situ* characterizations of NSB and NST cathodes. (a,e) GCD curves at 50 mA g⁻¹ versus Li/Li⁺; (b,f) CV curves at 0.1 mV s⁻¹; (c,g) *ex situ* FTIR and (d,h) Raman spectra of the electrode samples at different discharge and charge states in the first cycle in comparison with the corresponding products obtained in compatibility test (Figures S4.4 and S4.6); (i) schematic illustration of the proposed reaction mechanism for lithiation/delithiation of NSB and NST.

CV supports these observations. At a scan rate of 0.1 mV s⁻¹, the first cathodic scan displays two cathodic peaks at 2.33 and 1.56 V (Figure 4.2b), corresponding to the two plateaus in the

first galvanostatic discharge curve. Analogous to GCD curves in the following cycles, only a single cathodic peak and two small anodic peaks remain in the CV curves. These changes resemble prior results on 4-nitrobenzoic acid lithium salt (NBALS), which irreversibly convert to an azo compound during the first cycle,^[36] thereby modifying the redox-active species in subsequent cycles.

To examine the effects of the electrolyte on its electrochemical performance, the NSB cathode was also tested in the LiTFSI-DOL/DME electrolyte. However, cells exhibited immediate failure after the 1st discharge (Figure S4.3a). This instability was traced to the chemical compatibility of dissolved NSB with lithium metal, which differs between electrolytes (Figure S4.4). In the LiPF₆-EC/DMC electrolyte, no visible change of lithium foil was observed even after 48 h of exposure to dissolved NSB. In contrast, in the LiTFSI-DOL/DME electrolyte, spontaneous and rapid reaction occurred, with precipitates formed on the surface of the lithium foil within a short period of time. These compatibility tests in the two electrolytes, simulating the in-cell environment, provide direct evidence that the failure of LiTFSI-DOL/DME-based cells with NSB cathodes originates from their poor compatibility.

To further elucidate the failure mechanism, the reaction precipitate deposited on the surface of lithium metal, identified as the reduction product of NSB in LiTFSI-DOL/DME electrolyte, was collected and purified by recrystallization (named as NSB-R). Its ¹H NMR spectrum (300 MHz, DMSO-*d*₆, Figure S4.5) shows characteristic aromatic proton signals at δ 7.89 (d, J = 6.4 Hz, 2H) and 7.59 (d, J = 6.5 Hz, 3H), which are consistent with the spectra of azobenzene in the literature.^[329,330] FTIR and Raman spectra (red curves in Figure 4.2c and d) provide further evidence for its composition. FTIR analysis of NSB-R shows the disappearance of the $\nu_{\text{dimer}}(\text{NO})$ peaks at 1403 and 1392 cm⁻¹, while a new band at 1451 cm⁻¹ appears, attributable to the $\nu_{\text{azo}}(\text{N}=\text{N})$ stretch of *trans*-azobenzene.^[331] Its Raman spectrum also confirms this conversion, with the loss of azodioxy-dimer-associated $\nu_{\text{dimer}}(\text{NO})$ and $\nu_{\text{dimer}}(\text{N}=\text{N})$ bands at 1253 and 1405 cm⁻¹, respectively.^[36] New peaks emerge at 1143, 1440, and 1472/1492 cm⁻¹, corresponding to $\nu_{\text{azo}}(\text{CN})$, $\nu_{\text{azo}}(\text{N}=\text{N})$, and $\nu_{\text{azo}}(\text{CC})$ stretching vibrations, respectively, which are characteristic of *trans*-azobenzene.^[332] These results, together with the visual compatibility test (Figure S4.4), confirm that NSB undergoes spontaneous reduction to azobenzene (NSB-R) upon contact with lithium metal in LiTFSI-DOL/DME, whereas no such spontaneous reaction is observed in LiPF₆-EC/DMC. This raises the question of whether the same reduction occurs electrochemically in a cell with LiPF₆-EC/DMC, even though it does not proceed spontaneously

in this electrolyte. To address this and further probe the reaction mechanism, *ex situ* FTIR and Raman analyses were performed on NSB cathodes involving LiPF₆-EC/DMC electrolyte, and the results, along with those for NSB-R, are presented in [Figure 4.2c](#) and [d](#).

As seen in [Figure 4.2c](#) and [d](#), after discharge to 2.0 V (the first plateau), the characteristic signals of the azodioxide group in both spectra diminish, indicating the reduction by lithium. Meanwhile, in the FTIR spectra, a pair of new peaks emerges at 1479 and 1301 cm⁻¹, assigned to the asymmetric N=N→O (or mainly $\nu_{\text{azoxy}}(\text{N}=\text{N})$) stretching and symmetric N=N→O (or mainly $\nu_{\text{azoxy}}(\text{NO})$) stretching vibrations, respectively.^[333,334] In the Raman spectra, a pair of new peaks appears at 1440 and 1336 cm⁻¹, which are assigned to the N=N and N→O vibrations of the azoxy group, respectively.^[335,336] These observations suggest the formation of azoxy species at this stage. As the discharge proceeds further to 1.5 V, the azoxy-related peaks disappear from both spectra. Although no new FTIR peaks are clearly observed, a distinct Raman band emerges at 1370 cm⁻¹, which can be attributed to the formation of a lithiated azo (Li-N-N-Li) species.^[36,38] Upon subsequent charging, new features corresponding to the azo group appear in both the FTIR (1451 cm⁻¹) and Raman (1440 cm⁻¹) spectra. Additionally, the Raman spectrum exhibits bands that well match the characteristic $\nu_{\text{azo}}(\text{CN})$, $\nu_{\text{azo}}(\text{N}=\text{N})$, and $\nu_{\text{azo}}(\text{CC})$ vibrations of *trans*-azobenzene (or NSB-R) in both position and intensity.^[331,332] Together, these findings suggest that NSB undergoes an irreversible conversion to azobenzene during the first discharge-charge cycle. This transformation accounts for the transition of plateaus in GCD profiles and redox peaks in CV curves from the first to the second cycle, as the resulting azo species becomes the actual redox-active center in subsequent cycles. Accordingly, although the formation of the reduced azo species (NSB-R) in the presence of lithium metal in LiPF₆-EC/DMC is not spontaneous, such species is still formed during the electrochemical discharge/charge in a cell.

The electrochemical behavior of NST resembles that of NSB. As shown in [Figure 4.2e](#), when tested in LiPF₆-EC/DMC electrolyte, the first GCD cycle exhibits two discharge plateaus centered at 2.41 and 1.72 V, respectively, along with a pronounced charge plateau at 3.55 V. The initial discharge capacity reaches 209 mAh g⁻¹, approaching its theoretical value of 221 mAh g⁻¹. However, due to its high solubility in the electrolyte ([Figure S4.6](#)) and the occurrence of irreversible reactions, the initial CE is limited to 40.2%. From the 2nd cycle, the voltage profiles gradually evolve into a single discharge plateau at 1.75 V, and a sloping charge curve was centered at 3.51 V, accompanied by a rapid capacity fade. In the first CV scan, there are

two cathodic peaks at 2.19 and 1.55 V and an anodic peak at 3.61 V, corresponding well to the respective GCD plateaus. In the second cycle, the two-step discharge feature disappears, and the CV profile evolves into a single cathodic peak at 1.54 V and an anodic peak at 3.40 V, indicating a change in the redox mechanism. In the following cycles, the CV curves exhibit improved reversibility, with the cathodic peak stabilized at 1.68 V and an anodic response consistently maintained above 3.05 V.

When LiTFSI-DOL/DME electrolyte is used, NST-based cells also undergo inevitable failure after the first discharge ([Figure S4.3b](#)), which is attributed to the quick dissolution of NST and the spontaneous reaction of dissolved NST with the lithium metal anode in LiTFSI-DOL/DME electrolyte, as evidenced in [Figure S4.6](#). To further understand this degradation pathway, the reaction product (denoted as NST-R) formed on the surface of lithium metal after 168 h was characterized with ^1H NMR ([Figure S4.7](#)), FTIR, and Raman spectroscopies ([Figure 4.2g](#) and [h](#)). In pristine NST, characteristic azodioxide vibrations are observed at $1403/1392\text{ cm}^{-1}$ in the FTIR spectrum, and at 1253 cm^{-1} ($\nu_{\text{dimer}}(\text{NO})$) and 1401 cm^{-1} ($\nu_{\text{dimer}}(\text{N}=\text{N})$) in the Raman spectrum. These signals are substantially weakened in NST-R, while new peaks emerge at 1453 cm^{-1} in FTIR and 1426 cm^{-1} in Raman, assigned to the $\nu_{\text{azo}}(\text{N}=\text{N})$ vibration. These spectral changes confirm the spontaneous chemical reduction of NST into an azo compound in the compatibility test with lithium foil in LiTFSI-DOL/DME electrolyte, which ultimately leads to the failure of the cell.

The electrochemical transformation of NST was further investigated with two aims: to probe its reaction mechanism and to examine whether it proceeds electrochemically to the same product in $\text{LiPF}_6\text{-EC/DMC}$ electrolyte as it does spontaneously in LiTFSI-DOL/DME. To this end, *ex situ* FTIR and Raman analyses of NST electrodes in a $\text{LiPF}_6\text{-EC/DMC}$ cell were carried out and compared with those of NST-R ([Figure 4.2g](#) and [h](#)). Given its structural similarity to NSB, NST is expected to follow a comparable electrochemical redox pathway. As it is illustrated in [Figure 4.2g](#) and [h](#), upon discharge to 1.9 V, the characteristic peaks associated with the azodioxide group disappear, accompanied by the emergence of azoxy-related signals at 1479 cm^{-1} ($\nu_{\text{azoxy}}(\text{N}=\text{N})$) and 1304 cm^{-1} ($\nu_{\text{azoxy}}(\text{NO})$) in the FTIR spectrum and at 1335 cm^{-1} ($\nu_{\text{azoxy}}(\text{NO})$) and 1430 cm^{-1} ($\nu_{\text{azoxy}}(\text{N}=\text{N})$) in the Raman spectrum. When the discharge proceeds further to 1.5 V, these azoxy peaks disappear in both spectra, while a new Raman band appears at 1370 cm^{-1} , which is assigned to the Li-N-N-Li species. Upon charging to 3.8 V, the Li-N-N-Li signal vanishes in the Raman spectrum, whereas new peaks corresponding to the $\nu_{\text{azo}}(\text{N}=\text{N})$

vibration emerge in both FTIR and Raman spectra, consistent with those observed in chemically reduced NST-R. These results collectively confirm that NST undergoes an irreversible transformation into an azo compound during the first electrochemical cycle. This transformation explains the electrochemical behavior in subsequent cycles, where the resulting azo species functions as the redox-active material. Based on the results above, we propose the electrochemical reduction mechanism for NSB and NST in LIBs in [Figure 4.2i](#).

Additionally, comparative DFT calculations were conducted for NSB and NST ([Figure S4.8](#)) to elucidate the impact of *ortho*-methyl substitution on their electrochemical behavior. Although NSB and NST exhibit similar HOMO energy levels (-5.88 and -5.89 eV, respectively), the LUMO energy of NSB (-2.34 eV) is lower than that of NST (-2.09 eV). A lower LUMO level implies a higher tendency to undergo reduction, thereby facilitating electron injection into NSB at a higher reduction potential.^[337] As a result, in the first discharge, NSB shows a higher discharge plateau in the GCD profile and a more positive cathodic peak in the CV curve compared to NST in [Figure 4.2](#). Furthermore, NSB exhibits a narrower energy gap ($E_{\text{gap}} = 3.54$ eV) than NST ($E_{\text{gap}} = 3.80$ eV), suggesting a lower energy barrier and higher electronic conductivity according to molecular orbital theory.^[338,339] This accounts for the smaller voltage gap between the discharge and charge plateaus in the first cycle of NSB, indicating reduced polarization.

Based on electrochemical investigations on NSB and NST, we have found that, although both compounds are comparatively more stable in $\text{LiPF}_6\text{-EC/DMC}$ electrolyte than in LiTFSI-DOL/DME electrolyte, both compounds suffer from severe dissolution that leads to capacity fading. The *ortho*-methyl substitution in NST does not alleviate this issue, indicating that steric modification alone is insufficient. As previously discussed, high solubility is a major limitation of organic electrode materials,^[14,21] whereas introducing polar functional groups, such as carboxylates, has been shown to enhance intermolecular interactions and reduce solubility.^[27] Following this strategy, we introduced $-\text{COOH}$ and $-\text{COOLi}$ groups into NSB, yielding NSBA and LiNSBA, respectively, to improve cycling stability. NSBA was oxidized from 4-ABA, while LiNSBA was synthesized via neutralization of NSBA with LiOH in aqueous solution. The disappearance of the OH band at 1180 cm^{-1} in the Raman spectrum of NSBA, together with the shift of the carbonyl band from 1700 cm^{-1} in NSBA to 1613 cm^{-1} in LiNSBA in FTIR spectra, confirms the successful conversion ([Figure S4.9](#)).^[340,341] Additionally, the FTIR band at 1260 cm^{-1} for NSBA indicates a *trans*-dimer structure,^[327] which disappears after lithiation,

while a strong new band corresponding to the *cis* ON=NO configuration evolves at 1403 cm^{-1} in LiNSBA, suggesting a structural change upon salt formation. TGA (Figure S4.10a) shows that LiNSBA has a significantly higher decomposition temperature (435 $^{\circ}\text{C}$) than NSBA (196 $^{\circ}\text{C}$), indicating enhanced thermal stability and molecular polarity.^[342,343] Most importantly, the carboxylate substitution substantially reduces solubility in both electrolytes, outperforming both NSB and NST (Figure S4.10b). This markedly improves the compatibility of the materials with lithium anodes in both electrolytes, thereby enabling a direct comparison of their electrolyte-dependent behavior.

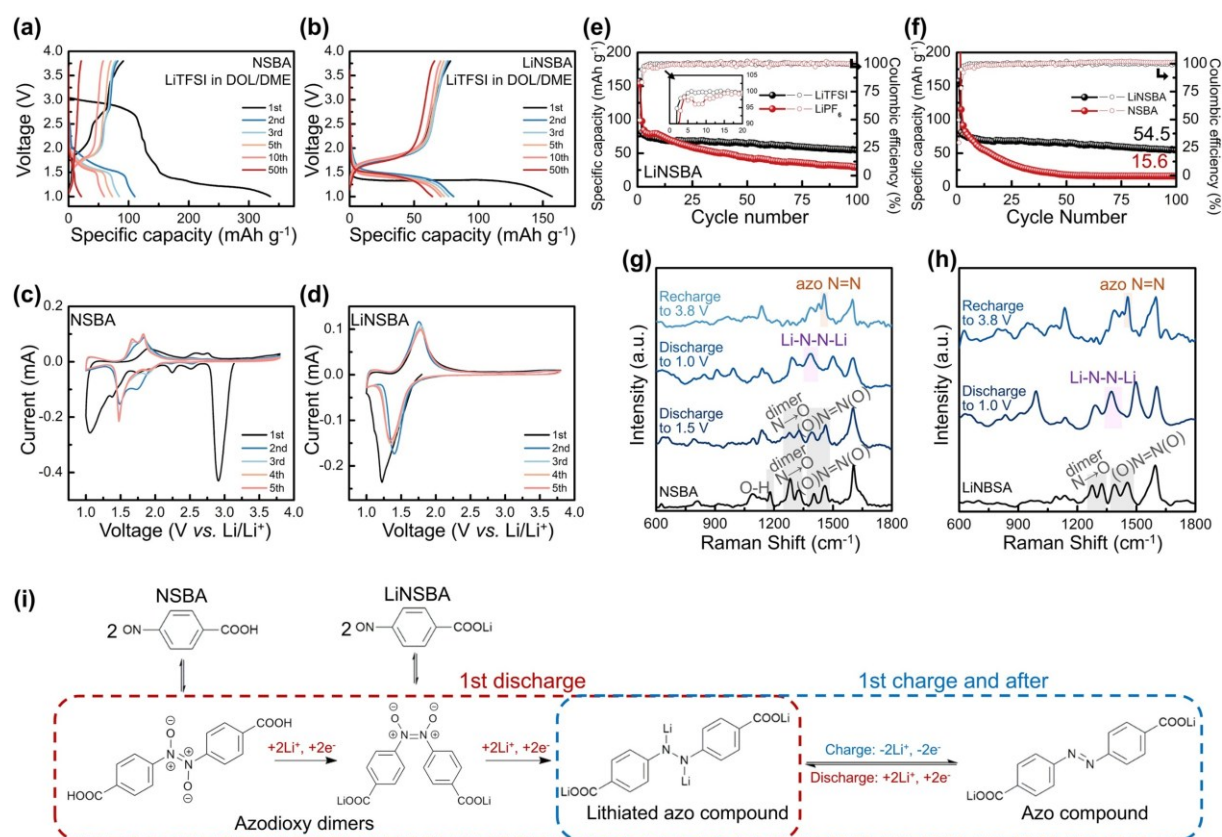


Figure 4.3. Electrochemical performance and *ex situ* characterizations of NSBA and LiNSBA cathodes. (a, b) GCD curves at 50 mA g^{-1} within 1.0–3.8 V vs. Li/Li⁺; (c, d) CV curves at 0.1 mV s^{-1} ; (e) cyclic performance and CE of LiNSBA cathode with different electrolytes at 50 mA g^{-1} ; (f) comparison of cyclic performance and CE of NSBA and LiNSBA cathodes in LiTFSI electrolyte at 50 mA g^{-1} ; (g, h) *ex situ* Raman spectra of the cathode samples at different discharge and charge states in the first cycle; (i) proposed electrochemical redox reaction mechanism for NSBA and LiNSBA.

The GCD curves of NSBA and LiNSBA cathodes in LiTFSI-DOL/DME electrolyte at 50 mA g^{-1} are compared (see Figure 4.3a and b). Importantly, both NSBA and LiNSBA exhibit

enhanced stability in LiTFSI-DOL/DME electrolyte compared with NSB and NST (their GCD curves are shown in [Figure S4.3](#)). NSBA delivers an initial discharge capacity of 336 mAh g⁻¹ with two distinct voltage plateaus at 2.93 and 1.21 V, respectively, corresponding to the insertion of 4 Li⁺ ions per dimer (2 Li⁺ ions per monomer), close to its theoretical capacity of 355 mAh g⁻¹. The plateau at 2.93 V disappears in the subsequent cycle, which can be attributed to the irreversible lithiation of the –COOH groups into –COOLi group.^[295] In contrast, LiNSBA exhibits an initial discharge capacity of only 157 mAh g⁻¹ with a single plateau at 1.33 V, indicating 2 Li⁺ insertion per dimer (1 Li⁺ per monomer). These results demonstrate that the introduction of two carboxylate substituents significantly alters the redox potentials, and apart from the lithiation plateau associated with the –COOH groups in NSBA, the overall reduction potentials are markedly lowered compared to those of NSB. This behavior is consistent with the observations reported by Luo et al. in an azobenzene system.^[38] During the first charge, NSBA and LiNSBA recover 91 and 78 mAh g⁻¹, respectively, corresponding to initial CEs of 27% and 50%, respectively. In subsequent cycles, their CEs both increase to above 95%, while the sloped lithiation/delithiation plateaus are retained at 1.44/1.75 V for NSBA and 1.55/1.80 V for LiNSBA.

Consistent with the GCD behavior, the CV curve of NSBA shows two distinct cathodic peaks at 2.91 and 1.05 V in the first scan ([Figure 4.3c](#)). The peak at 2.91 V corresponds to the lithiation of the –COOH groups, which does not appear in LiNSBA, where only a single cathodic peak at 1.22 V is observed in the first cycle. By comparing other peaks not associated with –COOH lithiation, it is evident that the reduction peaks shift to higher potentials in LiNSBA, which can be attributed to the presence of pre-introduced Li⁺ located on the non-conjugated carboxylate groups.^[344] In later cycles, NSBA displays a single cathodic peak at 1.47 V and a pair of closely spaced anodic peaks at 1.66 and 1.82 V, whereas LiNSBA displays a pair of stable redox peaks at 1.38/1.77 V. These results confirm that both NSBA and LiNSBA undergo structural transformation during cycling and demonstrate promising electrochemical behavior in LIBs.

We also compare the electrochemical performances of NSBA and LiNSBA cathodes in a LiPF₆-EC/DMC electrolyte, with the GCD profiles shown in [Figure S4.11](#). Notably, NSBA exhibits a significantly different behavior in LiPF₆-EC/DMC compared to that in LiTFSI-DOL/DME: only a single discharge plateau at 2.79 V is observed during the first cycle, without the second plateau or subsequent reversible cycling (see [Figure S4.11a](#)). In contrast, LiNSBA retains its characteristic charge-discharge profile in LiPF₆-EC/DMC, showing a single pair of sloping

lithiation/delithiation plateaus (see [Figure S4.11b](#)).

Overall, the GCD results demonstrate that modifying NSB to LiNSBA improves electrochemical performance in both electrolytes. First, in LiTFSI-DOL/DME, LiNSBA enables reversible charge-discharge cycling, whereas NSB fails after the first cycle. Second, in LiPF₆-EC/DMC, where NSB exhibits reversible cycling, LiNSBA delivers markedly enhanced stability ([Figure S4.11b](#) and [Figure 4.2a](#)). In this electrolyte, the capacity retention of LiNSBA reaches 50% after 10 cycles, significantly higher than NSB (18% after 10 cycles), indicating that carboxylate functionalization effectively mitigates dissolution-induced capacity fading. Thus, LiNSBA outperforms NSB in both electrolytes. To evaluate its long-term cycling performance in both electrolytes, extended cycling tests were conducted on LiNSBA cathodes in LiTFSI-DOL/DME and LiPF₆-EC/DMC. As shown in [Figure 4.3e](#), the long-term cycling performances of LiNSBA differ considerably between the two electrolytes. The initial discharge capacities are comparable: 157 mAh g⁻¹ in LiTFSI-DOL/DME and 153 mAh g⁻¹ in LiPF₆-EC/DMC. However, after 100 cycles at 50 mA g⁻¹, the capacity retention declines to 55 mAh g⁻¹ (35.0% retention relative to the 1st discharge and 68% relative to the 2nd, by which point most irreversible reactions are presumed to have occurred) in LiTFSI-DOL/DME and only 29 mAh g⁻¹ (18.9% relative to the 1st discharge and 30% relative to the 2nd) in LiPF₆-EC/DMC. Moreover, throughout the initial 15 cycles, the CE in LiPF₆-EC/DMC remains consistently lower than that observed in LiTFSI-DOL/DME. These observations can be attributed to the superior physicochemical properties of ether-based LiTFSI electrolytes, including stronger Lewis basicity, lower viscosity, better wettability, and higher ionic conductivity.^[109] Such features facilitate more stable solvation of Li⁺ ions, enhance electrode-electrolyte interfacial kinetics, and suppress irreversible side reactions, thereby improving electrochemical reversibility and cycling stability. Therefore, reducing the solubility of the active materials is essential to improve electrode compatibility and to take full advantage of advanced electrolyte systems.

Given the better cycling stability of LiNSBA in LiTFSI-DOL/DME electrolyte, we have further compared the cycling stability of NSBA and LiNSBA cathodes in this electrolyte at 50 mA g⁻¹ ([Figure 4.3f](#)). The results reveal that LiNSBA exhibits significantly better cyclability than NSBA, retaining 55 and 16 mAh g⁻¹ after 100 cycles, respectively. The superior cycling stability of LiNSBA is attributed to the substitution of the -COOH group with -COOLi, which enhances intrinsic conductivity and molecular polarity and inhibits dissolution by enhancing

the crystalline structure stability through the introduced O–Li···O coordination bonds.^[345,346]

To investigate their electrochemical redox mechanisms, *ex situ* Raman spectroscopy was performed on NSBA/LiNSBA cathodes at various charge/discharge states in [Figure 4.3g](#) and [h](#). For both NSBA and LiNSBA cathodes, characteristic vibrational bands assigned to the azodioxide group ($\nu_{\text{dimer}}(\text{NO})$ and $\nu_{\text{dimer}}(\text{N=N})$) are clearly observed in the pristine electrodes, confirming that both compounds exist in a dimeric form.^[347] Upon discharge of NSBA to 1.5 V, the $\nu(\text{OH})$ band at 1180 cm^{-1} significantly weakens, indicating the involvement of carboxylic acid groups in lithiation and suggesting a redox process converting –COOH to –COOLi. Further discharge to 1.0 V results in the marked decrease of the $\nu_{\text{dimer}}(\text{NO})$ and $\nu_{\text{dimer}}(\text{N=N})$ bands, accompanied by the appearance of a new band at 1370 cm^{-1} . This band is attributed to the lithiated azo species (Li–N–N–Li), consistent with previously reported spectra of lithiated azobenzene-4,4'-dicarboxylic acid lithium salt (ADALS).^[38] A similar spectral evolution is observed for LiNSBA, where the azodioxide bands diminish and the lithiated azo band emerges upon discharge to 1.0 V. During the initial lithiation cycle, oxygen is released from the organic cathodes, forming reactive oxygen species that are expected to engage side reactions with the lithium metal anode.^[348,349]

In the fully charged states of both cathodes, the original azodioxide signals do not reappear, while a new band at 1455 cm^{-1} emerges, corresponding to the N=N stretching of the azo configuration. Although this azo peak is less distinguishable in FTIR spectra ([Figure S4.12](#)), the overall FTIR profile of the charged products closely matches that of ADALS.^[38] These results provide strong evidence that both NSBA and LiNSBA undergo an irreversible transformation from azodioxide dimers to azo species after the first cycle, which then serve as active redox centers in subsequent cycles ([Figure 4.3i](#)).

However, the initial charge capacities of NSBA and LiNSBA are significantly lower than the theoretical extraction of 2 Li^+ per lithiated azo species, resulting in initial CE of only 27% and 50%, respectively (see their first cycle GCD in [Figure 4.3a](#) and [b](#)). This phenomenon has also been observed in a series of studies where NBALS was converted to an azo compound.^[36] One possible explanation is that the in situ formed azo products possess less coherent crystalline structures compared to pre-synthesized materials, leading to disrupted ion transport pathways and substantially reduced material utilization.^[350] In addition, some side products, such as electrolyte oxidation species, may remain embedded in the product matrix and further deteriorate the electronic conductivity.^[351–353]

4.3.2. Polymeric dinitrosobenzene

In addition to introducing polar functionalities and salt formation, polymerization represents another effective strategy to inhibit the solubilization and hence enhance the cycling performance of organic electrode materials.^[31,354] DNSB exists predominantly in a *trans*-polymer form at room temperature, as evidenced by the Raman band at 1441 cm^{-1} and the FTIR band at 1265 cm^{-1} , both attributed to the *trans*-azodioxide group (Figure S4.13a–c).^[355] Compared to mono-nitroso-substituted benzene (NSB), DNSB in the polymeric form exhibits significantly improved thermal stability, with the decomposition temperature enhanced from $75.4\text{ }^{\circ}\text{C}$ (NSB) to $165\text{ }^{\circ}\text{C}$ (DNSB) (Figure S4.13d). Moreover, DNSB shows poor solubility in both tested electrolytes (Figure S4.13e), which is expected to contribute to its enhanced structural stability during electrochemical cycling.

We first evaluated the electrochemical performance of DNSB physically mixed with Super-P as the conductive carbon (DNSB/SP) under a current density of 50 mA g^{-1} in two different electrolytes. In LiTFSI-DOL/DME electrolyte (Figure 4.4a), the first cycle exhibits a pair of distinct discharge/charge plateaus at 2.62/3.22 V, delivering a reversible capacity of 150 mAh g^{-1} . In subsequent cycles, the plateaus gradually evolve into sloping profiles accompanied by a steady capacity decline, reaching 41 mAh g^{-1} after 200 cycles. On the other hand, DNSB/SP in LiPF₆-EC/DMC electrolyte (Figure S4.14a) also displays a similar pair of voltage plateaus in the first cycle, with a slightly higher initial reversible capacity of 170 mAh g^{-1} . However, its cycling stability is markedly poorer (Figure S4.14b) with a rapid capacity decay to only 12 mAh g^{-1} after just 10 cycles, compared to 57 mAh g^{-1} in LiTFSI-DOL/DME at the same point. These results are consistent with the observations for LiNSBA, confirming that DNSB electrodes also exhibit significantly improved cycling performance in the LiTFSI-DOL/DME electrolyte.

However, the initial capacity of DNSB/SP remains significantly lower than its theoretical value of 396 mAh g^{-1} . This discrepancy can be attributed to the inherently poor electrical conductivity of the polymeric DNSB, which suffers from more hindered electron transport compared to its small-molecule counterparts. The reduced conductivity renders significantly lower material utilization.^[356] To address this limitation and enhance electrochemical performance, we have further optimized the electrode composition by employing two highly porous conductive carbons, BP2000 and KB, as alternatives to Super-P. Each was physically mixed with DNSB to yield DNSB/BP2000 and DNSB/KB, respectively. These carbons possess larger specific surface areas, which are expected to improve electron/ion transport within the polymer matrix

and facilitate more efficient redox reactions.^[357–359]

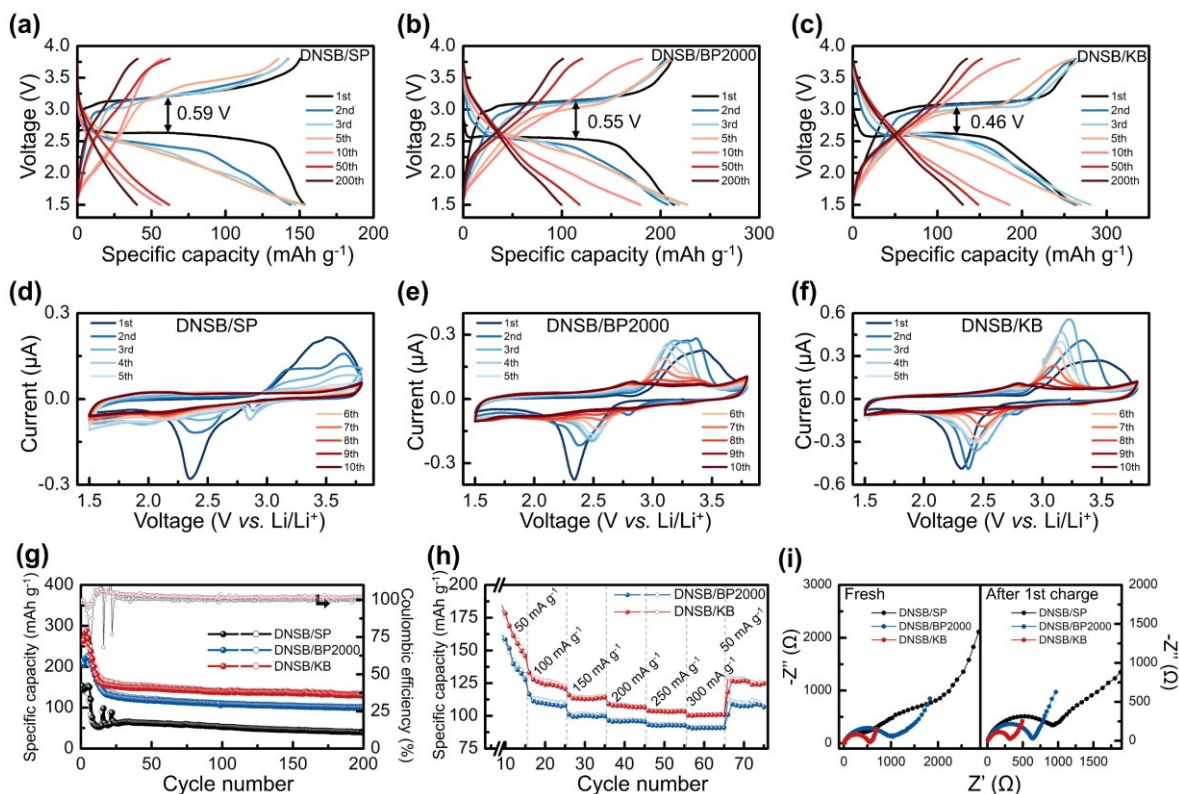


Figure 4.4. Electrochemical performances of DNSB physically mixed with three different conductive carbons as cathode materials in LIBs with LiTFSI-DOL/DME electrolyte. (a–c) GCD curves at 50 mA g^{-1} within 1.5–3.8 V vs. Li/Li⁺; (d–f) CV curves at 0.1 mV s^{-1} ; (g) cyclic performance and CE at 50 mA g^{-1} ; (h) capacities at varying current densities; (i) comparative Nyquist plots of three different cathode compositions tested at fresh and after the first cycle of GCD at 50 mA g^{-1} .

The electrochemical performances of DNSB cathodes mixed with different carbons are compared. At a current density of 50 mA g^{-1} in LiTFSI-DOL/DME electrolyte, all three electrodes exhibit similar initial voltage profiles with a pair of distinct discharge/charge plateaus in the voltage window of 3.8–1.5 V (Figure 4.4a–c), corresponding to the redox conversion of azodioxide to azo groups. However, the delivered capacities differ significantly depending on the conductive carbon used. DNSB/KB cathode achieved the highest reversible capacity of 278 mAh g^{-1} , followed by DNSB/BP2000 (215 mAh g^{-1}) and DNSB/SP (150 mAh g^{-1}). Furthermore, the voltage gap between the discharge and charge plateaus shows a consistent decreasing trend, from 0.59 V for DNSB/SP to 0.55 V for DNSB/BP2000, and further down to 0.46 V for DNSB/KB, indicating progressively reduced polarization and improved reaction kinetics with the use of more conductive and porous carbon matrices. This enhancement is

attributed to improved charge transport and more effective physical confinement of DNSB within the porous networks of BP2000 and KB.^[360–362]

CV results support these findings (Figure 4.4d–f). All electrodes exhibit a pair of redox peaks in the first scan, corresponding to the single pair of redox plateaus in GCD profiles. DNSB/KB electrode displays the most intense and symmetric redox peaks with the least separation of cathodic and anodic peak potentials, signifying the fastest redox kinetics. In contrast, the DNSB/SP electrode shows the broadest and least defined peaks with the largest peak-to-peak separation, suggesting sluggish reaction dynamics.^[363]

The impact of the conductive carbon on long-term cycling stability is presented in Figure 4.4g. Over 200 cycles at 50 mA g⁻¹, DNSB/KB cathode retains a specific capacity of 135 mAh g⁻¹, whereas the DNSB/BP2000 and DNSB/SP cathodes decay to 101 and 41 mAh g⁻¹, respectively. The relatively superior performance of DNSB/KB is further highlighted in the rate capability test (Figure 4.4h). At elevated current densities up to 300 mA g⁻¹, the DNSB/KB cathode maintains a higher capacity than its counterparts. Upon returning to 50 mA g⁻¹, over 90% of the original capacity is recovered. This rate capability confirms the high-rate redox activity of the KB-based system, attributable to its enhanced electronic and ionic conductivity.

The conductivity of DNSB cathodes with different conductive carbons is further evaluated from their EIS results before and after the first GCD cycle (Figure 4.4i, fitting results in Figure S4.15). In the Nyquist plots, the semicircle in the high-frequency region corresponds to the charge transfer resistance (R_{ct}), while the slope in the low-frequency region reflects the Warburg impedance associated with Li⁺ ion diffusion. Among the three cathodes, the KB-based one exhibits the lowest initial R_{ct} of 517 Ω , which further decreases to 316 Ω after the first cycle. This substantial reduction indicates a marked improvement in interfacial charge transfer and the formation of a more conductive and stable electrode-electrolyte interface. DNSB/BP2000 cathode also shows improved kinetics, with its R_{ct} dropping from 917 to 615 Ω after the first cycle. A moderate increase in ionic conductivity is observed, as evidenced by the slightly enhanced slope of the low-frequency region. In contrast, DNSB/SP cathode exhibits two depressed semicircles in the high- and mid-frequency regions, rather than a typical single R_{ct} arc followed by a Warburg line. This non-ideal impedance response suggests the presence of multiple interfacial processes. Since a stable solid electrolyte interphase (SEI) is not expected to form on the fresh cathode under these conditions, the additional semicircle is more likely attributed to the inefficient charge transfer between the DNSB active material and the carbon-

binder domain.^[364,365] The low specific surface area of Super-P results in poor electronic contact and nonuniform electron pathways, thereby increasing interfacial resistance and hindering charge transport. These impedance characteristics are consistent with the high polarization and poor electrochemical performance observed in the GCD and cycling results for the DNSB/SP cathode (Figure 4.4a and g).

The GCD profiles in Figure 4.4a–c reveal that the initially well-defined charge/discharge plateaus of DNSB gradually evolve into sloping profiles during cycling, accompanied by continuous capacity fading. This behavior suggests that DNSB, like other nitroso dimers, may undergo the irreversible transformation to azo in the first cycle under electrochemical conditions. To examine this hypothesis, further *ex situ* characterization was performed on cathodes at different charge/discharge states. Given its best electrochemical performance, the DNSB/KB electrode was selected for *ex situ* Raman, FTIR, and XPS analyses (Figure 4.5).

In the pristine state, Raman spectra (Figure 4.5a) exhibit characteristic bands for azodioxide dimer at 1311 and 1441 cm^{-1} , corresponding to the $\nu_{\text{dimer}}(\text{NO})$ and $\nu_{\text{dimer}}(\text{N}=\text{N})$ vibrations.^[355] After the first discharge, both peaks decrease significantly in intensity, indicating the reduction of the azodioxide structure. Simultaneously, a new band emerges at 1370 cm^{-1} , which is assigned to the symmetric stretching vibration of the N–N bond in a lithiated azo species ($\text{Li}-\text{N}-\text{N}-\text{Li}$), consistent with previously reported spectra for lithiated azobenzene derivatives.^[36,38] Upon charging (1C), the band at 1370 cm^{-1} disappears, indicating delithiation. However, the Raman spectrum does not return to its pristine state. Instead, a pair of new peaks appears at 1273 and 1314 cm^{-1} , attributed to the C–N(O) and C–N vibrations of an azoxy intermediate ($-\text{N}(\text{O})=\text{N}-$), along with a distinct band at 1442 cm^{-1} , characteristic of the azo group ($-\text{N}=\text{N}-$). Another new band at 1398 cm^{-1} also emerges, which can be assigned to the symmetric CH_3 bending mode found in azo polymers.^[366] These spectral changes suggest the formation of both azoxy and azo species following the first charge, implying that the electrochemical transformation proceeds via a multistep pathway involving partially reduced intermediates. In subsequent cycles, the intermediate peaks corresponding to azoxy species gradually diminish. During discharge, the peak at 1370 cm^{-1} becomes increasingly intense and better defined, indicating progressive accumulation of the $\text{Li}-\text{N}-\text{N}-\text{Li}$ species. In contrast, the corresponding azoxy-related bands (at 1273 and 1314 cm^{-1}) in the charged states fade continuously and become barely detectable by the 7th cycle (7C). From the 10th to the 15th cycle, the Raman spectra of both charged and discharged states become highly consistent, showing only two

dominant and reversible azo-related peaks, the 1370 cm^{-1} band at the discharge state and the 1442 cm^{-1} azo peak at the charged state.

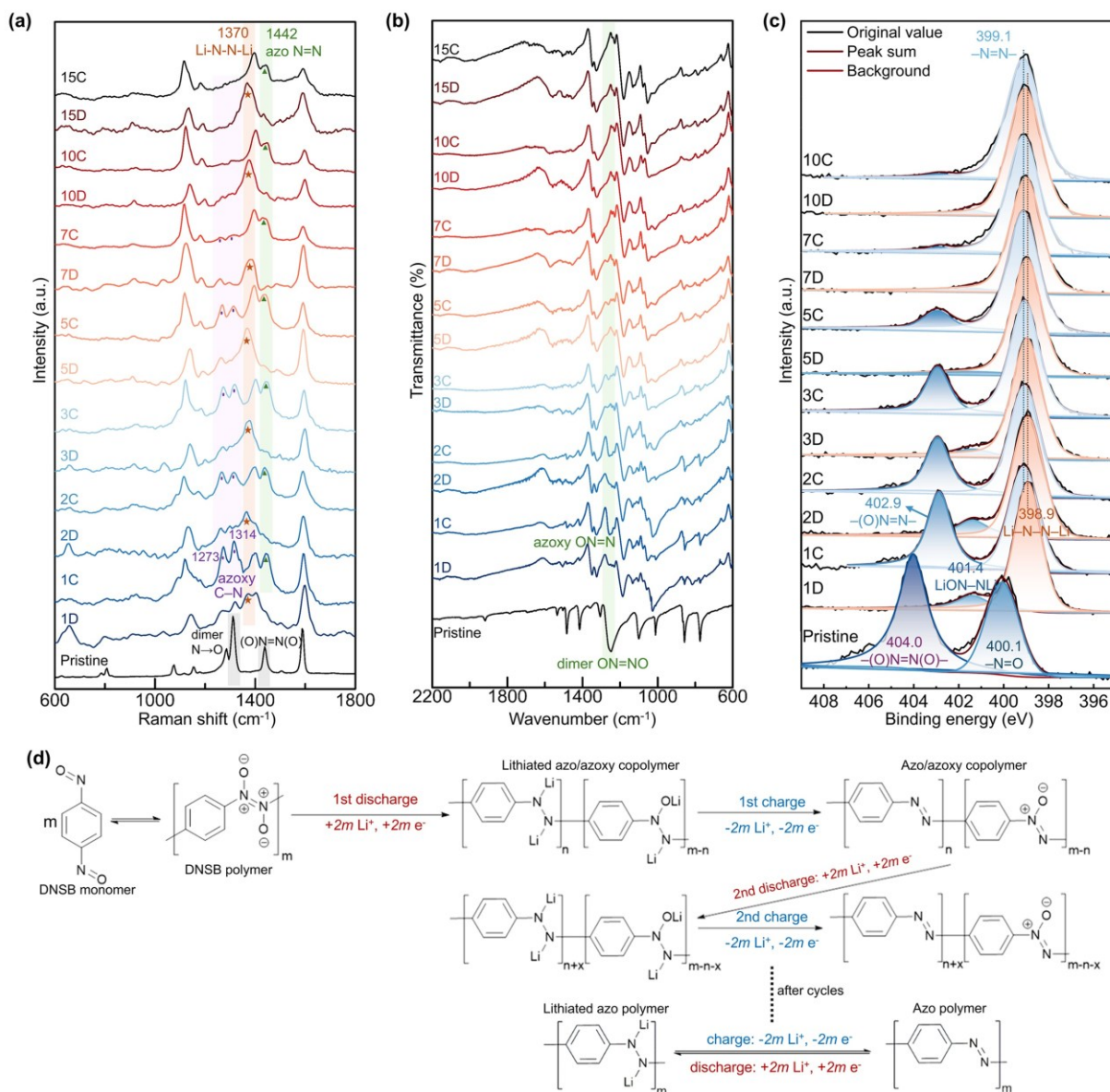


Figure 4.5. Elucidation of reaction mechanism of DNSB/KB cathodes with *ex situ* spectroscopic techniques. (a) Raman, (b) FTIR, and (c) XPS N 1s core level spectra of DNSB/KB cathodes at discharge/charge states during various cycles; (d) proposed reaction mechanism for DNSB.

FTIR spectra of DNSB cathodes at different cycles further support the gradual structural evolution during electrochemical cycling (Figure 4.5b). In the pristine, a strong absorption band is observed at 1265 cm^{-1} , which is attributed to the ON=NO stretching vibration of the azodioxide dimer structure. This peak serves as a fingerprint feature of the original DNSB molecular configuration.^[367,368] After the first discharge (1D), the band at 1265 cm^{-1} markedly

decreases in intensity, indicating the reduction and disruption of the dimeric ON=NO motif. Upon recharging (1C), this signal partially recovers, which may reasonably be attributed to the formation of azoxy-containing intermediates that also exhibit absorption near 1265 cm^{-1} .^[366] As cycling progresses, this band in the charged state continues to diminish and becomes barely detectable after the 7th cycle, further evidencing the consumption of the original azodioxide structure and azoxy intermediates. Beyond the 10th cycle, the FTIR spectra exhibit good reproducibility, with no apparent recovery of the azo/azoxy feature. This indicates that the transformation is largely complete, and the electrode surface is now dominated by the new, electrochemically active structure. Although the specific vibrational mode of azo group is less clearly resolved in FTIR due to spectral overlap and weaker absorption coefficients,^[366] the disappearance of the peak at 1265 cm^{-1} is ascribed to azodioxide/azoxy groups, and the stabilization of spectral features in later cycles strongly suggest that polymeric DNSB is gradually and irreversibly converted into a polymeric azo phase during cycling, in agreement with the Raman results.

The cycled electrochemical reaction is further confirmed by *ex situ* XPS N 1s spectra in [Figure 4.5c](#), where the C 1s peak at 284.6 eV is used as a reference binding energy. The pristine DNSB cathode exhibits two sharp and intense peaks at 404.0 and 400.1 eV, corresponding to the azodioxide ($-(\text{O})\text{N}=\text{N}(\text{O})-$) and terminal nitroso ($-\text{N}=\text{O}$) groups, respectively.^[369] Upon full discharge (1D), two new peaks appear at 401.4 and 398.9 eV, which are assigned to lithiated azoxy and lithiated azo species, respectively.^[38,300] After the first charge (1C), the original azodioxide- and nitroso-related peaks significantly diminish, while the azoxy features at 402.9 eV emerge, indicating a stepwise and irreversible transformation of the original redox centers. Meanwhile, the peak at 398.9 eV shifts slightly to 399.1 eV, in agreement with the reported “shift-to-higher” trend for azo/lithiated azo systems; however, its magnitude (+0.2 eV) is still smaller than the +0.6 eV characteristic of fully reversible azo couples,^[370,371] indicating incomplete delithiation of lithiated azo, which is consistent with the CE of <95% over the first ten cycles ([Figure 4.4g](#)). In the subsequent cycles, the proportion of the azoxy intermediate gradually decreases, as shown by quantitative XPS analysis ([Table S4.1](#)).^[372] The proportion of the azoxy intermediate decreases continuously from 41.7% after the 1C to less than 5% by the 7th cycle and becomes barely detectable thereafter, although a very weak residual signal can still be observed, indicating that the azoxy-to-azo conversion is nearly but not fully completed. In contrast, the azo-related peaks increase correspondingly from about 58% to more than 95%,

remaining as the dominant redox species during prolonged cycling. The XPS results revealing the structural evolution are in good agreement with the Raman and FTIR results, where vibrational signals of the azoxy intermediates also gradually disappear after several cycles, and only the reversible signals corresponding to lithiated/delithiated azo species remain. Together, as summarized in [Figure 4.5d](#), these spectroscopic findings confirm that DNSB undergoes an in situ conversion from an azodioxide dimer to a polymeric azo structure, which becomes the main redox-active phase upon cycling.

Notably, a slight positive shift of the azo peak, relative to the lithiated azo peak, can be observed upon the delithiation of the latter in later cycles, while the overall peak shift between the lithiated and delithiated states becomes progressively less pronounced (e.g., 10D/10C). The weakening peak shift can be attributed to the fact that only a fraction of the azo sites is electrochemically utilized, as reflected by the limited reversible capacity (181 mAh g^{-1}) compared with the theoretical value of 396 mAh g^{-1} . The reduced number of participating azo groups results in smaller variations in local electron density, leading to a less distinct binding energy difference between the charged and discharged states. This phenomenon may result from the restricted Li^+ transport and charge transfer in the formed azo polymer.

In the above DNSB cathodes with different conducting carbons, DNSB and the conducting carbons were simply physically mixed during the preparation of the cathode slurry. To overcome the intrinsic limitations of DNSB, such as its poor electronic conductivity and dissolution tendency, an encapsulation strategy was further developed by encapsulating DNSB within porous conductive carbon matrices (BP2000 and KB). This design aims to establish a more efficient electron-transport network to further enhance capacity utilization and improve cycling stability. BP2000 and KB were selected because of their large specific surface area (typically $1200\text{--}1500 \text{ m}^2 \text{ g}^{-1}$), open porous architecture, and high electrical conductivity, which collectively facilitate uniform dispersion of the active material within its pore structures, accelerate charge transport, and provide abundant pathways for ion and electron transfer.^[373,374] These features are particularly beneficial for organic cathodes with intrinsically low conductivity, as they help improve redox accessibility. The encapsulated DNSB-carbon composites, denoted as DNSB@BP2000 and DNSB@KB, were prepared through a solution-infusion process in toluene at a DNSB loading of 66 wt% (DNSB: carbon = 2:1 by weight). At this composition, the pore volume of the carbon hosts is sufficient to accommodate and fully confine DNSB.

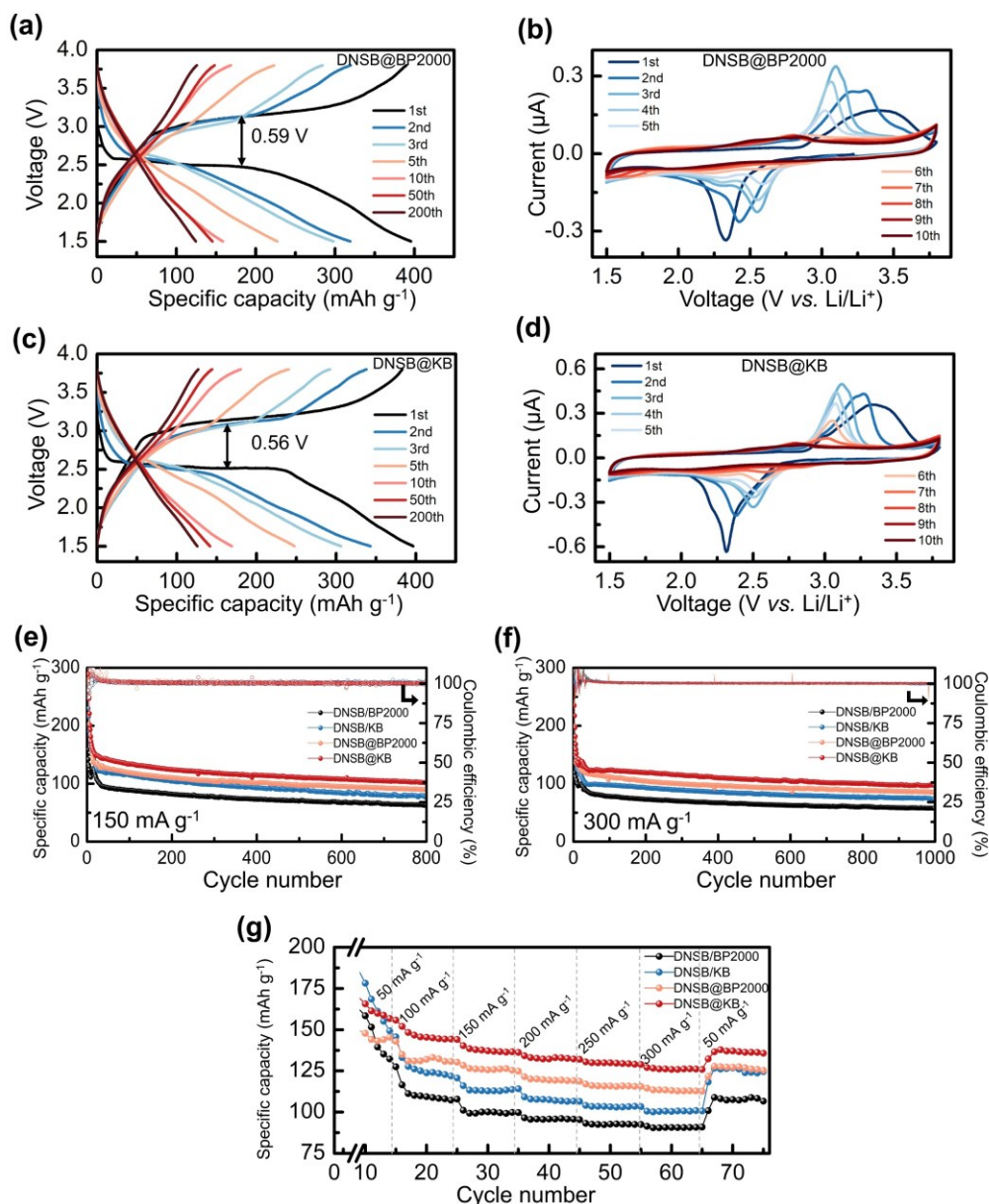


Figure 4.6. Electrochemical performances of DNSB@BP2000 and DNSB@KB cathodes in LiTFSI-DOL/DME electrolyte. (a, c) GCD curves at 50 mA g⁻¹ within 1.5–3.8 V vs. Li/Li⁺; (b, d) CV curves at 0.1 mV s⁻¹; (e, f) cyclic performance and CE at 150 and 300 mA g⁻¹; (g) capacities at varying current densities.

TGA (Figure S4.16) confirms successful encapsulation and provides two key pieces of evidence. First, the residual weights of DNSB@BP2000 and DNSB@KB after thermal decomposition are significantly higher than expected. Given that pure DNSB exhibits a weight loss of 93.86%, a 2:1 physical mixture would theoretically lose 61.94% of its mass. In contrast, DNSB@BP2000 and DNSB@KB exhibit only 41.55% and 45.91% weight loss, respectively. This discrepancy indicates that a substantial portion of DNSB is confined within the carbon pores, where its volatilization is suppressed and more carbonized residues are retained.^[375]

Second, the peak decomposition temperatures (175 and 144 °C for DNSB@BP2000 and DNSB@KB, respectively) of the composites are noticeably lower than that (203 °C) of pure DNSB, suggesting a reduced degree of polymerization after encapsulation within the porous carbons.^[376] This shift is consistent with the formation of smaller active material domains due to nanoscale confinement within the porous carbons.

Electrochemical evaluation (Figure 4.6) discloses the positive effects of encapsulation. With LiTFSI-DOL/DME electrolyte, both DNSB@BP2000 and DNSB@KB cathodes exhibit clear discharge/charge plateaus at ~2.52/3.13 V at 50 mA g⁻¹ during the first few GCD cycles (Figure 4.6a and c), consistent with the behavior observed above for the pristine DNSB cathodes in Figure 4.4. In the first GCD cycle, both composites deliver high initial reversible capacities, reaching 389 mAh g⁻¹ for DNSB@BP2000 and 383 mAh g⁻¹ for DNSB@KB, approaching the theoretical value of 397 mAh g⁻¹ (Figure 4.6a and c). Unlike three pristine cathodes (DNSB/SP, DNSB/BP2000, and DNSB/KB) that require a gradual activation process over the first several cycles (Figure 4.4), DNSB@BP2000 and DNSB@KB composites deliver the highest capacities in the first cycle that are close to their theoretical maxima, indicating efficient charge transport and improved material utilization. With continued cycling, these plateaus progressively evolve into sloped profiles, accompanied by gradual capacity fading. Interestingly, the encapsulated composites show slightly larger initial voltage gaps (0.59 V for DNSB@BP2000 and 0.56 V for DNSB@KB) than the physically mixed ones (0.55 V for DNSB/BP2000 and 0.46 V for DNSB/KB). The slightly increased polarization can be attributed to the occupation of internal pores by the encapsulated DNSB domains. This structural confinement improves electrochemical accessibility and utilization of the active material, although it simultaneously restricts Li⁺ diffusion within the confined pores, leading to moderate polarization.

Meanwhile, it is notable that DNSB@KB cathode consistently outperforms its counterparts (DNSB/BP2000, DNSB/KB, and DNSB@BP2000) across cycling and rate tests (Figure 4.6e–g). As shown in Figure 4.6e, DNSB@KB retains 102 mAh g⁻¹ after 800 cycles at 150 mA g⁻¹, markedly higher than those of DNSB@BP2000 (90 mAh g⁻¹), DNSB/BP2000 (63 mAh g⁻¹), and DNSB/KB (77 mAh g⁻¹). In a cycling test at a higher current density of 300 mA g⁻¹ (Figure 4.6f), DNSB@KB still maintains 97 mAh g⁻¹ after 1000 cycles, whereas the capacities of DNSB@BP2000, DNSB/KB, and DNSB/BP2000 decrease to 85, 73, and 58 mAh g⁻¹, respectively. The superiority of DNSB@KB cathode is further highlighted in the rate capability tests (Figure 4.6g, first 15 cycles in Figure S4.17). As the current density increases stepwise

from 30 to 300 mA g⁻¹, DNSB@KB sustains a reversible capacity of 126 mAh g⁻¹, compared with 113 mAh g⁻¹ for DNSB@BP2000, 101 mAh g⁻¹ for DNSB/KB, and 91 mAh g⁻¹ for DNSB/BP2000. Upon returning to 30 mA g⁻¹, DNSB@KB exhibits excellent recovery to 138 mAh g⁻¹, while DNSB@BP2000 and DNSB/KB recover to 127 mAh g⁻¹, and DNSB/BP2000 to 109 mAh g⁻¹. These results clearly indicate that encapsulation within the KB matrix provides the most effective stabilization of DNSB against dissolution and structural degradation under both moderate and high current densities.

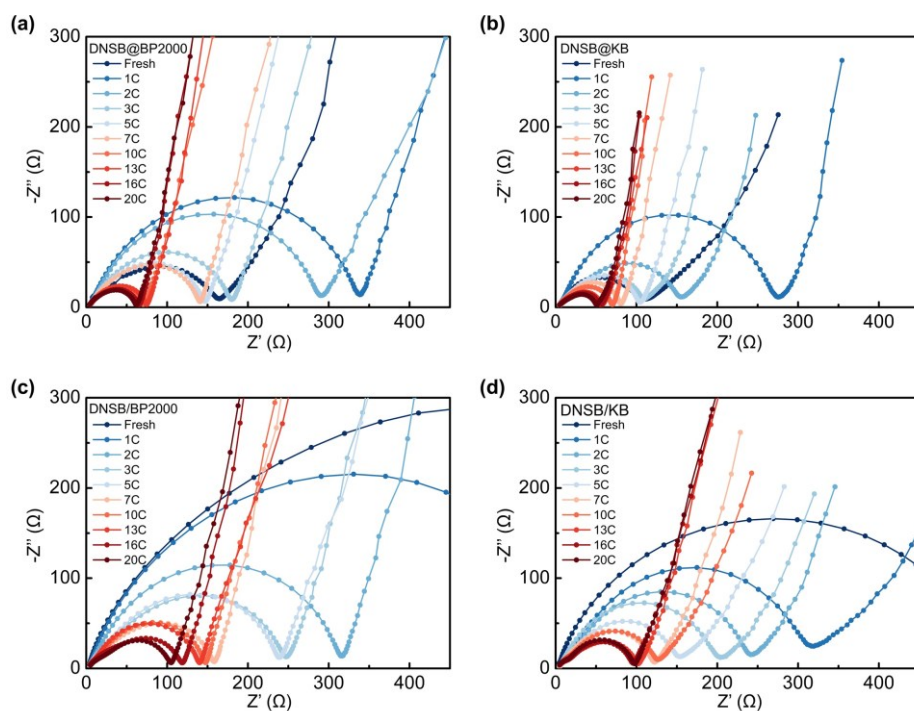


Figure 4.7. Nyquist plots of 4 different cathodes (a) DNSB@BP2000, (b) DNSB@KB, (c) DNSB/BP2000, and (d) DNSB/KB tested in fresh and after various cycles of GCD at 50 mA g⁻¹.

Figure 4.7 compares the EIS spectra of the four cathodes tested in fresh and after various GCD cycles at 50 mA g⁻¹. For the encapsulation cathodes (DNSB@BP2000 and DNSB@KB, Figure 4.7a and b), the fresh cathodes exhibit significantly lower R_{ct} than the physically mixed cathodes (DNSB/BP2000 and DNSB@KB in Figure 4.7c and d), confirming the benefit of the encapsulation strategy. Among them, DNSB@KB shows the lowest R_{ct} of 274 Ω, reflecting the superior conductivity and interfacial compatibility provided by the KB host.^[362,377] These observations highlight the dual importance of structural characteristics of the carbon matrix and

the way in which the active material is embedded within it. After the first cycle (1C), a contrasting trend is observed between the physical mixtures and the encapsulated composites. While DNSB/BP2000 and DNSB/KB exhibit a decrease in R_{ct} due to electrochemical activation, DNSB@BP2000 and DNSB@KB show a slight increase in the first cycle (relative to the fresh cathodes), although their absolute R_{ct} values remain lower than those of the corresponding mixtures throughout all tested cycles (Figure 4.7). This initial increase indicates that the structural evolution of DNSB into electrochemically generated azo-containing polymer species alters the electronic network within the electrode. The formation of these polymeric products introduces greater molecular complexity and partial loss of conjugation, which temporarily hinders charge transport and increases interfacial resistance.^[378,379] In subsequent cycles, the R_{ct} of the composites gradually decreases and is stabilized, suggesting progressive reorganization and stabilization of the electrode/electrolyte interface.^[380–382] Nevertheless, the polymeric framework formed during cycling remains intrinsically less conductive than the pristine DNSB, which is clearly manifested by the persistent polarization and continuous capacity fading observed during early cycling.^[21,383] These results demonstrate that both the irreversible structural evolution and the incomplete recovery of electronic conductivity contribute to the capacity degradation of electrodes. In addition, common degradation factors such as irreversible side reactions and the deterioration of electrical contact caused by volume changes during lithiation/delithiation may also play a role.^[384] However, the precise mechanism requires further investigation. By the 20th cycle, when the electrode compositions have been stabilized, as indicated by the CV and GCD results, the final R_{ct} ranking follows the order: DNSB@KB < DNSB@BP2000 < DNSB/KB < DNSB/BP2000, representing a progressive improvement in conductivity. This trend directly correlates with the observed cycling performance and confirms that enhanced charge transport is a key factor behind the improved electrochemical behavior.

4.4. Conclusion

This work provides a comprehensive understanding of the electrochemical behavior of aromatic nitroso compounds, including mono-nitroso small molecules (NSB, NST, NSBA, and LiNSBA) and polymeric di-nitroso DNSB, as cathode materials for LIBs. Electrochemical evaluations combined with *ex situ* FTIR, Raman, and XPS analyses have revealed a universal and irreversible redox pathway involving the transformation of azodioxide dimers into azo species, with DNSB undergoing a gradual conversion via azoxy intermediates over multiple cycles. Although the in situ-formed azo polymer exhibits low solubility and improved structural

stability compared to the small-molecule counterparts, the sluggish kinetics and poor conductivity result in restricted utilization of active sites and incomplete realization of the theoretical capacity. To address these limitations, we have employed an encapsulation strategy by confining DNSB within porous conductive carbons (KB and BP2000). This approach markedly improves charge transport and enhances electrochemical accessibility. Among the encapsulation composites, DNSB@KB exhibits the best overall performance, delivering near-theoretical initial capacity, best rate capability, and outstanding cycling stability, retaining 102 mAh g⁻¹ after 800 cycles at 150 mA g⁻¹ and 97 mAh g⁻¹ after 1000 cycles at 300 mA g⁻¹. Collectively, these findings uncover a fundamental and universal nitroso-to-azo conversion mechanism, establishing aromatic nitroso compounds as a mechanistically defined and tunable platform for constructing azo-type organic electrodes by in situ transformation, and provide valuable guidance for the rational design of organic cathode materials.

Chapter 5. Stabilization of *p*-Dinitrobenzene Cathodes through Electrode Surface Coatings

Abstract

Organic electrode materials have emerged as promising alternatives to conventional inorganic cathodes for lithium-ion batteries (LIBs), owing to their sustainability, structural tunability, and environmental benefits. Among these materials, *p*-dinitrobenzene (*p*-DNB) offers a high theoretical capacity of 319 mAh g⁻¹ through a reversible two-electron redox process. However, its practical application is limited by high solubility in organic electrolytes, leading to rapid capacity fading. In this work, two strategies were employed to improve the cycling stability of DNB-based cathodes. The first approach utilizes a poly(ethylene oxide) (PEO)-based solid polymer electrolyte to restrict the diffusion of dissolved species. The second approach involves applying poly(vinyl alcohol) (PVA) coatings on the electrode surface to suppress interfacial degradation. Electrochemical measurements demonstrate that although the PEO-based system preserves redox activity at elevated temperature, it suffers from performance decay due to thermal diffusion. In contrast, PVA-coated cathodes exhibit significantly improved long-term cycling stability at room temperature. The optimal PVA concentration results in a capacity of 178 mAh g⁻¹ after 150 cycles at 0.2 C. Electrochemical impedance spectroscopy and rate performance tests reveal that excessive coating thickness leads to increased interfacial resistance and polarization. These findings highlight the importance of optimizing polymer coatings to enhance the performance of organic electrode materials.

5.1. Introduction

Compared to conventional inorganic cathodes that often rely on scarce transition metals such as cobalt and nickel, organic electrode materials offer several notable advantages.^[41,385,386] These include the use of earth-abundant elements, high structural tunability, and generally lower environmental impact. In particular, small-molecule organic compounds stand out due to their high gravimetric capacity, clearly defined redox-active sites, and compatibility with low-temperature, solution-based synthesis.^[14,346,387] These features make them promising candidates for developing sustainable and cost-effective lithium-ion batteries (LIBs).

Among various redox-active organic molecules, nitroaromatic compounds such as *p*-dinitrobenzene (*p*-DNB) have attracted attention for their ability to undergo a reversible two-

electron redox process within a voltage window of 3.8 to 2.4 V vs. Li⁺/Li, yielding a high theoretical capacity of 319 mAh g⁻¹.^[35,388] Despite this favorable energy profile, the practical use of DNB is hindered by its high solubility in conventional liquid electrolytes, which causes rapid capacity fading during cycling. To address this issue, prior strategies have focused on molecular modifications, including polymerization, salt formation, or covalent functionalization.^[21,194,389,390] However, these approaches often involve complex synthesis steps or reduce the electrochemical activity of the material. Alternatively, physical strategies such as incorporating solid polymer electrolytes (SPEs) or applying polymer coatings on the electrode surface offer more accessible routes to suppress dissolution while preserving the intrinsic redox properties.

In this study, two complementary strategies for improving the stability of DNB-based cathodes have been introduced. First, a poly(ethylene oxide) (PEO)-based SPE was employed to limit the diffusion of dissolved intermediates and to provide mechanical support. Second, a poly(vinyl alcohol) (PVA) coating was applied onto the cathode surface, forming a protective layer that helps confine active species at the interface. Through electrochemical testing and spectroscopic analysis, it is demonstrated that the PVA coating, when optimized in thickness, effectively enhances cycling performance without significantly hindering charge transfer. These findings provide practical insights into balancing dissolution control and charge transport in organic cathode systems.

5.2. Experimental

5.2.1. Chemicals and materials

p-DNB (98%), PVA (weight-average molecular weight: 89,000–98,000 g mol⁻¹, 99+% hydrolyzed), PEO (average *M_v* 600,000), 2-propanol (≥ 99.5%), Nafion (5 wt% in mixture of lower aliphatic alcohols and water), ethanol (ACS reagent), lithium bis(trifluoromethane)sulfonimide (LiTFSI, 99.95%), and acetonitrile (ACN, 99.8%, anhydrous) were obtained from Aldrich and used as received. 1,3-dioxolane (DOL, 99%, Aldrich) and dimethoxyethane (DME, anhydrous, 99.5%, Aldrich) were dried and stored over a 4 Å molecular sieve before use. Super-P carbon black (IMERYS Graphite & Carbon, Belgium) and Celgard 2400 separator (Celgard LLC) were used as received. Deionized (DI) water was prepared using a Milli-Q purification system.

5.2.2. Preparation of PEO-based SPE

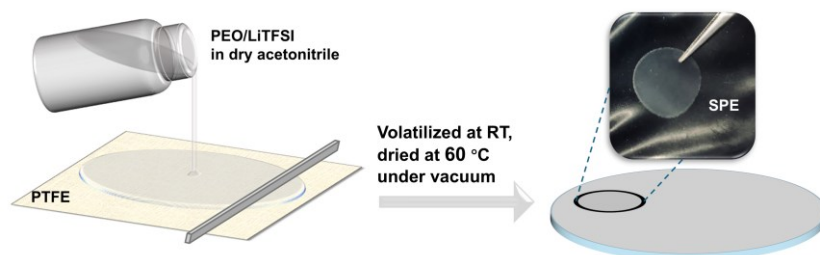


Figure 5.1. Schematic illustration of the preparation process for the PEO-based SPE film.

The PEO-based SPE was prepared by dissolving PEO and LiTFSI in anhydrous ACN at an [EO]:[Li⁺] molar ratio of 15:1, with a total polymer concentration of 10 wt%. The solution was stirred at room temperature until completely homogeneous then cast onto a clean polytetrafluoroethylene (PTFE) substrate. The cast film was dried under vacuum at room temperature for 12 h and subsequently at 60 °C under vacuum for 24 h to obtain free-standing films. The final thicknesses of SPE membranes were controlled to 45 μm and 90 μm , as shown in [Figure 5.1](#).

5.2.3. Fabrication of PVA-coated cathodes

To suppress interfacial dissolution of the active material, PVA coatings were applied directly onto prefabricated DNB cathodes (preparation process in [Section 5.2.5](#)). PVA was first dissolved in a water/2-propanol mixed solvent (90:10, v/v) to prepare coating solutions with different concentrations (0.3, 0.6, 0.9, 1.2, and 1.5 g L⁻¹). The solutions were stirred at 80 °C until fully transparent.

Table 5.1. Solution concentrations and corresponding mass ratios of PVA to DNB in the coating process.

Solution concentration, g L ⁻¹	Mass ratio (PVA: DNB)
0.3	0.75%
0.6	1.50%
0.9	2.25%
1.2	3.00%
1.5	3.75%

A fixed volume of PVA solution (25 μL per mg of active material) was drop-cast onto each electrode. The coating thickness was tuned by adjusting the solution concentration, corresponding to the designations PVA-0.3, PVA-0.6, PVA-0.9, PVA-1.2, and PVA-1.5. While

the total solution volume was kept approximately constant, the higher concentrations produced thicker coatings. The corresponding mass ratios of PVA to DNB are summarized in [Table 5.1](#). After coating, the electrodes were air-dried at room temperature and then vacuum-dried at 60 °C for 12 h prior to use. The entire fabrication process is illustrated in [Figure 5.2](#).

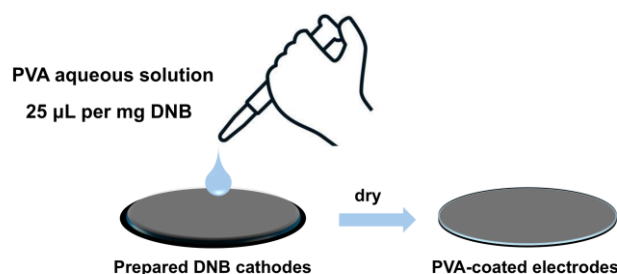


Figure 5.2. Schematic illustration of the PVA coating procedure on DNB cathodes.

5.2.4. Materials characterizations

X-ray diffraction (XRD) patterns were collected on a Rigaku SmartLab SE X-ray diffractometer with Cu K α radiation (1200 kW). Fourier-transform infrared (FTIR) spectra were obtained on a Thermo Scientific Nicolet 6700 Analytical FTIR spectrometer. Water contact angles were obtained using a CA instrument (AST Product, USA)

5.2.5. Electrochemical measurements

To fabricate the DNB cathodes, DNB powder, Super-P conductive carbon, and a binder (PEO for cells using SPEs; Nafion for cells with PVA-coated cathodes) were mixed at a weight ratio of 60:30:10. The mixture was dispersed in ethanol to form a homogeneous slurry, which was then cast onto carbon-coated aluminum foil discs. The average DNB loading was approximately 1.33 mg cm⁻², corresponding to ~2 mg of active material per electrode. The electrodes were dried at 60 °C for 8 h before use.

CR2025-type coin cells were assembled in an argon-filled glovebox using lithium metal as the anode. For cells employing an SPE, the PEO-based membrane served as both electrolyte and separator, and the cells were tested at 60 °C. For cells using PVA-coated cathodes, 1 M LiTFSI in a DOL/DME (1:1, v/v) solution was used as the liquid electrolyte, and double-layer Celgard 2400 membranes were employed as separators. These cells were tested at room temperature.

Galvanostatic charge–discharge (GCD) tests of the cells were undertaken on a battery testing system (Land, CT2001A, China). Electrochemical impedance spectroscopy (EIS) measurements were performed on an Metrohm Autolab PGSTAT128N electrochemical

workstation from 100 kHz to 0.01 Hz with an AC amplitude of 5 mV. EIS data analysis was performed by using Zview (Version v3.1, USA). For *ex situ* FTIR analysis, coin cells were cycled to selected states of charge or discharge, then disassembled in an argon-filled glovebox. The recovered cathodes were sealed and transferred under an inert atmosphere for spectroscopic characterization.

5.3. Results and discussion

DNB has been identified as a promising small-molecule organic cathode material for LIBs, exhibiting a reversible two-electron redox process within the voltage window of 3.8–2.4 V vs. Li^+/Li in 1 M LiTFSI DOL/DME electrolyte. This reaction corresponds to a theoretical capacity of 319 mAh g⁻¹. However, similar to other small-molecule organic electrodes, DNB suffers from significant capacity fading due to its high solubility in organic electrolytes. To address this limitation, two complementary strategies were investigated to improve cycling stability: (i) employing an SPE to restrict the diffusion of active species and (ii) applying polymer coatings to the electrode surface to suppress material loss at the interface.

5.3.1. Performance of DNB in PEO-based SPE

SPEs can physically hinder the dissolution of organic active species at room temperature and thereby improve cycling performance. In this work, a PEO–LiTFSI SPE system with an ethylene oxide to lithium ratio of 15:1 was employed for cells using DNB as the cathode material. This formulation provides a compromise between mechanical integrity and ionic conductivity, while its ether-based backbone resembles the solvation environment of conventional ether electrolytes, making it particularly suitable for evaluating the stability of nitroaromatic cathodes.^[132,391]

XRD analysis (Figure 5.3a) shows that the crystallinity of PEO-based SPEs decreases upon the addition of LiTFSI and further diminishes as the temperature rises from 25 °C to 60 °C, which at the same time facilitates Li^+ transport by increasing polymer chain mobility. In addition, FTIR spectroscopy (Figure 5.3b) confirms that DNB is chemically compatible with the PEO-based system. The characteristic nitro stretching vibrations of DNB remain unchanged upon mixing with the PEO binder (referred as cathode), indicating the absence of chemical interaction between the active material and polymer matrix.

Electrochemical testing was performed using cells containing SPEs of 45 μm or 90 μm, operated at 60 °C to ensure adequate ionic conductivity. The use of different thickness of SPEs

was designed to evaluate the trade-off between mechanical confinement and battery performance. The resulting GCD profiles (Figure 5.4a and b) shows voltage plateaus at 2.63/2.85 V at first discharge/charge, similar to those obtained in liquid electrolytes, confirming that the redox chemistry of DNB remained active. *Ex situ* FTIR measurements (Figure 5.4c) confirm the formation of the intermediate $\text{Li}_2\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ (lithiated DNB) after discharge to 2.4 V, as evidenced by the appearance of new peaks 1496 and 1387 cm^{-1} . Upon charging, the characteristic nitro peaks at 1540 and 1320 cm^{-1} reappear, confirming the reversible regeneration of DNB, in agreement with previous spectroscopic observations in liquid electrolyte systems.^[35] In subsequent cycles, the shape and position of the charge/discharge profiles remain largely unchanged, demonstrating the reversibility of the reaction during cycling.

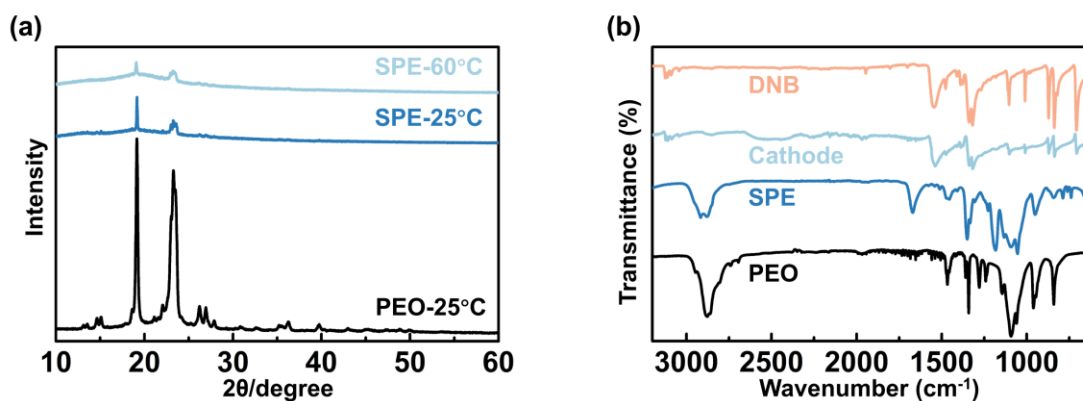


Figure 5.3. (a) XRD patterns of PEO and SPE at 25 °C and 60 °C; (b) FTIR spectra of PEO, SPE, DNB, and the composite cathode.

However, Figure 5.4d illustrates that the cycling performance of both SPE configurations remains unsatisfactory. The cell with SPE-45μm delivers an initial capacity exceeding 200 mAh g^{-1} during the first five cycles but declines rapidly, whereas the cell with SPE-90μm exhibits a delayed activation, reaching a maximum of 191 mAh g^{-1} by the 12th cycle, followed by a similar fading trend. These differences can be attributed to the effect of membrane thickness. Under the same electrolyte composition and testing conditions, the ionic conductivity of both SPEs is theoretically similar; however, increasing thickness extends the Li^+ transport pathway and raises bulk resistance, leading to slower electrode activation.

By the 50th cycle, although SPE-45μm retains a slightly higher capacity than SPE-90μm, both cells fall below 50 mAh g^{-1} . The severe degradation is likely caused by thermally driven diffusion of DNB and its intermediates into the polymer matrix, as indicated by the visible

darkening of the SPE layer in SPE-45 μm cells (Figure S5.1). This behavior is typical for small neutral molecules when combined with linear polymer matrices.^[392] Moreover, the thicker SPE provides a larger reservoir for dissolved species, which accelerates active-material loss and explains the poorer long-term stability of SPE-90 μm . These results suggest that although PEO-based SPE preserve the redox activity of DNB, they are insufficient to prevent molecular diffusion at elevated temperatures, which limits their effectiveness under practical conditions.

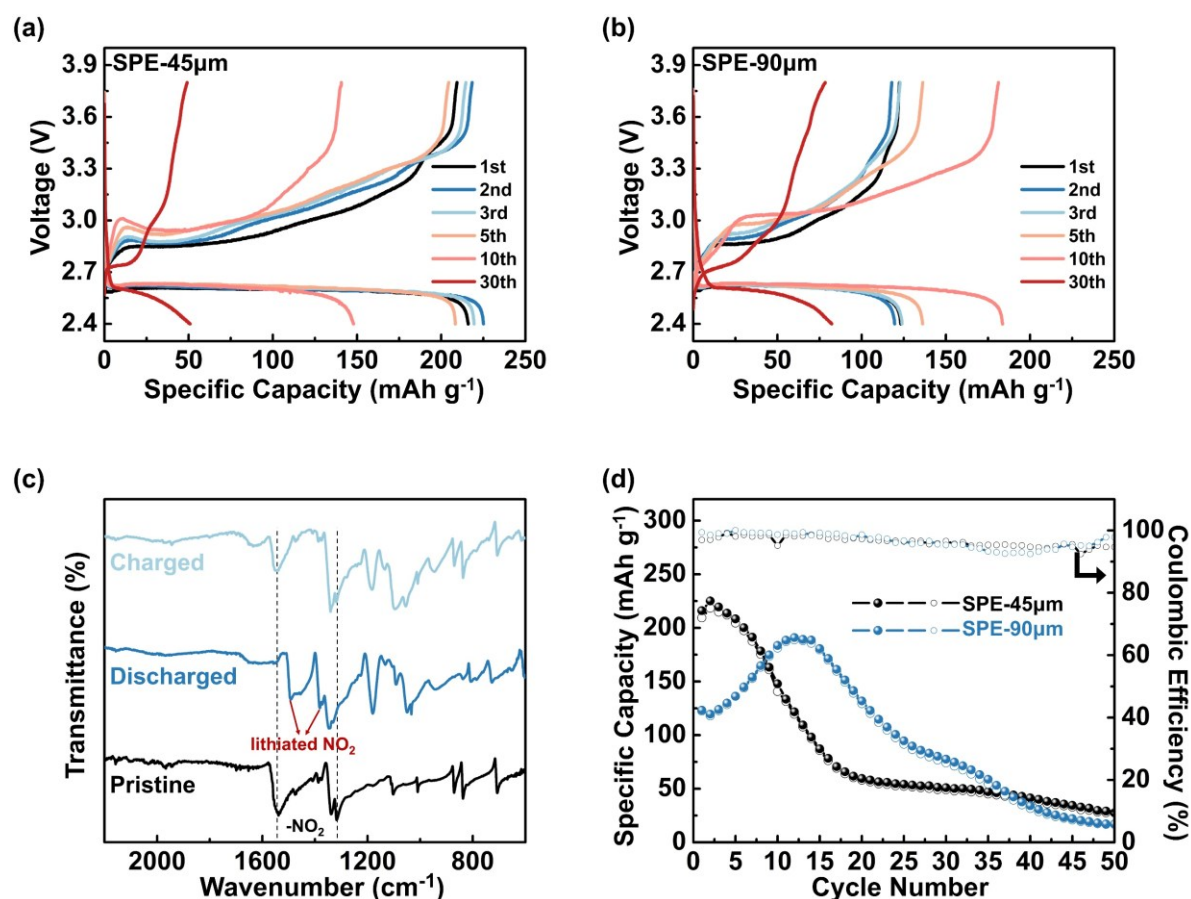


Figure 5.4. (a,b) GCD curves of cells with single and double PEO layers over 30 cycles at 60 °C at 0.2 C; (c) *ex situ* FTIR spectra of pristine, discharged, and recharged electrodes of cells using SPE-45 μm ; (d) cycling performance and Coulombic efficiency (CE) of cells with different PEO layer thicknesses.

5.3.2. Performance of DNB with PVA coating on the cathode surface

To overcome the shortcomings of PEO-based SPE, we examined an alternative strategy by applying a polymer coating directly onto the electrode surface. This method retains the advantages of liquid electrolytes for ion transport while introducing a physical polymer barrier to suppress dissolution of the active material. To ensure structural integrity, the coating process was designed to be mild and conducted in aqueous solution. PVA was selected based on its

hydrophilic, amorphous structure and previously reported ability to prevent polysulfide dissolution in lithium-sulfur batteries.^[393] A fixed amount of PVA solution was drop-cast per milligram of active material, and the coating thickness was controlled by adjusting the solution concentration.

FTIR spectra of the coated electrodes (Figure 5.5a) demonstrates that increasing PVA content led to stronger O–H stretching bands at 3550–3200 cm^{-1} , indicating higher polymer loading.^[394] Simultaneously, the intensity of nitro group peaks at 1540 and 1320 cm^{-1} decreased, suggesting progressive surface coverage by the PVA layer. Contact angle measurements (Figure 5.5b) corroborated this observation, showing a continuous decrease in contact angle as PVA content increased, consistent with enhanced hydrophilicity.

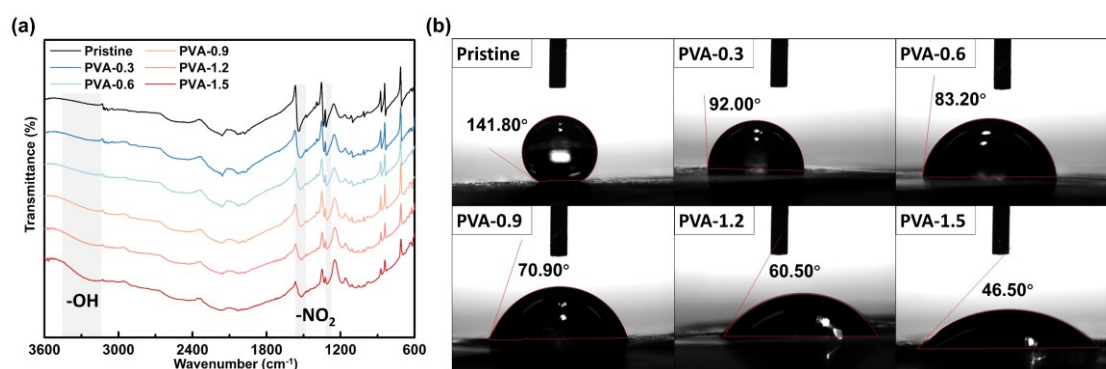


Figure 5.5. (a) FTIR spectra and (b) contact angles of the electrode samples without or with different content of PVA coating.

The effect of PVA coatings on electrochemical performance was evaluated under two small current densities, 0.1 C and 0.2 C (Figure 5.6a and b), to minimize polarization and better reflect the intrinsic cycling behavior.^[395] At 0.1 C, electrodes with PVA-0.3, PVA-0.6, and PVA-0.9 delivers initial discharge capacities of 289, 298, and 310 mAh g^{-1} , respectively, all exceeding the theoretical 90% utilization and outperforming the uncoated control (pristine, 285 mAh g^{-1}). These results indicate that a moderate PVA coating can effectively reduce active material loss in fresh batteries by providing physical confinement. In contrast, thicker coatings (PVA-1.2 and PVA-1.5) results in lower initial capacities (284 and 273 mAh g^{-1}), likely due to increased resistance at the interface.

During extended cycling at 0.1 C, PVA-0.3 exhibits higher capacity than the pristine electrode through the first 45 cycles but shows accelerated degradation afterward. By the 75th cycle, its capacity matches that of the pristine sample, suggesting partial coating detachment or

degradation. In contrast, PVA-0.6 and PVA-0.9 shows enhanced long-term stability. PVA-0.6 retains high capacity until the 140th cycle and concludes at 108 mAh g⁻¹ by the 150th cycle. PVA-0.9 performs even better, retaining 130 mAh g⁻¹ after 150 cycles, clearly surpassing the pristine sample (91 mAh g⁻¹). This suggests that a PVA concentration of 0.9 offers an optimal balance between dissolution suppression and charge transport. Upon further increasing the coating amount, PVA-1.2 exhibits a reduced initial capacity due to its elevated interfacial resistance. However, from the 52nd cycle onward, its performance surpasses PVA-0.3 and remains stable, finishing at 106 mAh g⁻¹ after 150 cycles. PVA-1.5 shows the lowest initial capacity and underperforms during the early stages, but exhibits the slowest long-term fading, ending at 102 mAh g⁻¹. These results highlight a trade-off between accessibility to redox-active sites and physical stabilization, where thicker coatings hinder ion/electron transport but improve retention over time.

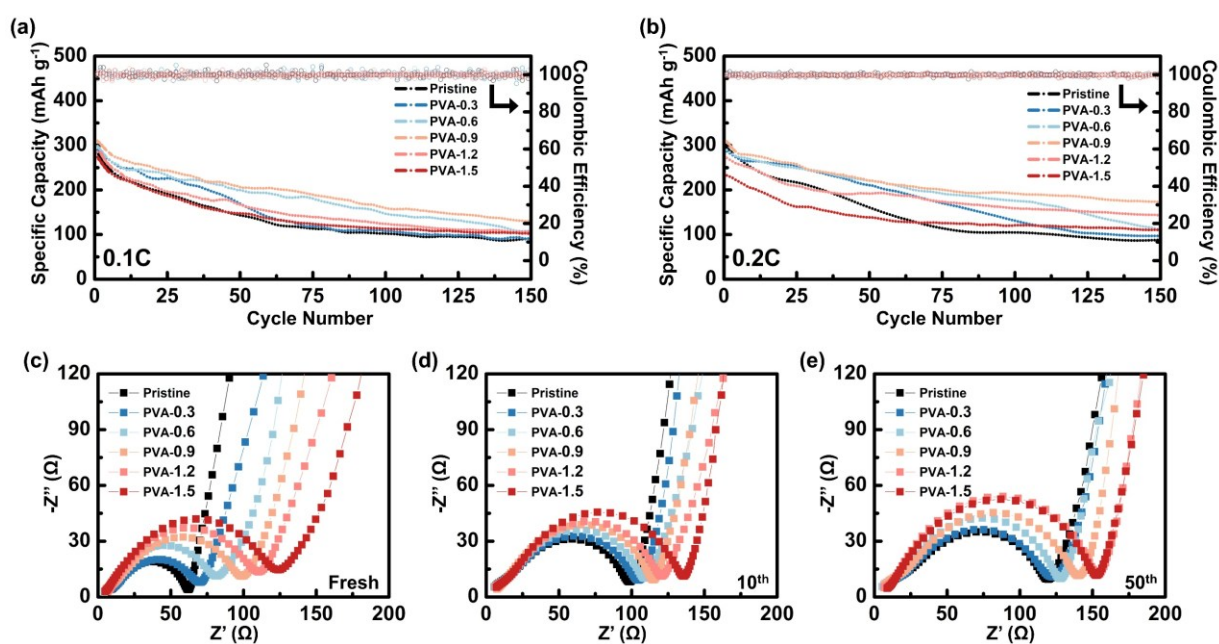


Figure 5.6. Electrochemical performance of PVA coated cathodes in LIBs: (a,b) cyclic performance and CE at 0.1 C and 0.2 C; (c-e) comparative Nyquist plots of fresh cells and cells tested after 10 and 50 cycles of GCD at 0.1 C.

At an increased current density of 0.2 C, the influence of PVA coating amount remains more evident. The fading rate slows progressively as coating concentration increases from PVA-0.3 to PVA-0.6. After 150 cycles, the two electrodes retain 97 and 111 mAh g⁻¹, respectively, both outperforming the pristine sample (88 mAh g⁻¹). PVA-0.9 again demonstrates the best performance, maintaining 178 mAh g⁻¹, confirming its effectiveness under both slow and

moderate current densities.

In contrast, PVA-1.2 and PVA-1.5 again exhibits limitations under faster cycling conditions. PVA-1.2 delivers only 272 mAh g⁻¹ in the first cycle at 0.2 C, lower than its value at 0.1 C. Its capacity remains similar to the pristine sample during the first 40 cycles but later surpasses PVA-0.3 and PVA-0.6, eventually reaching 143 mAh g⁻¹ at the 150th cycle. PVA-1.5 follows a similar pattern, starting with the lowest capacity among all electrodes (232 mAh g⁻¹) and remaining below the control for over 60 cycles, but stabilizing at 111 mAh g⁻¹ in the later stages, demonstrating strong long-term confinement despite compromised kinetics.

To investigate the impact of PVA coating on interfacial processes and resistance evolution during cycling, EIS was conducted on selected cells at the fresh state, after 10 cycles, and after 50 cycles at 0.1 C, as shown in [Figure 5.6c–e](#). The Nyquist plots exhibit a characteristic semicircle in the high-to-medium frequency region, corresponding to the charge-transfer resistance (R_{ct}), followed by a linear tail in the low-frequency region, which is associated with the Warburg impedance related to lithium-ion diffusion within the electrode. The equivalent circuit models used for fitting are adapted according to the electrode condition. For the pristine electrode at the fresh state, no surface film is present, and the impedance response is well fitted using a simple model composed of bulk resistance of the cell (R_e), R_{ct} , and Warburg element (Z_w) ([Figure S5.2a](#)). In contrast, all coated electrodes at the fresh state, as well as all samples after cycling, displays an additional high-frequency semicircle, requiring the inclusion of a surface film resistance (R_{sf}) in the equivalent circuit ([Figure S5.2b](#)), which reflects the presence of polymer-derived or solid electrolyte interphase (SEI) layers.^[396,397]

Table 5.2. Fitting results of *ex situ* EIS data (unit: Ω).

		Pristine	PVA-0.3	PVA-0.6	PVA-0.9	PVA-1.2	PVA-1.5
Fresh	$R_{sf} (\Omega)$	—	8.502	12.52	16.05	18.30	18.93
	$R_{ct} (\Omega)$	54.19	58.34	58.55	84.43	90.78	87.97
10 th	$R_{sf} (\Omega)$	17.82	18.18	18.51	19.35	19.53	25.54
	$R_{ct} (\Omega)$	73.98	78.16	82.43	97.23	91.89	101.8
50 th	$R_{sf} (\Omega)$	20.09	20.35	20.52	22.94	38.88	44.23
	$R_{ct} (\Omega)$	99.48	101.7	107.8	107.2	113.2	119.5

As summarized in [Table 5.2](#), both R_{sf} and R_{ct} are clearly dependent on coating amount across all three electrochemical states. At the fresh state, R_{sf} and R_{ct} increase progressively with increasing coating concentration. PVA-1.2 and PVA-1.5 exhibit much higher initial resistances

compared to PVA-0.3 and PVA-0.6. This trend is attributed to the insulating nature of PVA, which partially blocks charge transfer at the electrode-electrolyte interface. The elevated R_{sf} and R_{ct} values in thick coatings explain the reduced first-cycle discharge capacities observed earlier. Moreover, even after prolonged cycling, the heavily coated electrodes retain higher R_{sf} and R_{ct} values than those with thinner coatings. This persistent resistance buildup limits the rate performance and active material utilization of heavily coated electrodes, despite their improved long-term capacity retention. These findings reveal that increased coating amount enhances the physical stability of electrodes but comes at the cost of higher interfacial resistance and diminished reaction kinetics.

To further elucidate the evolution of interfacial resistance during cycling, [Figure 5.7](#) highlights *ex situ* EIS results for all six electrodes. For every sample, R_{ct} progressively increases with cycling, indicating degradation of the conductive network and diminished charge transfer kinetics. In parallel, R_{sf} also shows an upward trend with cycling. Notably, the pristine electrode exhibits no R_{sf} at the fresh state but develops a visible R_{sf} during cycling, suggesting gradual SEI formation. By contrast, coated electrodes present a measurable R_{sf} even at the fresh state due to the pre-existing polymer layer, which further increases upon cycling. For instance, R_{sf} in PVA-1.5 increases from 18.93 Ω at the fresh state to 44.23 Ω after 50 cycles, indicating a significant buildup of surface-layer resistance during prolonged operation. This evolution underscores the combined influence of the polymer coating and SEI thickening on interfacial resistance.

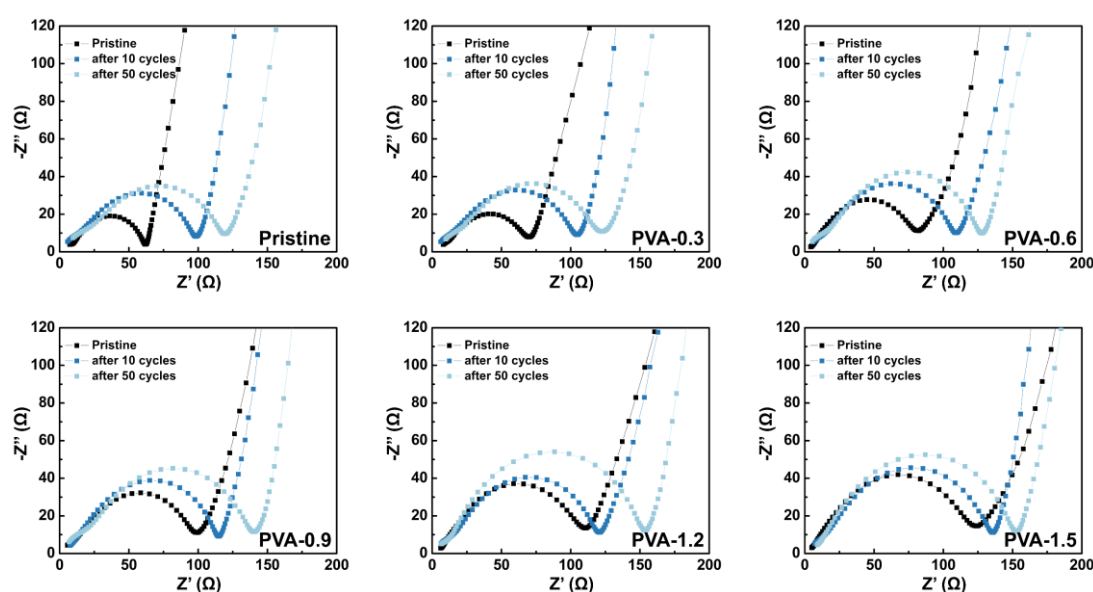


Figure 5.7. *Ex situ* EIS results of cells using 6 different electrode samples without or with

different content of PVA coating.

To assess the rate performance of the PVA-coated electrodes, GCD tests were performed under increasing current densities ranging from 0.2 C to 1 C (Figure 5.8a). All electrodes display decreasing capacity with increasing current density, a typical outcome due to shorter ion diffusion time and increased polarization. However, the extent of capacity loss varies significantly with coating amount. Thinner coatings, including PVA-0.3, PVA-0.6, and PVA-0.9, retain higher capacities at fast rates, while thicker coatings such as PVA-1.2 and PVA-1.5 exhibit greater capacity decline, indicating increased resistance to ion transport under high-rate conditions.

Additionally, the CE curves in Figure 5.8a provide further insight into the effect of PVA coating on redox reversibility during rate changes. During the initial discharge at each elevated current density, the CE of PVA-coated electrodes drops more significantly below 100% as the coating concentration increases, indicating a larger degree of irreversible capacity loss at high rates. In contrast, when the current density returns to 0.2 C after high-rate cycling, the CE values of electrodes with higher PVA concentration rise progressively above 100%, revealing a clear trend. This behavior suggests that thicker coatings, while initially impeding complete lithiation or delithiation at fast rates, help retain active species and promote recovery of capacity upon rate reduction.

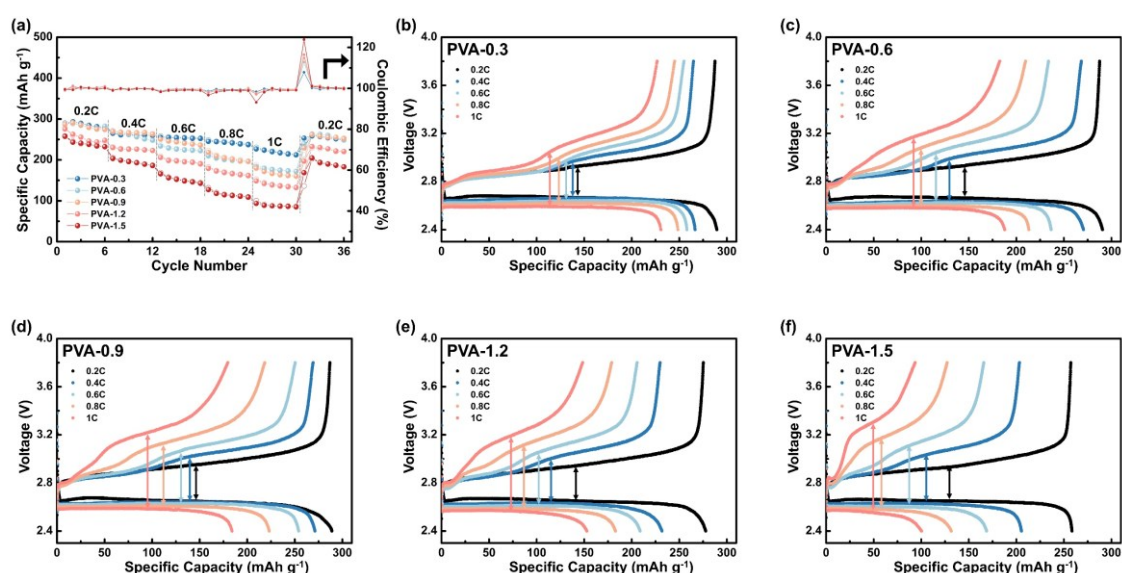


Figure 5.8. (a) Rate performance of PVA-coated electrodes under varying C-rates from 0.2 C to 1 C; (b–f) GCD curves of first discharge/charge at each rate for PVA-coated electrodes.

To further analyze the electrochemical polarization, the voltage gap between charge and

discharge curves at 50% state of charge (SOC) across different rates was extracted in [Figure 5.8b–f](#). These voltage differences provide a quantitative measure of overpotential under dynamic conditions. As shown in [Table 5.3](#), at low current densities (e.g., 0.2 C), voltage gaps across different electrodes remain similar. However, as current increases, the gaps widen, particularly for thicker coatings. For instance, at 1 C, the voltage gap increases from 0.4517 V (PVA-0.3) to 0.7421 V (PVA-1.5), reflecting the pronounced impact of interfacial resistance and reduced conductivity in thickly coated electrodes.

Table 5.3. Voltage gap at 50% SOC under various C-rates for PVA-coated electrodes (unit: V)

C rate	PVA-0.3	PVA-0.6	PVA-0.9	PVA-1.2	PVA-1.5
0.2C	0.2586	0.2700	0.3016	0.2892	0.2815
0.4C	0.2927	0.3621	0.3683	0.3711	0.3984
0.6C	0.3205	0.4231	0.4294	0.4467	0.4976
0.8C	0.3698	0.4957	0.5181	0.5395	0.6132
1C	0.4517	0.5853	0.6210	0.6297	0.7421

These results reaffirm that although PVA coatings effectively stabilize DNB and suppress dissolution, excessive coating amount significantly compromises rate performance due to additional mass-transfer limitations. Among all samples, PVA-0.9 strikes the best balance, with moderate voltage polarization and superior capacity retention across the full range of current densities.

5.4. Conclusions

This work presents two practical approaches for improving the cycling performance of DNB-based cathodes in LIBs. The use of a PEO-based SPE enables reversible redox activity at elevated temperature, but the performance is limited by the thermal diffusion of dissolved species into the electrolyte matrix. On the other hand, the application of PVA coatings on the cathode surface effectively suppresses material dissolution and significantly improves capacity retention at room temperature. Among the coating formulations tested, the electrode with a moderate PVA loading (PVA-0.9) achieves the best overall performance, retaining a specific capacity of 178 mAh g⁻¹ after 150 cycles at 0.2 C. However, further increases in coating amount lead to higher interfacial resistance and reduced rate capability. EIS analysis confirms that both charge-transfer and surface film resistances increase with PVA content and evolve during cycling. These results demonstrate that polymer coating is an effective strategy to stabilize

organic electrodes, and that careful optimization of coating amount is essential to balance ionic conductivity and long-term stability.

Chapter 6. Contributions and Significance of Thesis Research, and Suggestions for Future Work

6.1. Contributions and significance of thesis research

This thesis makes several significant contributions to the field of electrochemical energy storage by advancing the understanding and application of azo-, nitroso-, and nitro-based organic cathodes for LIBs. The research addresses critical challenges related to dissolution, conductivity, and stability by integrating molecular design, electrode engineering, and electrolyte optimization, thereby providing both mechanistic insights and practical strategies to overcome the intrinsic limitations of organic electrodes. The key contributions are as follows:

i) Mechanistic investigation of new redox-active systems

A central contribution of this thesis is the mechanistic clarification of nitrogen-containing organic cathode materials, particularly azo and nitroso compounds, which remain far less understood than the widely studied carbonyl systems. By combining systematic electrochemical testing with *ex situ* characterizations, this thesis establishes a coherent picture of the structural evolution and redox processes in these systems.

In **Chapter 3**, the redox behavior of azo dye cathodes, with a focus on MO and related derivatives, is systematically investigated. *Ex situ* characterizations during charge/discharge cycling confirm that the azo ($-N=N-$) group serves as the reversible redox center. This work provides detailed mechanistic demonstrations of the redox chemistry of azo-dye-based OCMs in LIBs. Beyond clarifying the mechanism, this study establishes the feasibility of employing low-cost, commercially available dyes as cathode materials, thereby validating a new class of organic electrodes and opening new directions for material selection in azo-based systems.

In **Chapter 4**, the electrochemical mechanisms of nitroso-based compounds are elucidated. Small molecules, such as NSB, NST, NSBA, LiNSBA, along with polymeric DNSB, are examined. Spectroscopic analysis reveals a common irreversible transformation from nitroso groups ($-N=O$) into azo-type species through azoxy intermediates during initial cycles. The identification of $Li-N=N-Li$ and $N=N$ coordination states provides new mechanistic insights. More importantly, the discovery that nitroso groups can *in situ* transform into azo-type redox centers suggests a novel design principle, enabling the construction of electrodes where nitroso

precursors evolve into more stable azo polymers during cycling, offering a previously unexplored route to stabilize organic cathodes. Beyond mechanistic clarification, this chapter underscores molecular design as a critical pathway for stabilization, showing that approaches such as lithiation and polymerization can establish new principles for improving durability and guiding the development of next-generation OCMs.

ii) Insights into electrolyte compatibility with different OCMs

Another important contribution of this thesis is the systematic evaluation of how electrolyte environments influence the performance and stability of OCMs. Since many OCMs suffer from dissolution and interfacial instability in conventional carbonate-based electrolytes, understanding their compatibility with alternative systems is essential. Through comparative studies, this work demonstrates how electrolyte chemistry directly governs solubility, redox reversibility, and long-term cycling, thereby providing guidance for tailoring electrolytes to the unique requirements of organic electrodes.

In **Chapter 4**, this thesis clarifies the electrolyte compatibility of nitroso-based cathodes, an aspect that had remained poorly understood. NSB and NST show reversible cycling in carbonate electrolytes but fail in ether systems, whereas NSBA, LiNSBA, and polymeric DNSB display lower solubility in both, with ether electrolytes offering better stability. Among them, DNSB performs best due to its polymeric backbone, which suppresses dissolution and enables extended cycling. These results establish a clear link between molecular structure and electrolyte environment, and the contribution of this work lies in demonstrating that electrolyte compatibility must be systematically tailored to molecular motifs, providing design principles for stabilizing organic cathodes.

In **Chapter 5**, PEO-based SPEs are employed with *p*-DNB cathodes. The SPEs suppress dissolution at room temperature, but at elevated temperatures, despite maintaining redox activity, melting of the PEO matrix weakens confinement and causes capacity fading. This highlights the critical need to balance ionic conductivity (which generally increases with temperature) with effective solubility suppression in polymer electrolytes, underscoring that SPE systems for organic cathodes require more refined design to achieve both stability and performance.

iii) Exploration of electrode engineering strategies for improved performance

A further contribution of this thesis lies in developing electrode engineering strategies to suppress dissolution, enhance conductivity, and improve the long-term cycling stability of organic cathodes. Since many OCMs are intrinsically soluble and poorly conductive, electrode-level design provides an essential pathway to stabilize active species and ensure efficient charge transport. This work demonstrates how polymer coatings, carbon encapsulation, and composite architectures can be used to control dissolution, reduce charge-transfer resistance, and improve utilization efficiency.

In **Chapters 3 and 4**, this thesis contributes by demonstrating that carbon encapsulation is a powerful and generalizable strategy for stabilizing soluble organic cathodes. By embedding both azo dyes such as MO and nitroso-based polymers such as DNSB into conductive porous carbons, the work shows that nanoscale confinement and enhanced conductivity can simultaneously suppress dissolution, lower charge-transfer resistance, and extend long-term cycling stability. This establishes carbon-based composites as a versatile and scalable design principle, providing a clear pathway to translate otherwise unstable organic molecules into practical cathode materials for lithium-ion batteries.

In **Chapter 5**, PVA coatings are introduced onto *p*-DNB electrodes as protective barriers that reduced active-material dissolution and preserved mechanical integrity at the electrode–electrolyte interface. Electrochemical testing confirms that optimized coating thickness significantly extends cycle life, whereas excessively thick layers increase interfacial resistance and polarization, highlighting the importance of balancing protection and transport. Beyond the specific case of *p*-DNB, this work demonstrates a broadly applicable and scalable strategy for stabilizing water-insoluble organic cathodes, offering a practical route to mitigate dissolution and enhance cycling stability for potentially practical applications.

iv) Broader impact on sustainable energy storage

abundant energy storage. By shifting away from transition-metal-based cathodes and establishing viable strategies for stabilizing organic electrodes, it supports global efforts to reduce reliance on critical metals, mitigate environmental impact, and promote recyclable, circular battery chemistries. As energy storage demand continues to accelerate, the insights developed here provide guiding principles for designing scalable and environmentally friendly cathodes that can meet future energy needs.

6.2. Suggestions for future work

While the advances achieved in this thesis mark important steps forward, several challenges remain unresolved, pointing to fertile directions for future research.

- i) First, molecular design must balance stability with energy density. Polymerization can effectively suppress dissolution, but excessive chain growth often lowers the number of accessible redox sites. Salt formation offers another approach, as ionic interactions help immobilize active molecules and improve their cycling stability. Future work should focus on combining these strategies in a controlled way—for instance, using partial polymerization or selecting appropriate counterions—to reduce solubility while retaining sufficient redox activity. The integration of computational prediction with targeted synthesis will be valuable for guiding the design of such balanced systems.
- ii) Second, interfacial engineering with SSEs remains a major bottleneck. For polymer-based SSEs, the main limitation is their modest ionic conductivity at room temperature, which restricts practical operation and often necessitates elevated temperatures that accelerate dissolution, diffusion, and side reactions of organic electrodes. Future efforts should therefore focus on designing new polymer electrolytes or polymer hybrids incorporating ionic liquids, plasticizers, or tailored segmental mobility to achieve high conductivity at room temperature while preserving mechanical strength and stability against organic species. Inorganic SSEs present a different set of challenges: oxide-based electrolytes typically suffer from high interfacial resistance, whereas sulfide-based electrolytes, although highly conductive, are chemically unstable and have been demonstrated in only a few all-solid-state cells with narrow voltage windows and poor long-term stability. Addressing these issues may require interfacial engineering through artificial interlayers, chemical surface modification, or buffer phases, as well as compositional tuning and protective coatings to stabilize sulfide phases. Looking ahead, hybrid SSEs that combine the interfacial adaptability of polymers with the conductivity of inorganic phases, together with in situ characterization of solid–solid interfaces, offer a promising pathway toward stable and efficient organic-based solid-state batteries.
- iii) Third, while OCMs already demonstrate promising tunability and sustainability, their energy density and cycling stability still leave room for improvement compared with commercial cathode materials. In particular, the relatively low intrinsic conductivity of

many OCMs requires higher carbon content in electrodes, which reduces volumetric energy density. Addressing these challenges will require not only the development of active materials with higher conductivity and redox efficiency, but also systematic optimization of electrode formulations. Composite structures with conductive carbons, careful binder selection, and tailored electrode architectures can enhance electronic pathways and structural stability. In parallel, pairing with compatible electrolytes and improving cell assembly will be equally important. Such integrated efforts will be critical to narrowing the performance gap and advancing OCM-based batteries toward practical applications.

- iv) Finally, the chemical space of organic cathodes remains far from fully explored. Beyond a few model compounds, many molecular families are still under-investigated for their potential in multi-electron storage. Future studies should couple material discovery with mechanistic analysis, where the coordination of *in situ* spectroscopy with DFT calculations and kinetic modeling will be essential for establishing structure–stability relationships and guiding the rational design of more durable redox chemistries.

The following section outlines, case by case, how the projects presented in chapters 3 to 5 can be further developed.

- i) **Chapter 3:** Future work on azo dye cathodes should take advantage of the rich and diverse library of commercially available dyes, which provide a low-cost and accessible pool of candidates far beyond the few model compounds studied to date. Exploring this chemical space, particularly azo derivatives with higher redox site density and lower solubility, could reveal new materials with improved stability and capacity. Rational molecular modification through substituents offers a means to tune redox potential and reversibility, while electrode engineering can further enhance performance.
- ii) **Chapter 4:** Among the nitroso compounds investigated herein, DNSB emerges as the most promising candidate due to its polymeric backbone and reduced solubility, which enable superior cycling stability compared with small-molecule analogues. Building on these mechanistic insights, future efforts should focus on tuning the degree of polymerization of DNSB to achieve a balance between capacity and cyclability, for example through controlled synthesis or by confining polymerization within defined structural frameworks. In addition, the discovery that nitroso groups can transform *in*

situ into azo-type redox centers suggests a new design principle: constructing precursors that potentially evolve into more stable azo frameworks during cycling and extending this concept to the design and investigation of a broader range of nitroso compounds.

- iii) **Chapter 5:** To further approach practical application, *p*-DNB cathodes should be systematically studied in a wider range of electrolyte environments to determine which systems are most compatible with its redox chemistry. In particular, the use of SSEs could help physically suppress dissolution, while advanced liquid electrolytes such as high-concentration or fluorinated formulations may provide improved cycling stability compared with conventional systems. At the same time, electrode-level engineering remains a practical lever: tuning particle size, optimizing the ratio of active material to conductive carbon, embedding *p*-DNB within porous carbons, and developing polymer-based composites can collectively improve conductivity, structural integrity, and resistance to dissolution. By coupling these electrolyte and electrode strategies, future work can more clearly define the practical viability of DNB and outline its potential role in organic cathode development.

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Appendix A

Supplementary Information

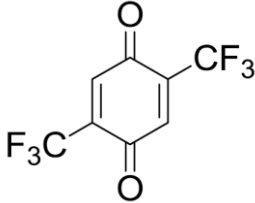
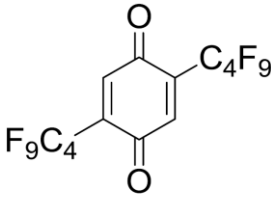
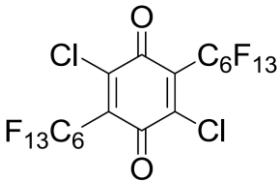
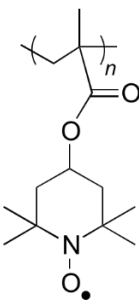
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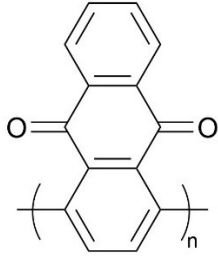
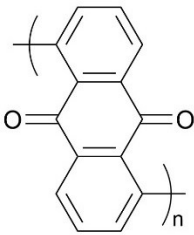
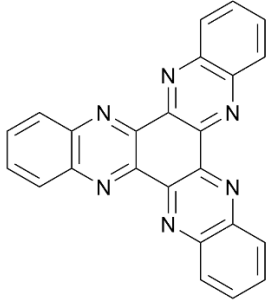
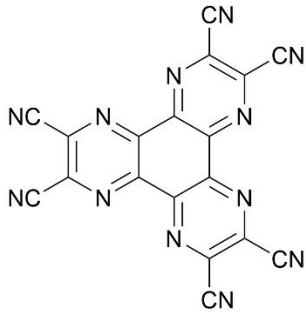
Electrochemical Performances of Azo Dyes as Organic
Cathodes for Lithium-Ion Batteries

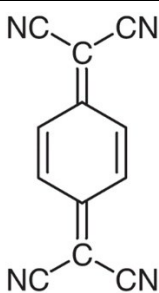
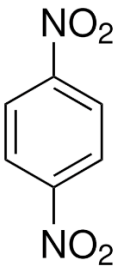
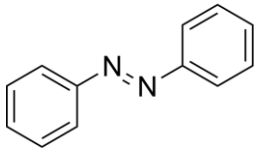
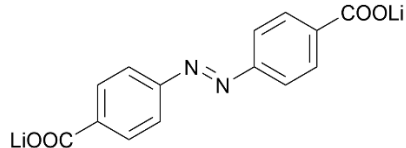
Table S3.1. Prices of raw materials obtained from Thermo Fisher and MSE Supplies LLC.

Chemical name	Product No.	Pack size	Total price (USD)	Unit price (USD/kg)
Methyl orange (MO)	AAA1760436	500 g	164.3	328.6
Methyl red (MR)	AAA1669036	500 g	337.50	755
Orange G (OG)	18-612-086	1 kg	1025	1025
Congo red (CR)	ICN10509990	500 g	540	1080
Lithium cobalt oxide (LiCoO ₂)	PO0129	500 g	344.90	689.8
Lithium nickel manganese cobalt oxide (LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂ , NMC811)	PO5038	500 g	512.95	1025.9
Lithium Manganese Oxide (LiMn ₂ O ₄)	PO0126	500 g	408.95	817.9
Lithium Iron Phosphate (LiFePO ₄)	PO0127	500 g	414.95	829.9

Table S3.2. Prices of organic cathode materials for LIBs reported in the literature.

Organic positive electrode	Product No.	Unit price (USD/kg)	Ref.
 2,5-bis(trifluoromethyl)-1,4-benzoquinone (CF₃-BQ)	NA	multi-step synthesis required	[28]
 2,5-bis(perfluorobutyl)-1,4-benzoquinone (Rf₄-BQ)			
 2,5-bis(perfluorohexyl)-3,6-dichloro-1,4-benzoquinone (Rf₆-Cl-BQ)			
 Poly(4-methacryloyloxyTEMPO) (PTMA)	NA	multi-step synthesis required	[398]

 Poly(1,4-anthraquinone) (P14AQ)	NA	multi-step synthesis required	[399]
 Poly(1,5-anthraquinone) (P15AQ)	NA	multi-step synthesis required	
 Hexaazatrinaphthylene (3Q)	NA	multi-step synthesis required	[400]
 Hexaazatriphenylenehexa carbonitrile (6CN)			

 7,7,8,8-tetracyanoquinodimethane (TCNQ)	AC169360100	16680	[401]
 <i>P</i>-dinitrobenzene (<i>p</i>-DNB)	AAA1029322	8680	[35]
 Azobenzene (AB)	AC401542500	2622	[36]
 Azobenzene-4,4'-dicarboxylic acid lithium salt (ADALS)	NA	multi-step synthesis required	[38]

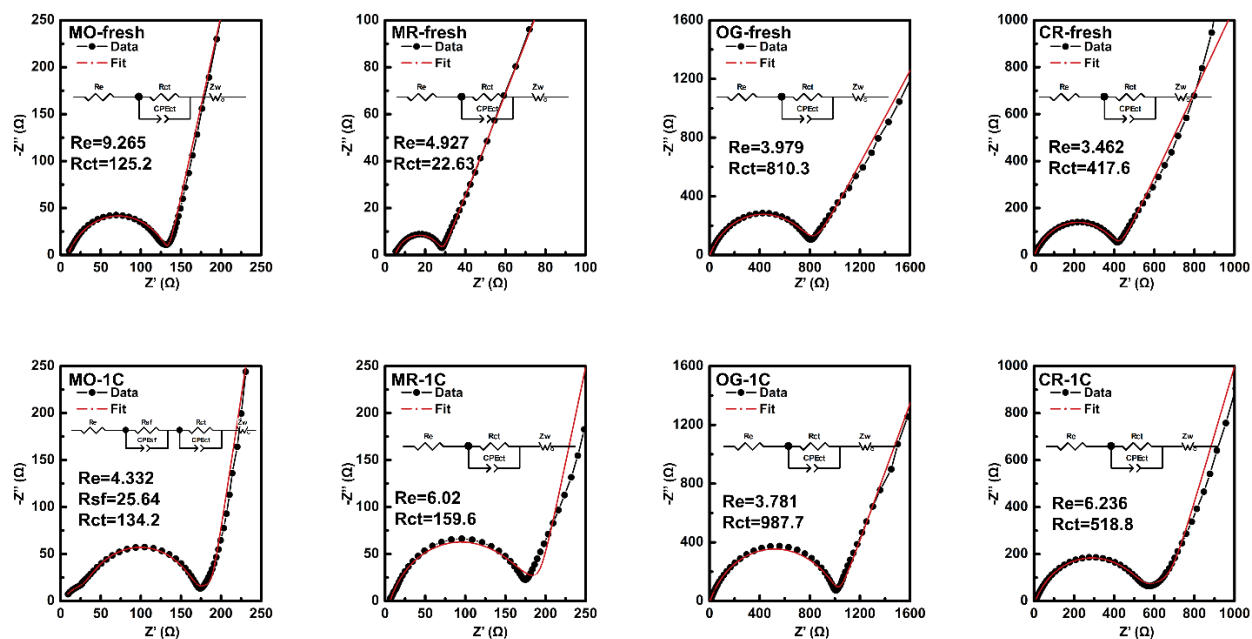
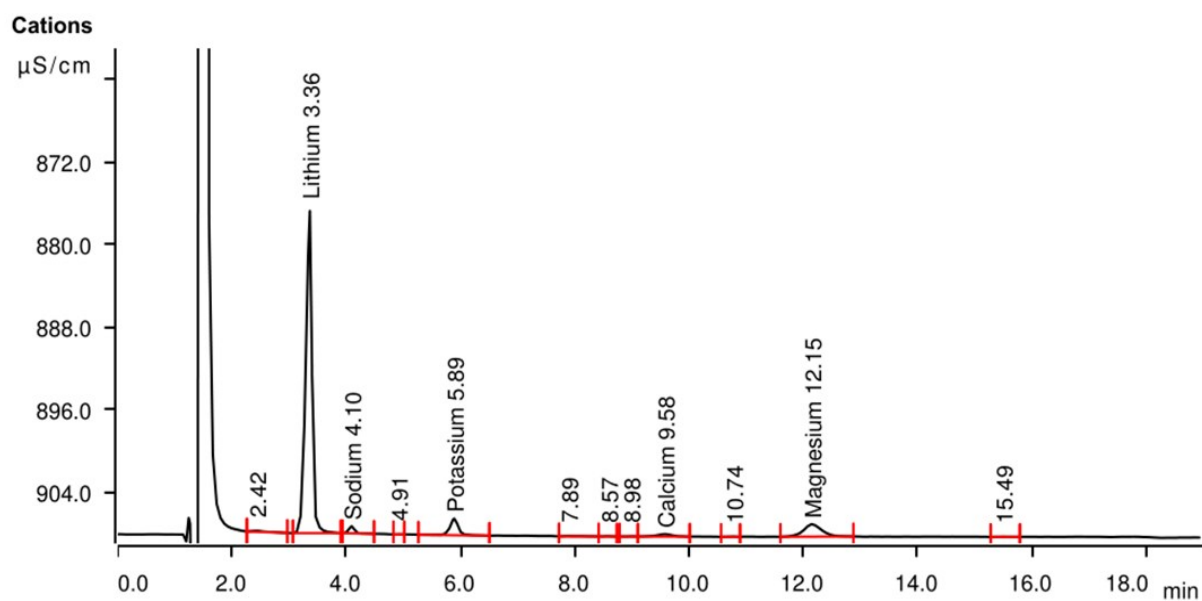


Figure S3.1. EIS results and fitting plot of four batteries at the fresh state and after the first charge.



Peak number	Retention time min	Area (μS/cm) x min	Height μS/cm	Concentration ppm	Component name
1	2.418	0.0258	0.095	invalid	
2	3.363	3.9694	31.262	5.244	Lithium
3	4.095	0.0760	0.691	0.206	Sodium
4	4.912	0.0012	0.013	invalid	
5	5.888	0.2737	1.609	2.047	Potassium
6	7.890	0.0110	0.029	invalid	
7	8.567	0.0040	0.026	invalid	
8	8.980	0.0033	0.019	invalid	
9	9.578	0.0756	0.237	-0.153	Calcium
10	10.737	0.0036	0.019	invalid	
11	12.147	0.4503	1.198	1.503	Magnesium
12	15.493	0.0040	0.016	invalid	

Figure S3.2. Ion chromatography results of MOLS.

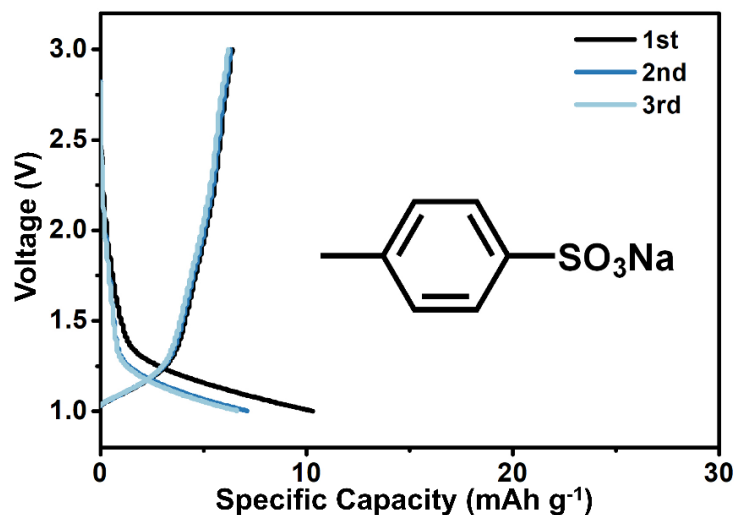


Figure S3.3. Galvanostatic charge–discharge (GCD) curves of a cell with sodium *p*-toluenesulfonate cathode at 30 mA g⁻¹ within 1.2–3.0 V versus Li⁺/Li (the electrodes were fabricated with the same procedure as azo dye cathodes except with the use of Nafion as the binder).

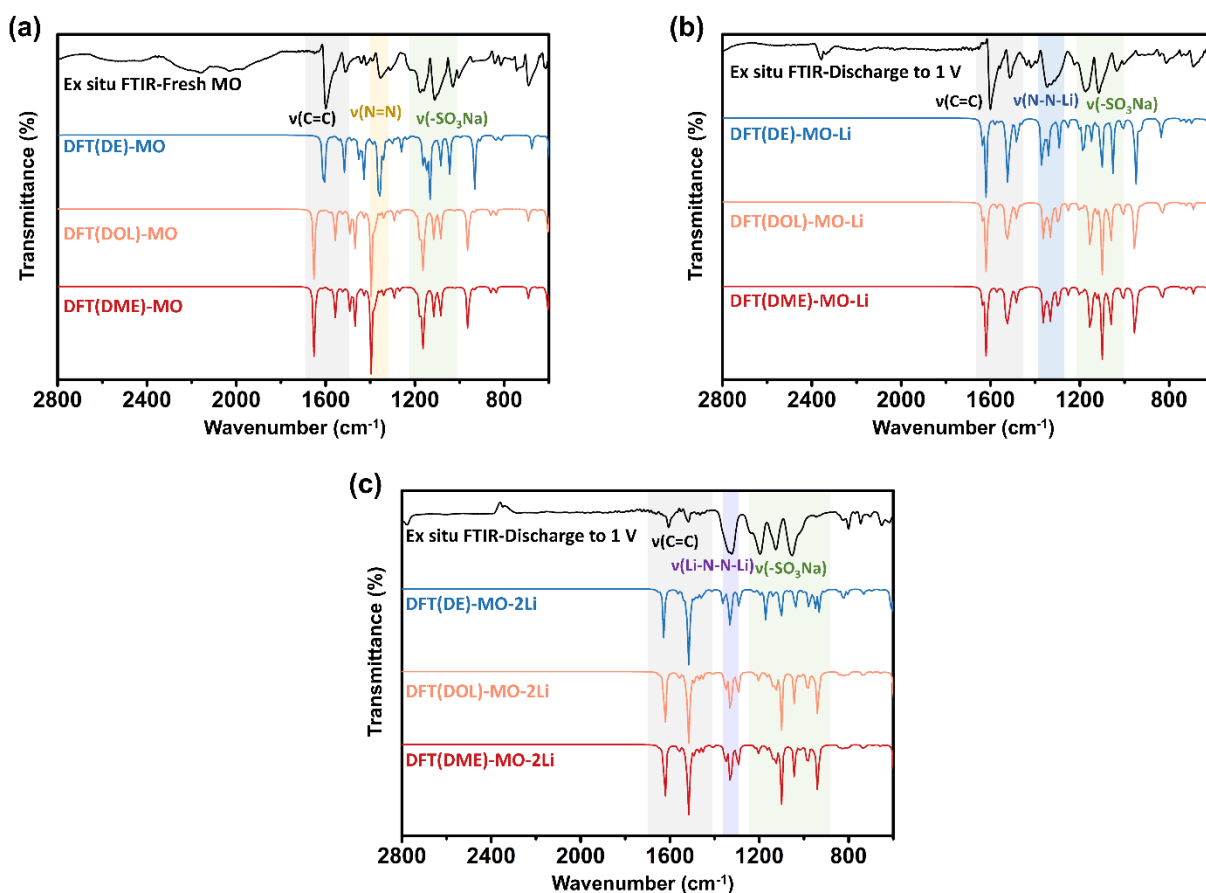


Figure S3.4. Comparative experimental IR spectra and DFT-simulated spectra of MO, MO-Li, and MO-2Li in different solvent models.

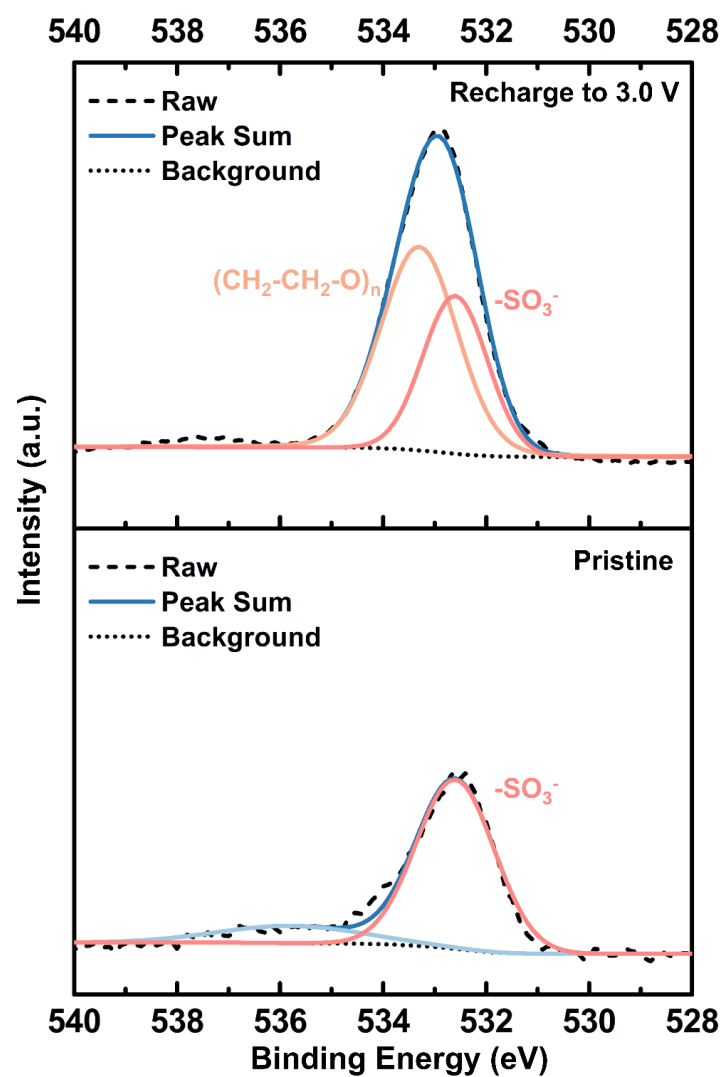


Figure S3.5. O 1s XPS spectra of MO electrodes before and after the 1st GCD cycle.

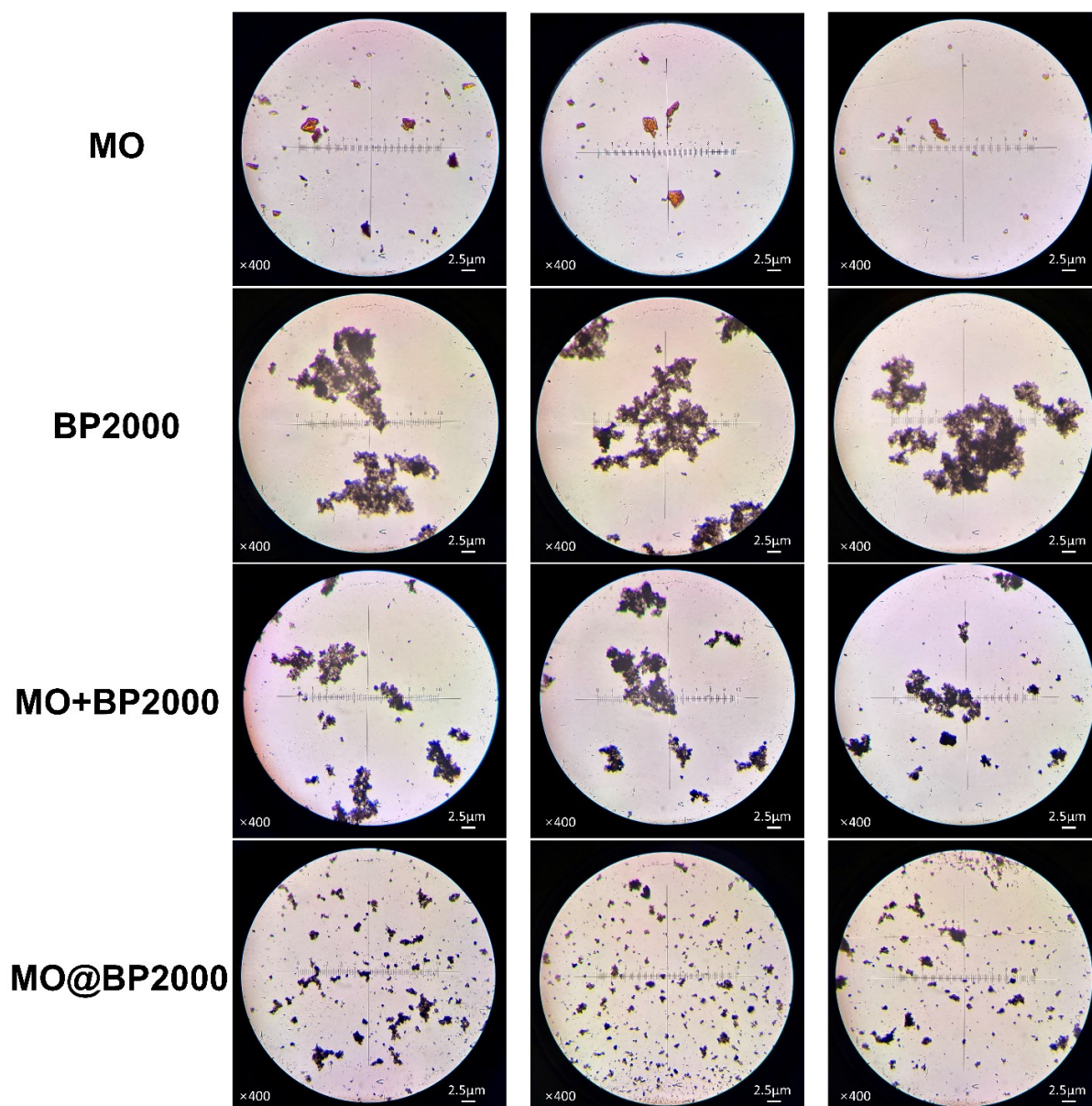


Figure S3.6. Optical microscopy images of pristine MO, pristine BP2000, physical mixture of MO and BP2000, and MO@BP2000 composite (magnification: 400×).

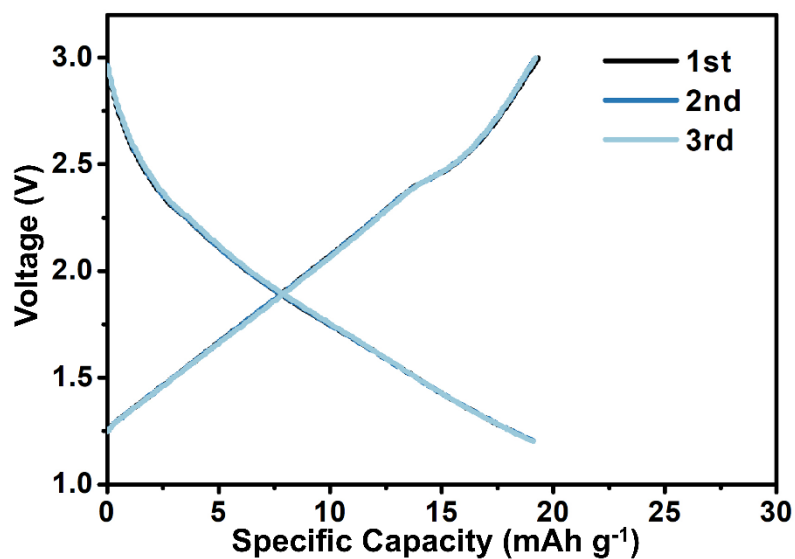


Figure S3.7. GCD curves of a cell with BP2000 cathode at 30 mA g^{-1} within 1.2–3.0 V versus Li^+/Li (the electrodes were fabricated with the same procedure as azo dye cathodes).

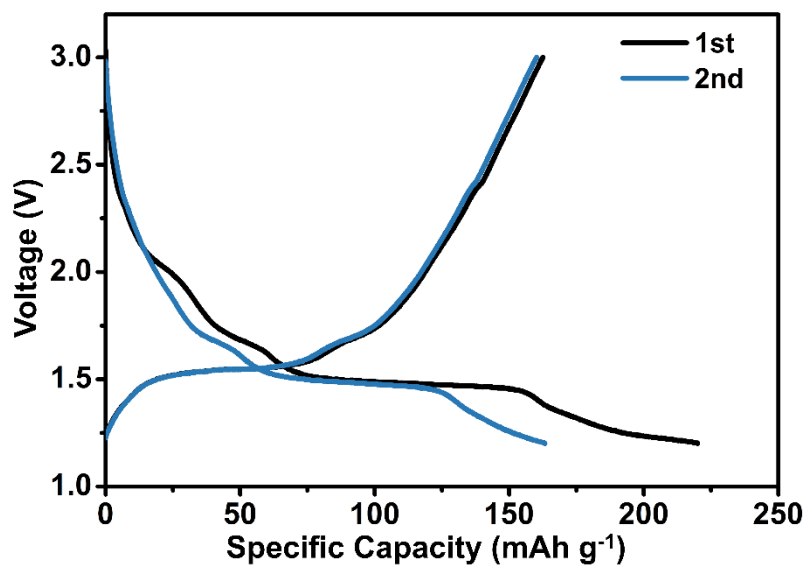


Figure S3.8. GCD curves of the first two cycles during the rate performance test of MO@BP2000 electrode.

Appendix B

Supplementary Information

for

Revealing the electrochemical evolution of nitroso-to-azo
cathodes for lithium-ion storage

Compatibility Test of Nitroso Compounds with Lithium in Electrolytes

To evaluate the chemical stability of various nitroso compounds in different electrolytes, a compatibility test was conducted using Li metal disks. Specifically, 50 mg of each active material was dissolved in 2 mL of two different electrolyte systems: 1 M LiTFSI in DOL/DME (1:1, v/v) and 1 M LiPF₆ in EC/DMC (1:1, v/v). After confirming dissolution or dispersion behavior through visual inspection, a clean lithium metal disk was added to each solution under an argon atmosphere. The vials were then sealed and stored statically under inert conditions to prevent ambient contamination. Photographs were taken at selected time intervals to monitor any morphological or colorimetric changes of the lithium surface, serving as an indication of possible side reactions or degradation pathways between the active material and lithium in each electrolyte environment.

Following the stability test, significant instability of the nitroso compounds was observed in the 1 M LiTFSI in DOL/DME electrolyte, as evidenced by noticeable changes to the Li metal surface. To further investigate the chemical byproducts formed during this process, the electrolyte solution was processed after removing the Li disk. The remaining solution was concentrated under reduced pressure, and the residue was subjected to recrystallization by slow addition into poor solvent (deionized water). The resulting solid was collected, washed thoroughly with water three times to remove residual salts and soluble impurities, and then dried under vacuum at 80 °C for 24 h.

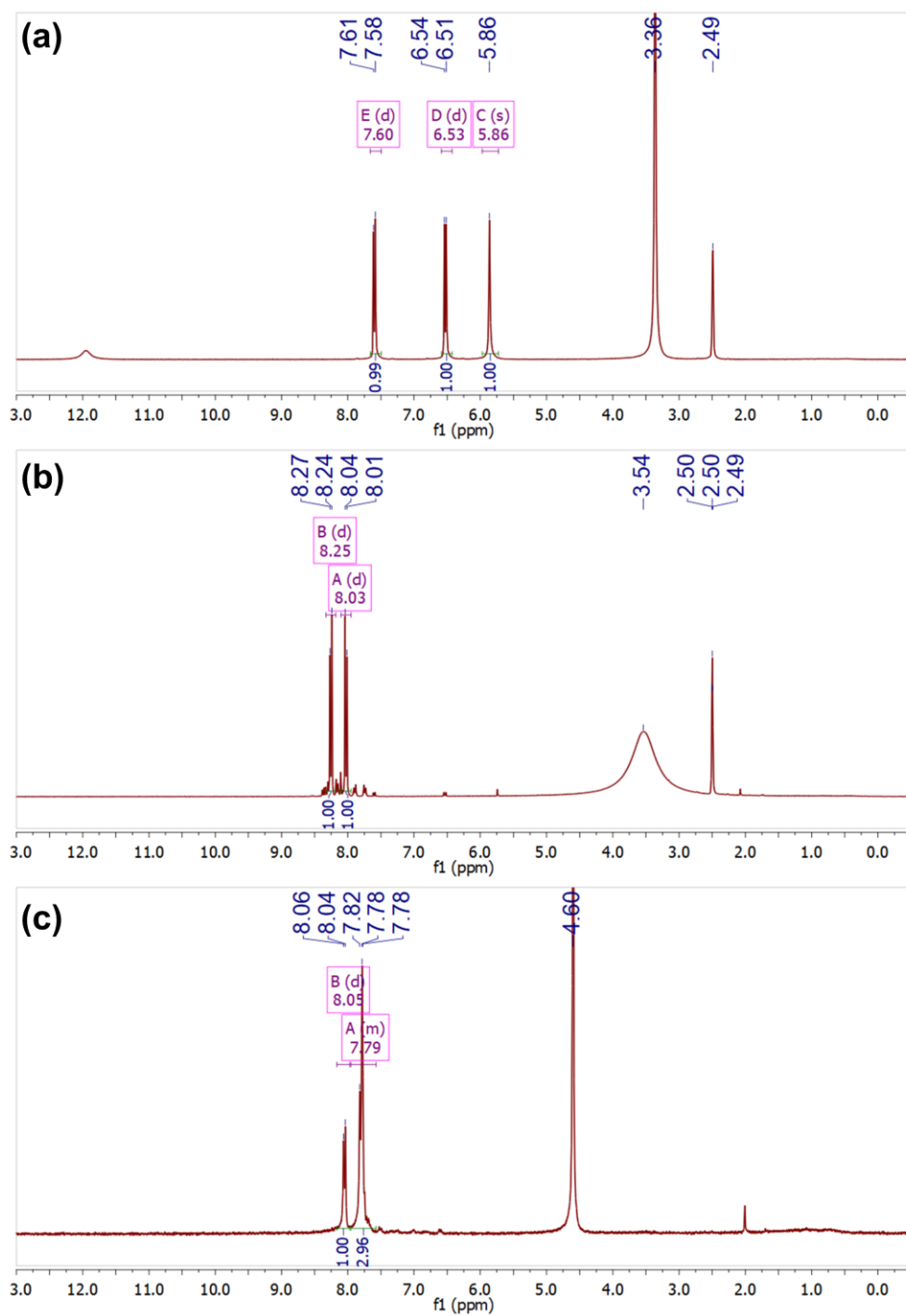


Figure S4.1. ^1H NMR spectra of (a) 4-aminobenzoic acid, (b) synthesized NSBA, and (c) synthesized LiNSBA.

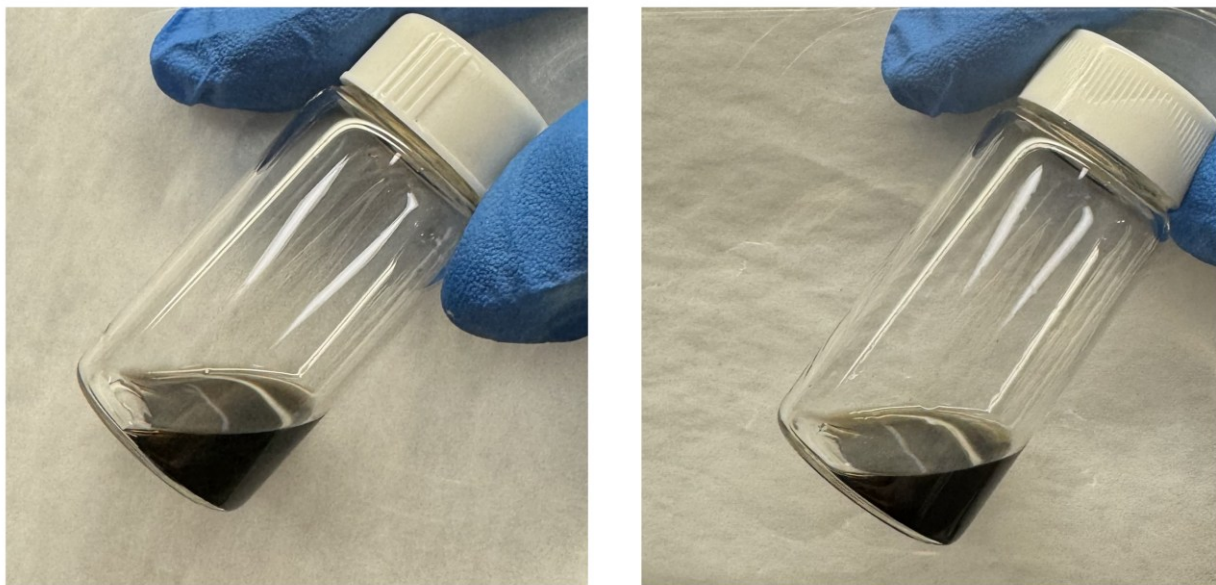


Figure S4.2. The dissolution test for 50 mg NSB in 2 mL of LiPF₆-EC/DMC (left) and LiTFSI-DOL/DME (right) electrolytes.

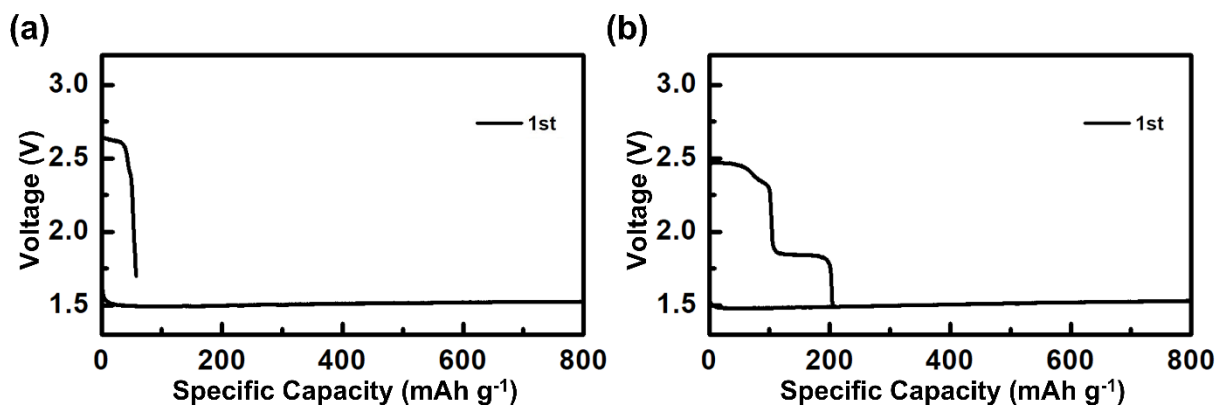


Figure S4.3. GCD curves of (a) NSB and (b) NST cathodes in 1M LiTFSI in DOL/DME electrolyte at a current density of 50 mA g⁻¹.

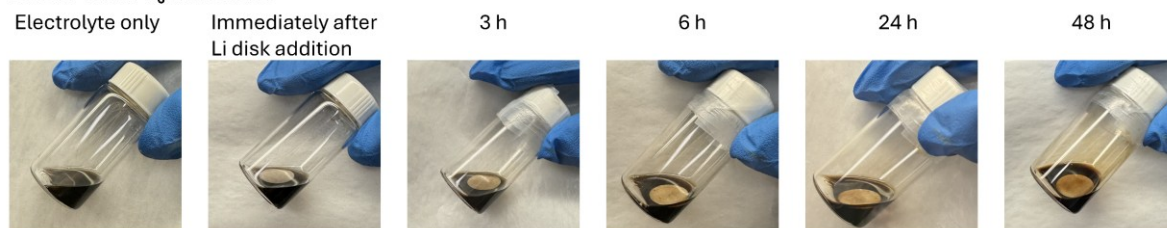
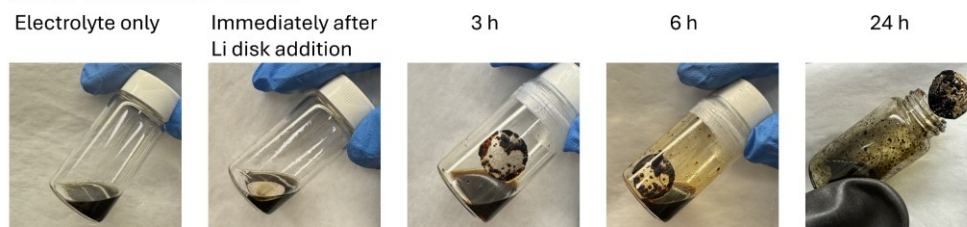
NSB in 1M LiPF₆ in EC/DMC**NSB in 1M LiTFSI in DOL/DME**

Figure S4.4. Compatibility tests of NSB and Li metal disks in two electrolytes: 1M LiPF₆ in EC/DMC (top row) and 1M LiTFSI in DOL/DME (bottom row). Each row shows (from left to right) the electrolyte containing NSB before Li addition, immediately after the addition of the Li disk, and after 3, 6, 24, and (for LiPF₆) 48 h.

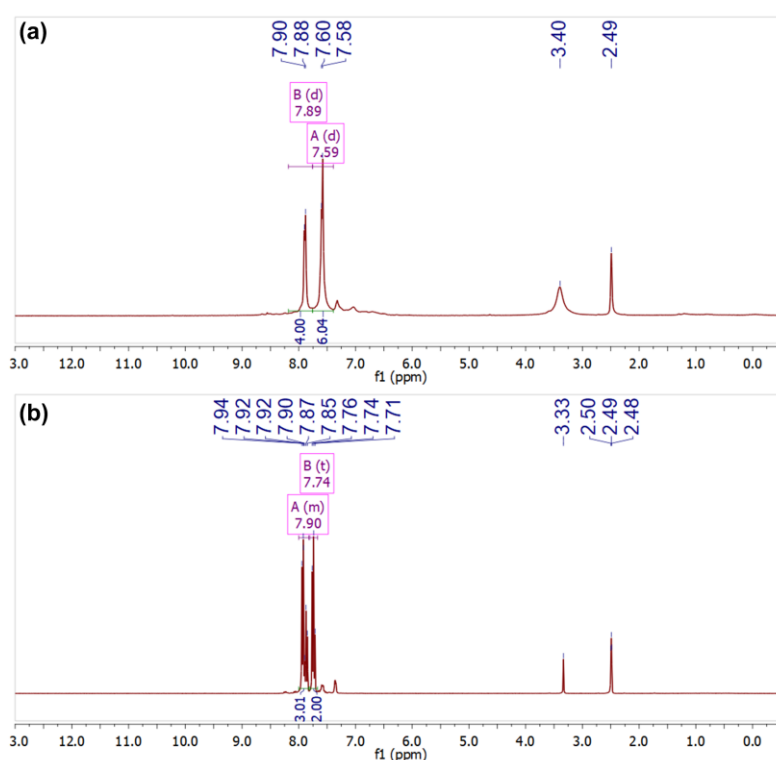


Figure S4.5. ¹H NMR spectra of (a) NSB and (b) NSB-R.

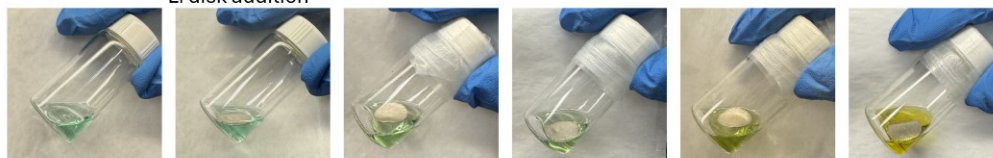
NST in 1M LiPF₆ in EC/DMCElectrolyte only Immediately after
Li disk addition**NST in 1M LiTFSI in DOL/DME**Electrolyte only Immediately after
Li disk addition

Figure S4.6. Compatibility tests of NST and Li metal disks in two electrolytes: 1 M LiPF₆ in EC/DMC (top row) and 1M LiTFSI in DOL/DME (bottom row). Each row shows (from left to right) the electrolyte containing NSB before Li addition, immediately after the addition of the Li disk, and after 3, 6, 24, 48 and (for LiPF₆) 168 h.

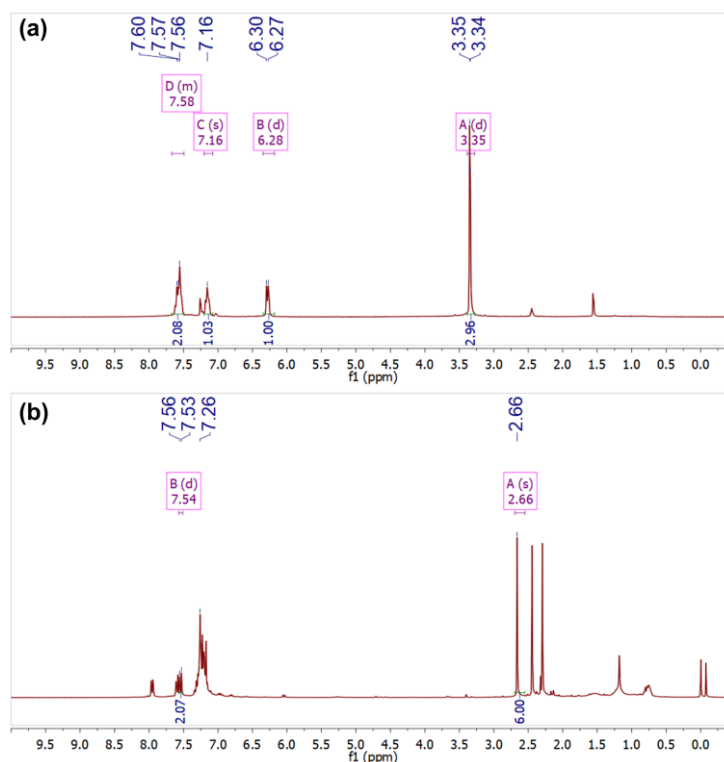


Figure S4.7. ¹H NMR spectra of (a) NST and (b) NST-R. The peaks ascribed to NST disappears in (b). The spectrum of NST-R exhibits characteristic peaks of *o,o'*-azotoluene.^[402]

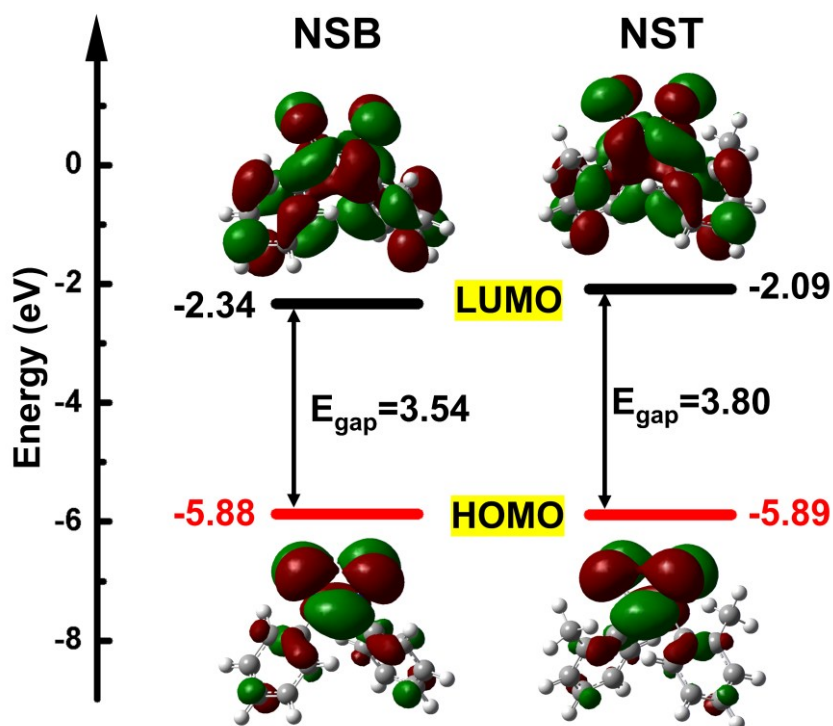


Figure S4.8. Calculated molecular orbitals (HOMO/LUMO) of NSB and NST by DFT.

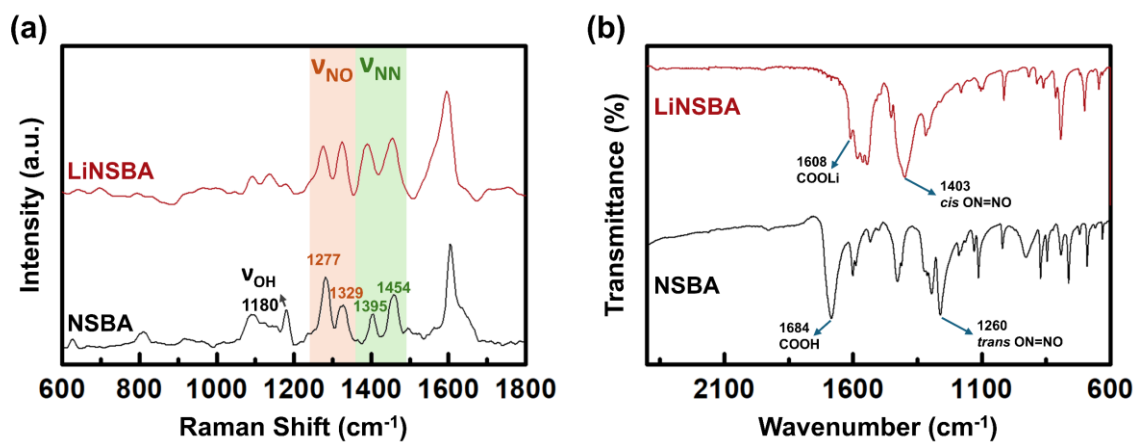


Figure S4.9. Comparative (a) Raman and (b) FTIR spectra of NSBA and LiNSBA.

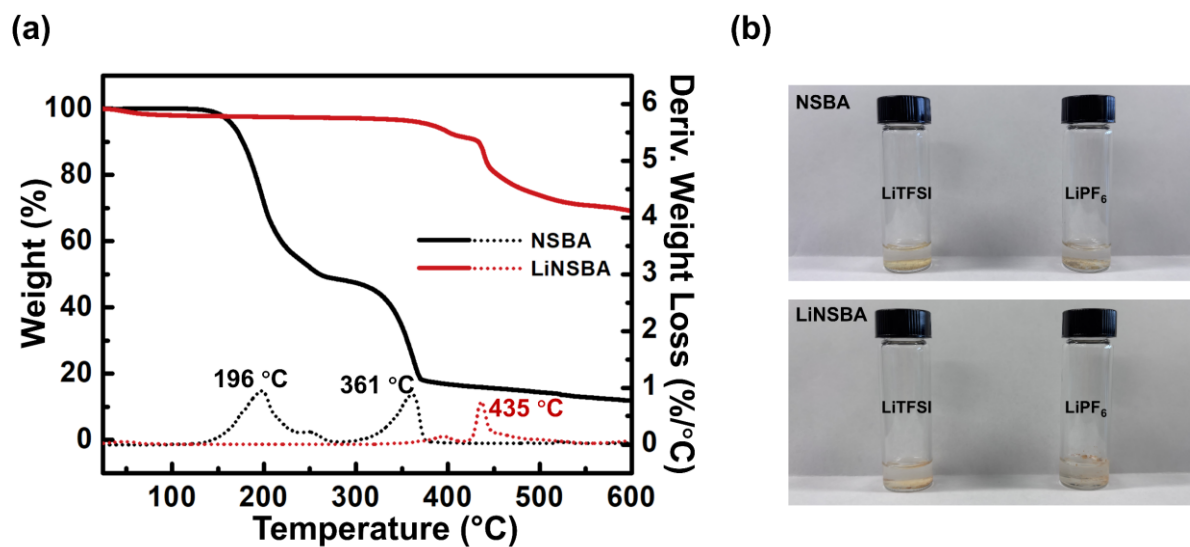


Figure S4.10. (a) Comparative TG and DTG curves of NSBA and LiNSBA; (b) solubility tests of NSBA and LiNSBA in electrolytes.

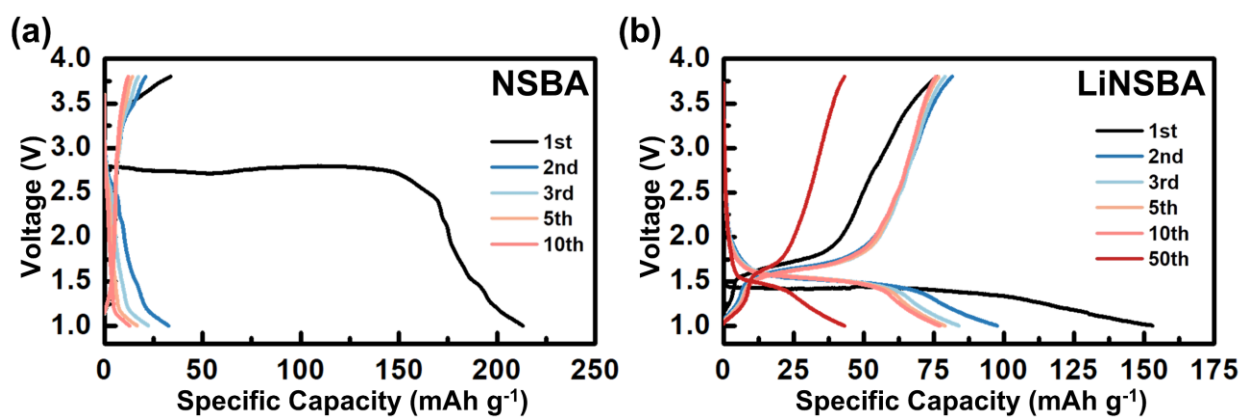


Figure S4.11. GCD curves of (a) NSBA and (b) LiNSBA cathodes in 1 M LiPF₆ in EC/DMC electrolyte at a current density of 50 mA g⁻¹.

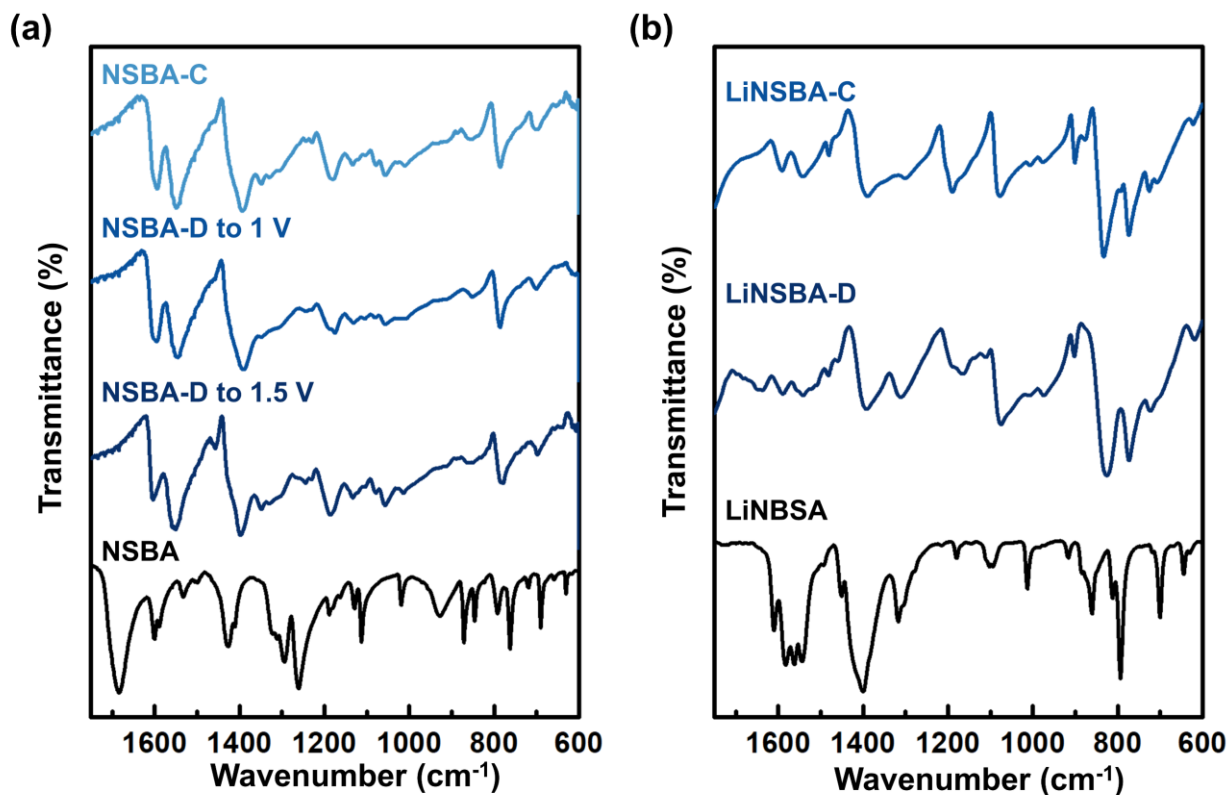


Figure S4.12. *Ex situ* FTIR spectra of (a) NSBA and (b) LiNSBA cathode samples at different discharge and charge states in the first cycle in comparison with relative reduced product.

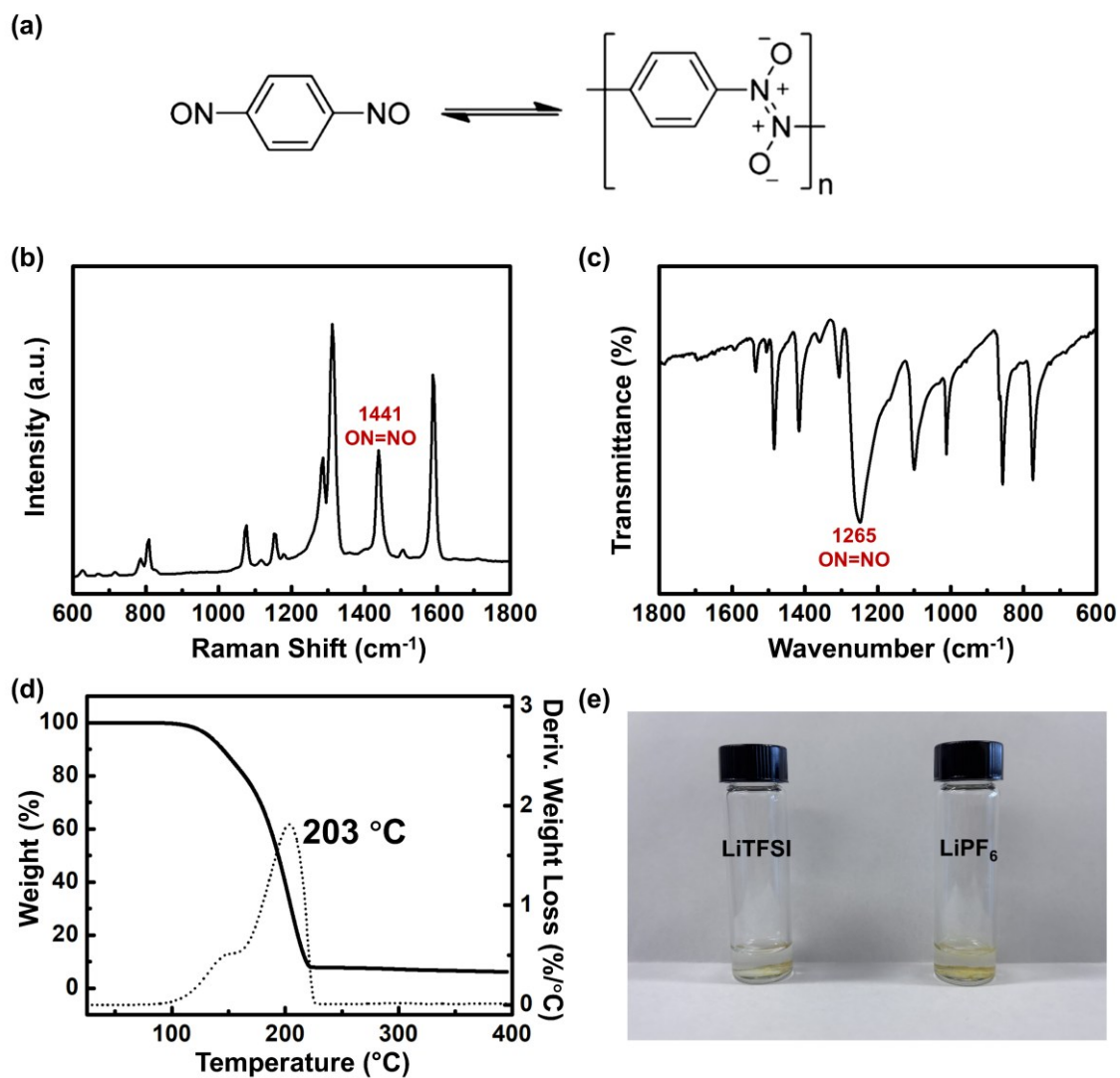


Figure S4.13. (a) Illustration of polymerization of DNSB; (b–d) Raman spectrum, FTIR spectrum, and TGA curve of DNSB; (e) solubility tests of DNSB in LiTFSI-DOL/DME (left) and LiPF₆-EC/DMC (right) electrolytes.

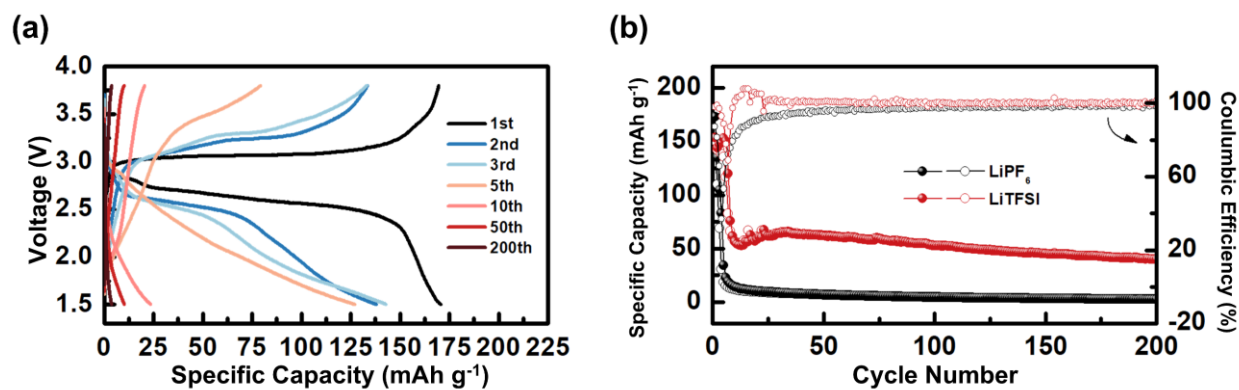


Figure S4.14. (a) GCD curves of DNSB/SP cathode in 1 M LiPF₆ EC/DMC electrolyte at 50 mA g⁻¹; (b) cycling performance of DNSB/SP cathode in two electrolytes at 50mA g⁻¹.

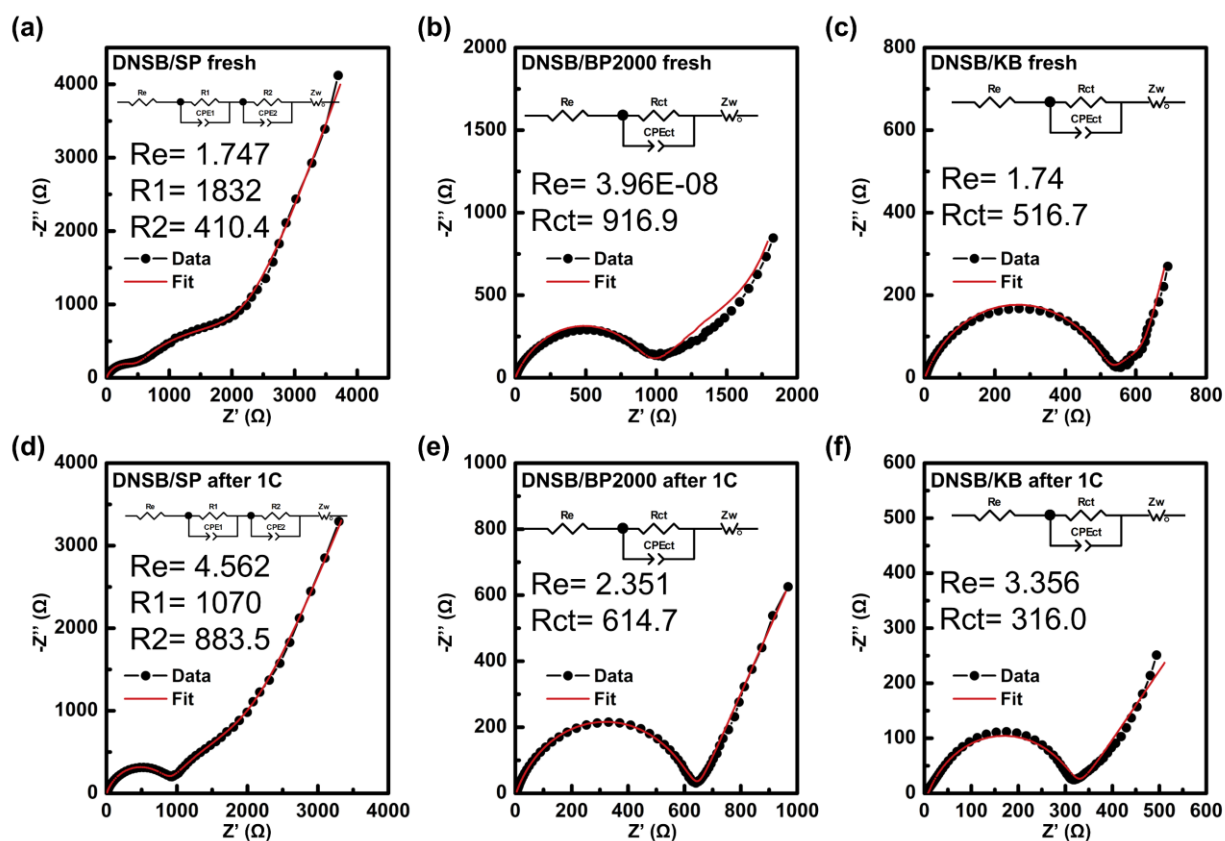


Figure S4.15. EIS results and fitting plot of DNSB/SP, DNSB/BP2000, and DNSB/KB cathodes with at fresh state and after 1st cycle at 50 mA g⁻¹.

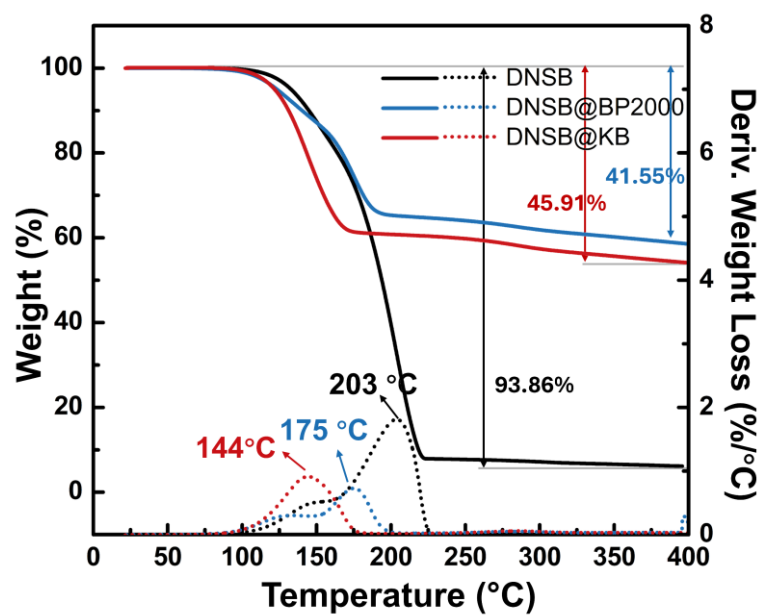


Figure S4.16. TGA and DTG curves of DNSB, DNSB@BP2000, and DNSB@KB under N₂.

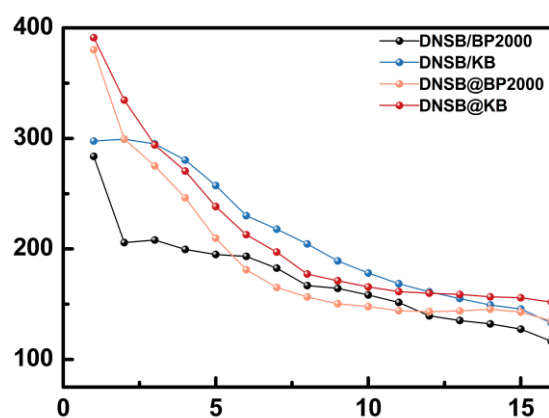


Figure S4.17. First 15 cycles of rate performance tests for DNSB/BP2000, DNSB/KB, DNSB@BP2000, and DNSB@KB cathodes in LiTFSI-DOL/DME electrolyte.

Table S4.1. Quantitative XPS peak area analysis of nitrogen species at different cycles for the DNSB/KB cathode.

Cycles	Integral area			Area fraction	
	Species A	Species B	Sum area	A fraction	B fraction
Pristine	28026.23	16979.24	45005.47	0.622729	0.377271
1C	15272.89	21338.34	36611.23	0.417164	0.582836
2C	11455	24520.01	35975.01	0.318415	0.681585
3C	9201.572	28393.21	37594.78	0.244757	0.755243
5C	4520.323	35878.88	40399.2	0.111891	0.888109
7C	1191.731	40218.69	41410.42	0.028779	0.971221
10C	1390.58	41389.38	42779.96	0.032505	0.967495

Notes:

Species A corresponds to azodioxide ($-(O)N=N(O)-$) in the pristine state and azoxy ($-(O)N=N-$) in the cycled samples.

Species B corresponds to terminal nitroso ($-N=O$) in the pristine state and azo ($-N=N-$) in the cycled samples.

Quantitative XPS analysis reveals a continuous transformation of nitrogen species during cycling. The proportion of Species A (azoxy) decreases steadily from 41 % in 1C state to below 5 % after the 7th cycle, while Species B (azo) correspondingly increases from 58 % to >95 %. This confirms the progressive and nearly complete azoxy-to-azo conversion during repeated lithiation/delithiation, in agreement with the spectroscopic observations discussed in [Figure 4.5](#).

Appendix C

Supplementary Information

for

Stabilization of *p*-Dinitrobenzene Cathodes through Electrode Surface Coatings

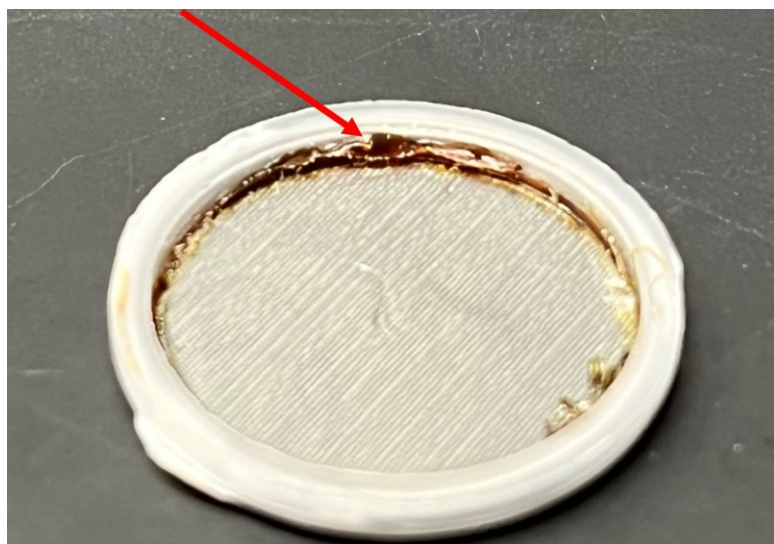


Figure S5.1. Photograph of an opened coin cell after 30 cycles at 0.2 C using single layer PEO-based SPE. A gel-like substance is observed leaking from the electrode edge, accompanied by electrolyte discoloration. This phenomenon indicates the migration and accumulation of dissolved active species within the polymer matrix during extended cycling.

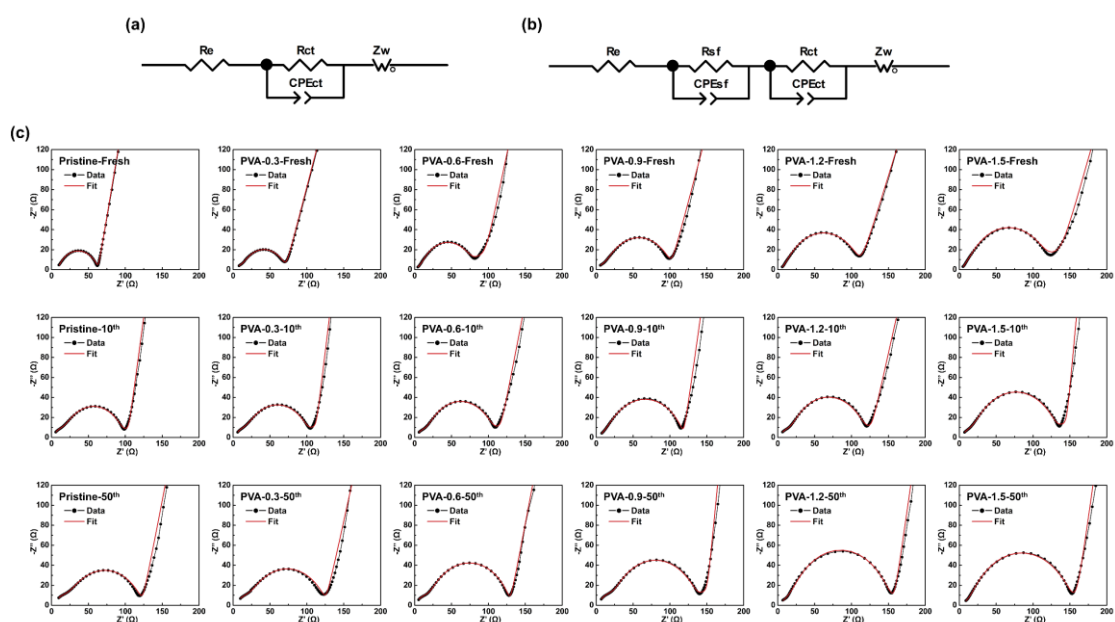


Figure S5.2. (a,b) Equivalent circuit models used for pristine (a) and coated or cycled (b) electrodes. R_e : bulk resistance; R_{ct} : charge-transfer resistance; R_{sf} : surface film resistance; CPE: constant phase element; Z_w : Warburg element; (c) Nyquist plots and fitting curves of batteries.