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Electrolyte Composition Governs Polysulfide Shuttling and Electrochemical Stability in Li/FeS₂ Batteries: Organic, Ionic Liquid, and Hybrid Electrolytes Compared

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Abstract

Iron pyrite (FeS₂) is a promising, earth-abundant cathode material for secondary lithium batteries, offering a theoretical specific capacity of 894 mAh g⁻¹. A central obstacle to its practical deployment is polysulfide (PS) shuttling, which causes capacity fade, anode corrosion, and diminished Coulombic efficiency. While conventional organic electrolytes (OE) provide high ionic conductivity, they exacerbate PS dissolution; ionic liquid electrolytes (ILE) suppress shuttling but suffer from high viscosity and reduced rate capability. Here we report a systematic comparison of Li/FeS₂ coin half-cells assembled with three electrolytes: OE (1.0 M LiPF₆ in 1:1 v/v EC:DMC [ethylene carbonate:dimethyl carbonate]), ILE (1.0 mol LiTFSI in 9 mol Pyr₁₄FSI), and a 1:1 v/v hybrid blend (ME: mixed electrolyte composed of OE and ILE). Structural characterization by X-ray diffraction (XRD) and Raman spectroscopy confirms phase-pure pyrite-phase cathodes. Cyclic voltammetry (CV) reveals that the ME produces the most reproducible redox profiles across three cycles, indicating superior electrochemical reversibility. Galvanostatic charge-discharge (GCD) measurements show that the ILE initially retains capacity more effectively than OE during formation cycling, while the ME yields the smoothest and most ordered voltage profiles throughout extended cycling. Quantitative UV-Vis spectroscopy of 1,3-dioxolane (DOL) soaks from post-cycled cell components demonstrates that the ME incurs the lowest total sulfur loss (13.14-13.16%), compared with 15.30-15.33% for ILE and 19.52-19.53% for OE, a 33% reduction relative to OE. These results establish that a hybrid ionic-organic electrolyte simultaneously enhances ionic transport and suppresses PS dissolution, offering a practical and scalable route toward high-stability FeS₂-based lithium cells.

Keywords: iron pyrite; lithium battery; ionic liquid electrolyte; polysulfide shuttling; hybrid electrolyte; UV-Vis spectroscopy; galvanostatic cycling; Beer-Lambert analysis

1. Introduction

Mounting scientific consensus on anthropogenic climate change, coupled with the finite supply of fossil fuels that currently underpin global energy infrastructure, has made the large-scale deployment of clean energy technologies one of the defining engineering challenges of the twenty-first century^{1,2}. Electrification of transportation and industry demands reliable, high-performance energy storage that can be manufactured at scale and integrated with intermittent renewable sources. Solid-state and advanced lithium-based battery systems have emerged at the forefront of this effort, offering attractive combinations of energy density, cyclability, and form-factor flexibility that have enabled transformative progress in portable electronics, electric vehicles, and grid-scale storage^{3,4}. The continued expansion of these applications, however, depends critically on developing electrode and electrolyte chemistries that simultaneously deliver higher capacity, improved safety, and lower manufacturing cost than the present generation of lithium-ion cells⁵⁻⁹.

The growing demand for high-energy-density, low-cost electrochemical storage has renewed interest in conversion-type cathode materials that can transcend the capacity limitations of conventional intercalation chemistries¹⁰. Pyrite (FeS_2) is particularly attractive in this context: it is geologically abundant, minimally toxic, and capable of delivering a theoretical specific capacity of 894 mAh g^{-1} through a two-electron conversion reaction with lithium. Its established commercial role as a cathode in primary (non-rechargeable) lithium batteries further validates its compatibility with lithium metal anodes and standard cell architectures¹⁰⁻¹⁴. Nevertheless, translating these attributes into viable secondary (rechargeable) cells remains challenging. Three principal degradation pathways have been identified: (i) mechanical pulverization of the active material upon volume expansion during lithiation^{15,16}, (ii) poor electronic conductivity of intermediate conversion products¹², and (iii) polysulfide (PS) shuttling^{10,13,16}.

Polysulfide shuttling is arguably the most insidious of these failure mechanisms¹⁷⁻²¹. During electrochemical cycling of Li/FeS_2 cells, elemental sulfur and Li_2S are generated as intermediate and final discharge products, respectively^{12,14,22,23}. Both species can dissolve into the electrolyte to form soluble polysulfide anions (Li_2S_x , $x = 2-8$)^{18-21,24}. These dissolved species migrate down the concentration gradient from the cathode toward the lithium metal anode, where they are chemically reduced to regenerate shorter-chain polysulfides that diffuse back toward the cathode. The resulting parasitic redox shuttle irreversibly consumes active material, corrodes the lithium anode, and drives self-discharge^{18,19,21,25}. PS shuttling is widely recognized as the dominant capacity-fade mechanism in Li-S -type cells, yet quantitative, component-resolved studies of its magnitude in Li/FeS_2 systems remain scarce²⁶.

Electrolyte composition is the primary determinant of PS solubility and transport^{27,28}. The Lewis basicity (electron-donor strength) of the solvent governs how strongly it solvates dissolved polysulfide anions: high-donor solvents dramatically increase PS solubility, while low-donor solvents suppress it²⁷. Bis(trifluoromethanesulfonyl)imide (TFSI^-)-based ionic liquid electrolytes (ILEs) are inherently weak Lewis bases, and this property has been exploited to mitigate PS shuttling in both Li-S and Li/FeS_2 cells^{10,29,30}. Evans et al. demonstrated that a TFSI -based ILE

(0.6 M LiTFSI in Pyr₁₃TFSI) delivered more than a fourfold improvement in capacity retention relative to a conventional carbonate electrolyte in Li/FeS₂ cells¹⁰. Beyond PS suppression, ILEs offer non-flammability, negligible vapor pressure, a wide electrochemical stability window, and broad thermal stability, safety attributes of increasing importance for practical battery deployment^{27,31,32}.

Despite their advantages, ILEs are limited by high viscosity, which reduces ionic conductivity and rate capability relative to conventional organic electrolytes (OEs)³¹⁻³³. This viscosity-conductivity trade-off motivates the development of mixed electrolyte (ME) systems in which the complementary properties of ILEs and OEs are combined. Guerfi et al. demonstrated that blending an ionic liquid with an organic electrolyte yielded a non-flammable, high-conductivity system with improved electrochemical performance relative to either component alone³⁴. However, systematic studies quantifying how hybrid electrolytes influence PS shuttling in Li/FeS₂ cells, and whether the PS-suppression benefits of the ILE are preserved upon blending, have not been reported.

In this work, we present a direct, three-way comparison of Li/FeS₂ coin half-cells assembled with: (i) a conventional OE (1.0 M LiPF₆ in 1:1 v/v EC:DMC), (ii) an ILE (1.0 M LiTFSI in 9 M Pyr₁₄FSI), and (iii) a 1:1 v/v ME composed of the OE and ILE. Cathode phase identity and structural integrity are confirmed by XRD and Raman spectroscopy before cycling. XRD is used to assess the cathode's post-cycling integrity. Electrochemical performance is assessed by CV and GCD over both formation and extended cycling protocols. Critically, we quantify PS dissolution in each system using ex-situ UV-Vis absorption spectroscopy of DOL soaks from post-cycled cell components, an approach adapted from Lapp et al.³⁵, providing a comparative, and component-resolved measurement of sulfur loss across these three electrolyte classes. Our results demonstrate that the ME uniquely combines favorable electrochemical kinetics with suppressed PS dissolution, establishing hybrid electrolyte design as a promising and practical strategy for improving the cycling stability of FeS₂-based lithium cells.

2. Experimental

2.1 Cathode Preparation

Commercial FeS₂ powder was mechanically milled at 100 rpm for 60 h using a planetary ball mill. The milled powder was transferred to a sealed container and stored in an argon-filled glovebox (H₂O, O₂ < 0.5 ppm) prior to electrode fabrication. Cathode slurries were prepared by first combining 80 wt% FeS₂ with 10 wt% conductive carbon (Super P) in a mortar and pestle, followed by addition of 10 wt% poly(vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP). The resulting slurry was stirred overnight to ensure homogeneity. Electrodes were cast onto 1.55 cm-diameter stainless-steel spacers using a doctor-blade technique, dried in ambient air for 1 h, and then transferred to a vacuum oven at 120 °C for 12 h to remove residual solvent and adsorbed moisture. All electrodes were stored in the argon glovebox until cell assembly.

2.2 Sulfurization of FeS₂ Powder

For thin-film characterization specimens, a supplementary sulfurization process was employed using a three-zone tube furnace (MELLEN). Approximately 0.5 g of elemental sulfur powder per gram of FeS₂ was placed in Zone A (180 °C) to serve as the sulfur vapor source, while the FeS₂ powder was positioned in Zone B (500 °C). Zone B was ramped to target temperature over 45 min; Zone A was ramped over 30 min. Sulfurization proceeded for 4 h total. After the initial Zone B ramp, nitrogen carrier gas was introduced to distribute sulfur vapor uniformly across the FeS₂ bed. This procedure was employed to maintain stoichiometric sulfur content and prevent sulfur-deficient phase formation during high-temperature processing, consistent with previously reported sulfurization protocols for FeS₂ cathode materials ⁹.

2.3 Structural Characterization

X-ray diffraction (XRD) patterns were collected using an Aeris X-ray diffractometer (Malvern Panalytical) in Bragg–Brentano geometry with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) to confirm phase identity and assess structural changes upon electrochemical cycling. Diffraction data were analyzed by comparison with the ICDD reference pattern 01-071-0053 for cubic pyrite (Pa $\bar{3}$, Z = 4). Raman spectra were acquired with a LabRAM HR Evolution spectrometer (Horiba Scientific) using a 532 nm excitation laser focused through a 50 $\times$ objective; laser power was kept below 1 mW at the sample surface to avoid photo-induced phase transformation. Electrochemical cell assembly and testing resulted in Figure S1 and S2. Field-emission scanning electron microscopy (FESEM) was performed on a Phenom G2 instrument (Thermo Fisher Scientific) to assess electrode morphology before (Figure S3) and after cycling (Figure S4, Figure S5, and Figure S6).

2.4 Electrochemical Cell Assembly and Testing

All 2032-type coin half-cells were assembled in an argon glovebox (H₂O, O₂ < 0.5 ppm) using lithium metal foil as the counter/reference electrode and Whatman GF/D glass-fiber separators. Three electrolyte formulations were evaluated: (i) OE: 1.0 M LiPF₆ in 1:1 v/v ethylene carbonate (EC) / dimethyl carbonate (DMC) (battery grade, Sigma-Aldrich); (ii) ILE: 1.0 M LiTFSI in 9 M 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide (Pyr₁₄FSI); and (iii) ME: 1:1 v/v blend of OE and ILE.

Electrochemical impedance spectroscopy (EIS) was performed at open-circuit voltage over the frequency range 100 kHz to 10 mHz with a perturbation amplitude of 10 mV (Supplementary Figure S7). Galvanostatic charge-discharge (GCD) measurements were performed on an MTI 8-channel battery analyzer at a constant current of 0.56 mA ($\sim 0.1 \text{ A g}^{-1}$ based on active material mass) over a potential window of 0.5–3.1 V vs. Li/Li⁺. Cells underwent three formation cycles, followed by ten additional cycles to assess intermediate-term stability; selected cells were cycled for up to 100 cycles to evaluate long-term performance (Supplementary Figures S8–S10). Cyclic voltammetry (CV) was conducted using a CH Instruments 660D potentiostat in a two-electrode configuration at a scan rate of 0.1 mV s⁻¹ over the range 0.5–3.1 V (3 cycles). Gravimetric specific capacity (C_m , mAh g⁻¹) was calculated as:

$$C_m = I \times \frac{(t_2 - t_1)}{m} \quad (1)$$

where I is the applied current (A), t_1 and t_2 are the start and end times of the half-cycle (h), and m is the active material mass (g).

2.5 UV-Vis Spectroscopy and Polysulfide Quantification

After three formation cycles, cells were disassembled in the argon glovebox and individual components (cathode, separator, and lithium anode) were soaked in 1,3-dioxolane (DOL, anhydrous, 99.8%, Sigma-Aldrich) for a minimum of 24 h to extract dissolved polysulfide species. UV-Vis absorption spectra were collected over 250-750 nm on a PerkinElmer Lambda 950 spectrophotometer using 1.0 cm pathlength quartz cuvettes. All sample spectra were baseline-corrected by subtraction of the pure DOL solvent spectrum measured under identical conditions.

Polysulfide concentrations were determined by Beer-Lambert analysis ($A = \epsilon bc$) using literature molar absorptivity values: S_8 at 260–280 nm ($\epsilon = 7000 \text{ M}^{-1} \text{ cm}^{-1}$)³⁶; S_4^{2-} at 306–410 nm ($\epsilon = 1033 \text{ M}^{-1} \text{ cm}^{-1}$)³⁶; $S_3^{\bullet-}$ at 611 nm ($\epsilon = 4115\text{--}4500 \text{ M}^{-1} \text{ cm}^{-1}$)^{36,37}; and S_6^{2-} at 325 nm ($\epsilon = 2575 \text{ M}^{-1} \text{ cm}^{-1}$)³⁸. Because literature ϵ values were employed, all concentrations are reported as estimates and should be interpreted comparatively rather than as absolute values. The total dissolved sulfur concentration was calculated as:

$$[S]_{lost} = 8[S_8] + 6[S_6^{2-}] + 4[S_4^{2-}] + n[S_n^{m-}] \quad (2)$$

The mass of sulfur lost to dissolution (m_{slot}) and the percentage of total cathode sulfur lost ($\%S_{lot}$) were derived following Lapp et al.³⁵:

$$\%S_{lost} = [S]_{lost} \times V_e \times MW(S) \quad (3)$$

$$\%S_{lost} = 100\% \times \frac{m_{S_{lost}}}{m_{S_0}} \quad (4)$$

where V_e is the electrolyte volume and m_{S_0} is the initial sulfur mass in the cathode, computed from the loaded FeS_2 mass and the stoichiometric sulfur fraction ($2 \times MW(S) / MW(FeS_2)$). Figure S11 summarizes the polysulfide species concentrations in anode, separator, and cathode of the OE, ILE, and ME after 3 cycles.

3. Results and Discussion

3.1 Structural Characterization of the Pyrite Cathode

Figure 1 shows the XRD pattern of a representative pre-cycled cathode. Diffraction peaks at $2\theta = 31.5^\circ, 35.7^\circ, 39.4^\circ, 43.0^\circ, 46.0^\circ, 54.9^\circ, 73.6^\circ$, and 80.8° index unambiguously to the (111), (200), (210), (211), (220), (311), (321), and (420) reflections of cubic pyrite-phase FeS_2 (space group $Pa\bar{3}$, ICDD 01-071-0053)^{39–43}. No secondary phases (e.g., marcasite, pyrrhotite, or mackinawite) were detected, confirming phase-pure cathode preparation. The relatively narrow diffraction peaks

indicate well-developed crystallinity, consistent with a slurry-cast electrode derived from commercially sourced FeS₂ powder.

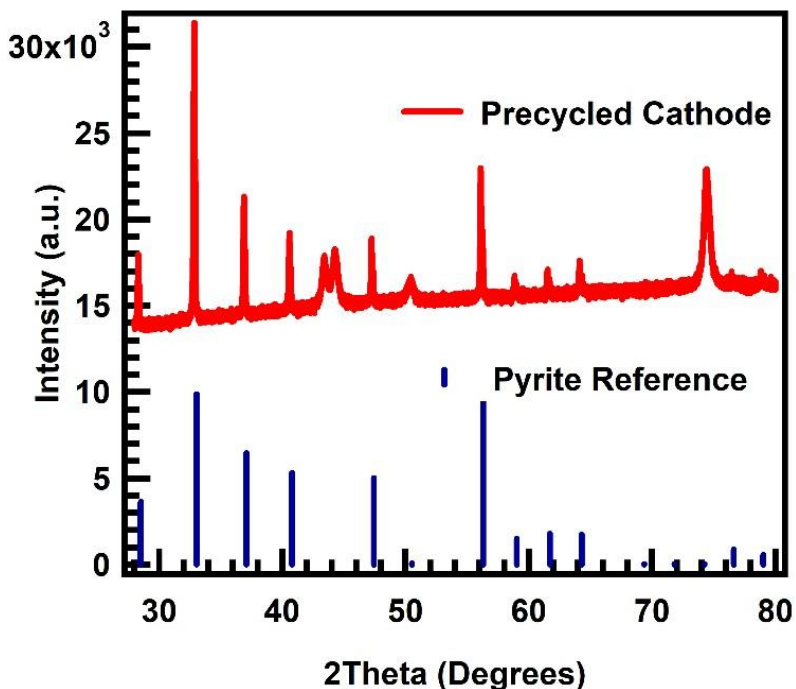


Figure 1. XRD pattern of the pre-cycled FeS₂ cathode. All diffraction peaks index unambiguously to cubic pyrite ($Pa\bar{3}$, ICDD 01-071-0053); no secondary phases are detected.

The corresponding Raman spectrum (Figure 2) exhibits three characteristic peaks at approximately 342 cm⁻¹ (E_g), 378 cm⁻¹ (A_g), and 430 cm⁻¹ (T_g), in excellent agreement with reported pyrite vibrational modes³⁹⁻⁴³. The A_g mode, arising from symmetric S-S bond stretching, is the most intense feature. Additional bands at ~1350 cm⁻¹ (D band) and ~1600 cm⁻¹ (G band) confirm the presence of the Super P conductive carbon additive. Together, XRD and Raman spectroscopy unambiguously establish the pyrite-phase identity of all cathodes prior to electrochemical testing.

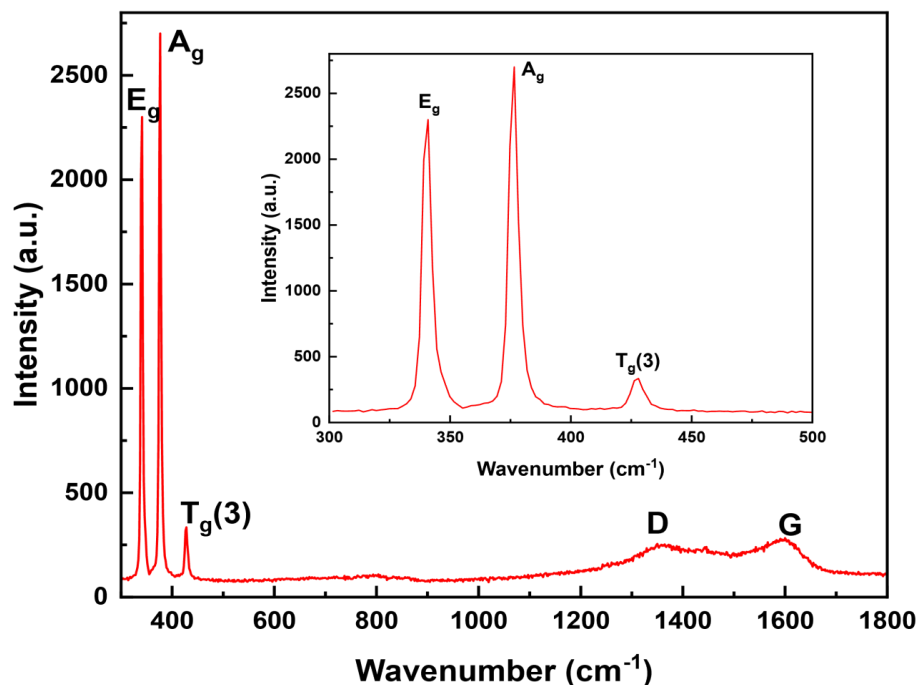


Figure 2. Raman spectra of the pre-cycled FeS_2 cathode. Inset (expanded view, $300\text{--}500\text{ cm}^{-1}$): characteristic pyrite vibrational modes at 342 cm^{-1} (E_g), 378 cm^{-1} (A_g), and 430 cm^{-1} (T_g). Main panel (full range): D ($\sim 1350\text{ cm}^{-1}$) and G ($\sim 1600\text{ cm}^{-1}$) bands of the Super P carbon additive are resolved.

Post-cycling XRD patterns for cathodes recovered from OE (red), ILE (blue), and ME (green) cells are compared with the pristine pattern in Figure 3. The pyrite reflections are attenuated in all three post-cycled samples relative to the pristine cathode, consistent with partial electrochemical conversion of FeS_2 during cycling. Importantly, the ME-cycled cathode retains the most intense and well-defined diffraction peaks among the three, indicating the greatest degree of structural preservation. The OE-cycled cathode exhibits the most pronounced peak broadening and intensity loss, suggesting more extensive and irreversible conversion or amorphization - consistent with the highest PS dissolution losses measured for OE by UV-Vis analysis (Section 3.4).

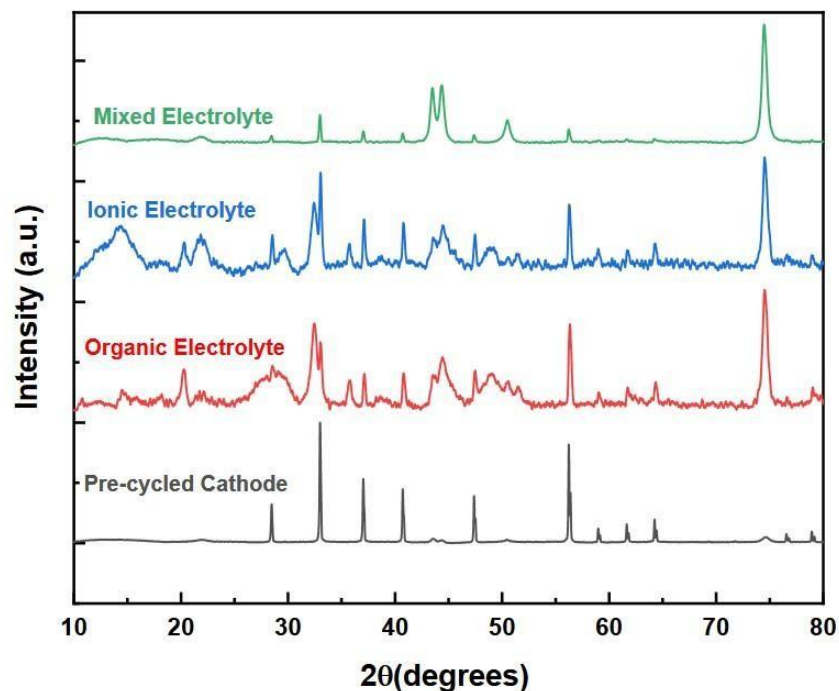


Figure 3. XRD patterns of the FeS_2 cathode before cycling (pre-cycled, bottom) and after 3 cycles in OE (red), ILE (blue), and ME (green). Peak attenuation in all post-cycled samples reflects partial FeS_2 conversion; the ME-cycled cathode retains the most structurally intact pyrite phase.

3.2 Cyclic Voltammetry

Figure 4 presents cyclic voltammograms of cells assembled with OE, ILE, and ME, each scanned at 0.1 mV s^{-1} for three consecutive cycles. All three electrolyte systems display a characteristic anodic peak near 2.1 V vs. Li/Li^+ and a broad cathodic envelope between 0.8 and 1.2 V vs. Li/Li^+ , consistent with the multi-step conversion of pyrite with lithium^{12,14,22,23}. The anodic peak corresponds to re-oxidation of Li_2S and metallic iron toward FeS_x intermediates, while the broad cathodic feature reflects sequential lithiation through soluble polysulfide intermediates to Li_2S and Fe^0 .

The OE cell (Figure 4a) displays the broadest cathodic features and the greatest attenuation across successive cycles, reflecting progressive active-material loss due to PS dissolution in the high-donor carbonate solvent. The ILE cell (Figure 4b) exhibits the most well-resolved and symmetric redox peaks in cycles 1 and 2, consistent with slower, more reversible reaction kinetics enabled by suppressed PS solvation in the ionic liquid medium; however, a slight shift and broadening in cycle 3 suggests the onset of interfacial changes. Most significantly, the three CV cycles of the ME cell (Figure 4c) overlay most closely with one another, demonstrating superior cycle-to-cycle reproducibility. The minimal variation in peak position and current between cycle 1 and cycle 3 in the ME indicates a more stable electrode-electrolyte interface and more reversible electrochemical processes, prerequisites for long-term cycling stability.

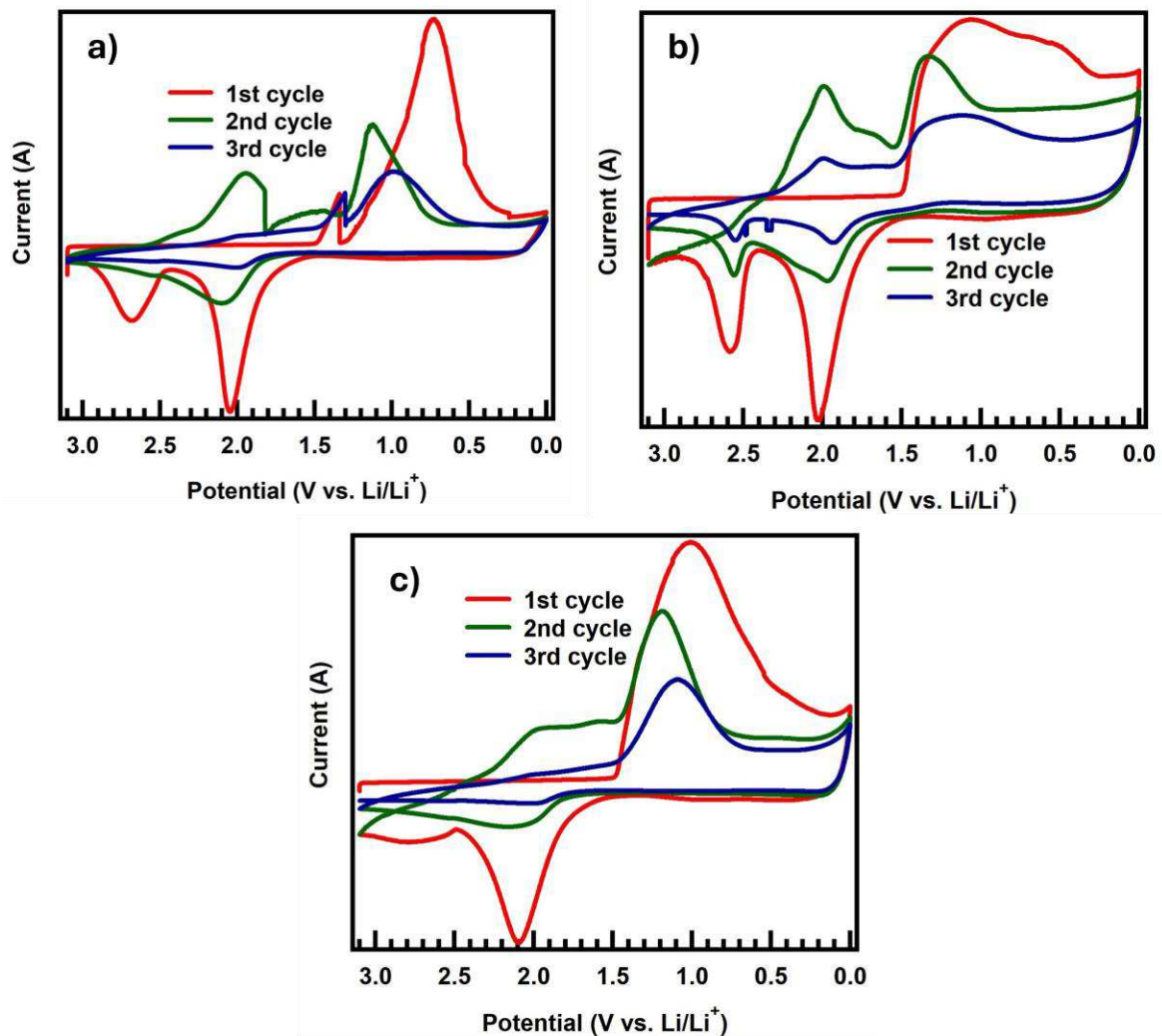


Figure 4. Cyclic voltammograms (0.1 mV s^{-1} , $0.5\text{--}3.1 \text{ V}$, 3 cycles) of Li/FeS_2 cells assembled with (a) OE, (b) ILE, and (c) ME. The ME produces the most reproducible redox profiles across successive cycles, indicating superior electrochemical reversibility. Cycle number is indicated in the legend.

3.3 Galvanostatic Charge-Discharge

Galvanostatic charge-discharge profiles for the three formation cycles are presented in Figure 5. The ILE cell (Figure 5b) retains capacity most effectively during formation, consistent with a beneficial solid electrolyte interphase (SEI) formed in the low-donor TFSI⁻-based ionic liquid environment^{10,35}. The OE cell (Figure 5a) undergoes the most rapid capacity decline across the three formation cycles, attributable to accelerated PS dissolution in the high-donor carbonate solvent. The ME cell (Figure 5c) produces notably smoother and more ordered voltage profiles than either the OE or ILE, with clearly defined discharge plateaus indicative of well-controlled, stepwise conversion reactions and minimal parasitic side reactions.

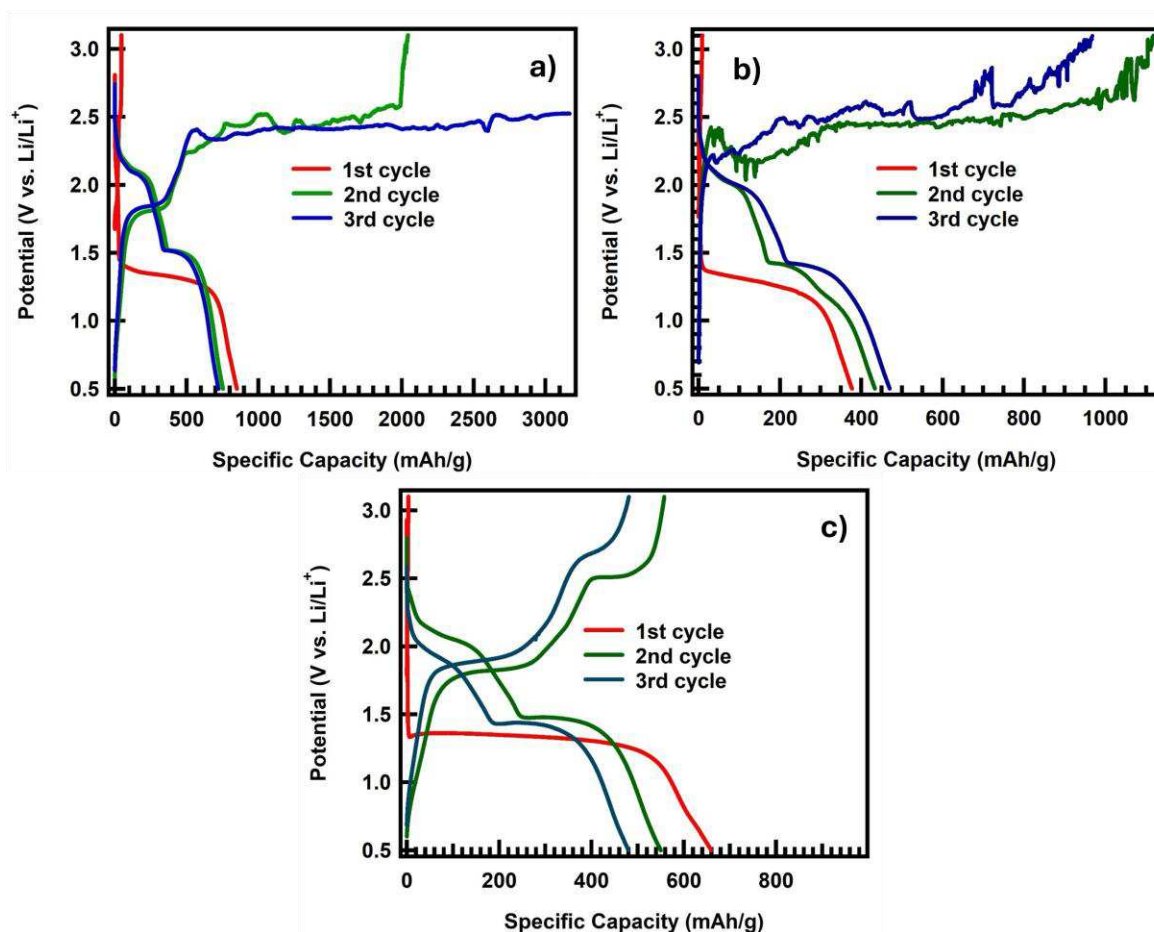


Figure 5. GCD profiles (0.56 mA, 0.5-3.1 V) for the first three formation cycles in cells assembled with (a) OE, (b) ILE, and (c) ME. The ILE shows superior initial capacity retention; the ME exhibits the smoothest and most ordered voltage profiles across all three cycles.

Figure 6 shows GCD profiles for ten additional cycles (cycles 4-13) collected immediately following the formation protocol. The ILE cell undergoes more pronounced capacity fade during extended cycling than during formation, suggesting that the protective SEI formed in the ionic liquid is not indefinitely stable under continuous cycling conditions. The OE and ME cells also exhibit declining specific capacity with cycle number, as anticipated for a conversion cathode operated without polysulfide-trapping strategies. Critically, the ME cell (Figure 6c) maintains more uniform voltage profiles throughout the ten extended cycles compared with either the OE (Figure 6a) or ILE (Figure 6b), consistent with its ability to moderate both ionic transport and PS loss simultaneously.

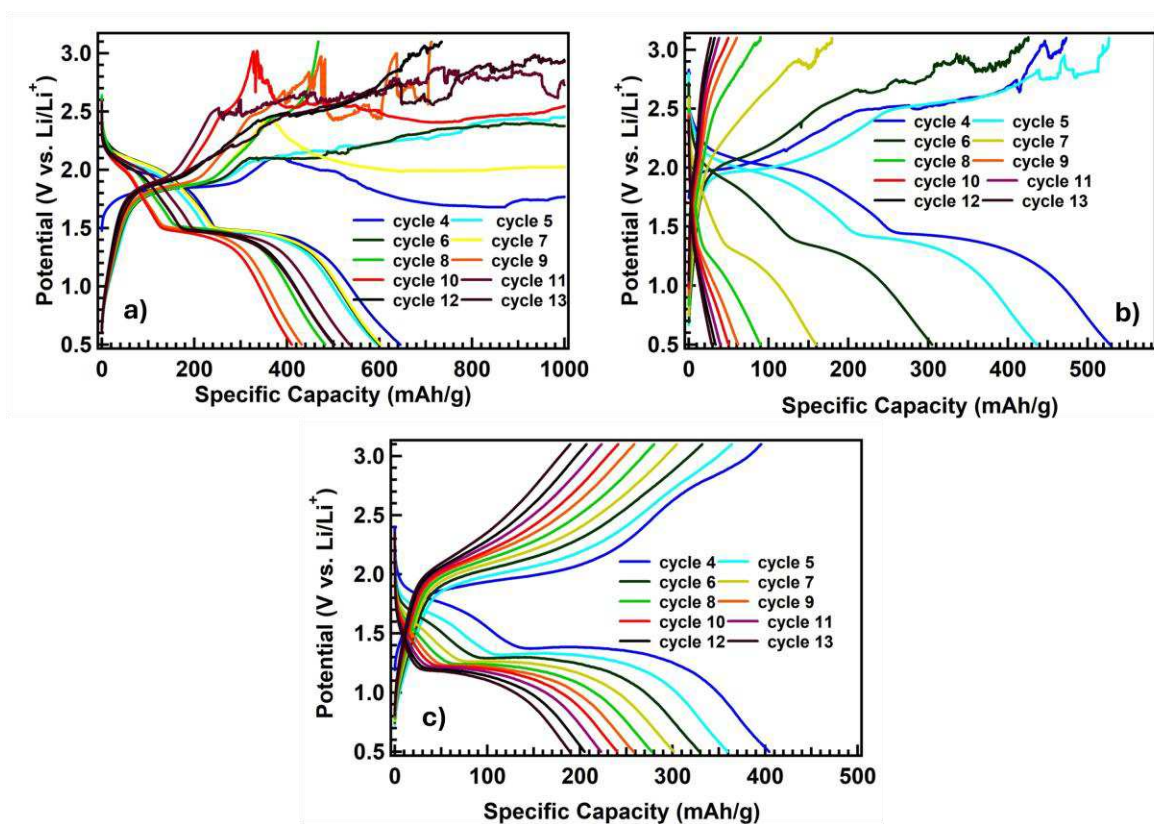


Figure 6. GCD profiles for 10 additional cycles (cycles 4-13) following the formation protocol in cells assembled with (a) OE, (b) ILE, and (c) ME. The ME maintains the most consistent voltage profiles across extended cycling, reflecting balanced ionic transport and polysulfide suppression.

Taken together, the GCD data support a mechanistic picture in which the ME achieves a balance between two competing requirements: the OE component provides high ionic conductivity that supports efficient charge transport, while the ILE component suppresses PS dissolution. Neither pure electrolyte achieves this balance independently: the ILE is conductivity-limited during extended cycling, and the OE is stability-limited by excessive PS shuttling. The 1:1 ME blend appears to access a favorable intermediate regime. Figure S1 and S2 showcase the discharge specific capacity and Coulombic efficiency vs cycle number for OE, ILE, and ME over 100 cycles along with the capacity retention vs cycle number over 100 cycles. Figure S3, S4, S5, and S6 demonstrate the FESEM images of the precycled FeS₂ cathode, postcycled FeS₂ cathode in OE for three cycles, postcycled FeS₂ cathode in ILE for three cycles, and postcycled FeS₂ cathode in ME for three cycles, respectively. Future rate capability studies and electrochemical impedance spectroscopy (EIS, Supplementary Figure S7) will be required to precisely deconvolve the conductivity and interfacial resistance contributions of each electrolyte component. Figure S8, S9, and S10 present the GCD profiles at the 10th, 20th, 30th, 40th, 50th, 60th, 70th, 80th, 90th, and 100th for OE, ILE, and ME, respectively.

3.4 UV-Vis Spectroscopy and Polysulfide Quantification

To quantitatively assess PS dissolution, UV-Vis absorption spectra were collected from DOL soaks of the post-cycled cathode, separator, and lithium anode of cells subjected to three formation cycles. Figure 7 presents spectra from OE cells. Absorbance features are identified at wavelengths characteristic of S_8 (~ 260 and ~ 270 nm), S_6^{2-} (~ 325 nm), S_4^{2-} (~ 306 and ~ 410 nm), and $S_3^{\bullet-}$ (~ 611 nm), consistent with the expected polysulfide speciation in lithium–sulfur-type systems^{36–38} in cathode and separator as summarized in Table S1. Absorbance for anode are measured for wavelengths for S_8 (~ 267 and ~ 278 nm), S_6^{2-} (~ 363 and 488 nm), S_4^{2-} (~ 310 and ~ 441 nm), as summarized in Table S2. The presence of absorbance in all three component soaks (cathode, separator, and anode) confirms that PS species migrate through the full cell during cycling, as expected for an unimpeded shuttle mechanism.

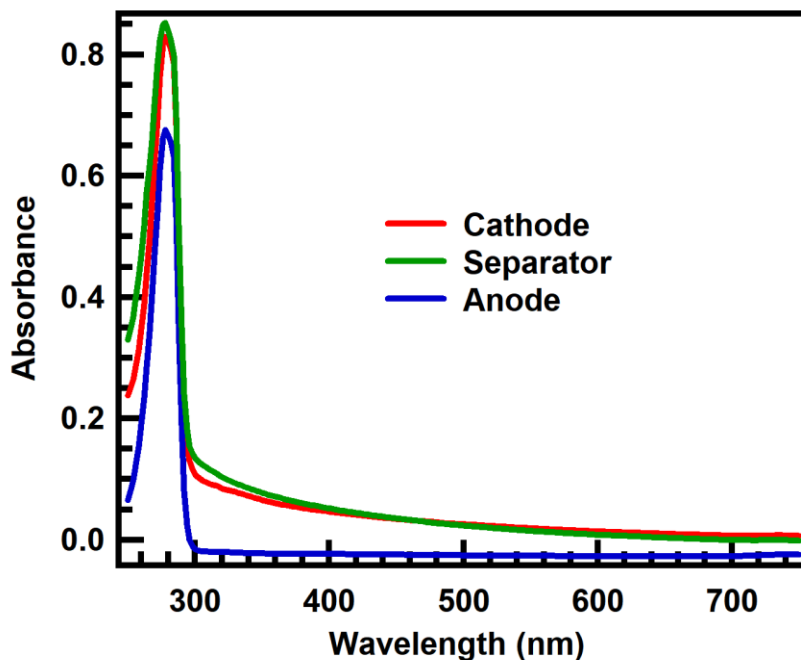


Figure 7. UV-Vis spectra of DOL soaks from post-cycled (3 cycles) cell components in OE: cathode (red), separator (green), and anode (blue).

Polysulfide concentrations derived from Beer-Lambert analysis of the OE cell components are summarized in Tables S3–S5. In the cathode soak (Table S3), S_4^{2-} is the most abundant species ($573 \mu\text{M}$), followed by S_8 ($51 \mu\text{M}$), S_6^{2-} ($43 \mu\text{M}$), and $S_3^{\bullet-}$ ($9\text{--}10 \mu\text{M}$). The dominance of S_4^{2-} near the cathode is consistent with its role as a principal intermediate in the stepwise reduction of elemental sulfur. In the separator soak (Table S4), S_6^{2-} becomes the most concentrated species ($391 \mu\text{M}$), with substantial S_4^{2-} ($220 \mu\text{M}$) also present, reflecting selective transport of longer-chain polysulfides across the separator. The anode soak (Table S5) shows the lowest total PS concentrations, consistent with partial chemical reduction of shuttled PS species at the lithium metal surface.

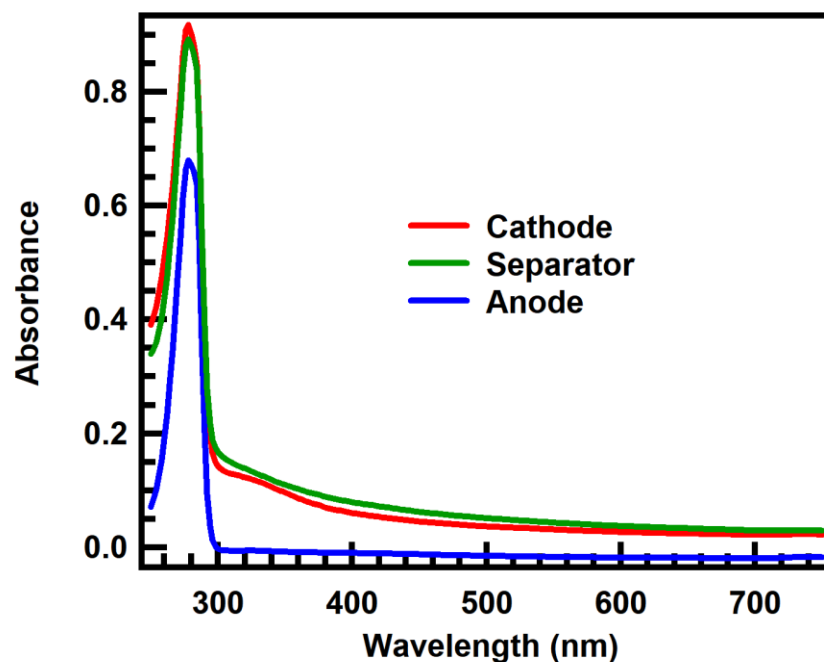


Figure 8. UV-Vis spectra of DOL soaks from post-cycled (3 cycles) cell components in ILE: cathode (red), separator (green), and anode (blue). Reduced absorbance intensity in the separator and anode soaks relative to OE reflects suppressed PS transport in the low-donor ionic liquid medium.

Corresponding spectra and concentration data for the ILE cells are shown in Figure 8 and Tables S6-S8. The ILE cell exhibits reduced PS concentrations in the separator and anode soaks relative to OE, consistent with suppressed polysulfide transport in the low-donor ionic liquid medium. However, the ILE cathode soak shows slightly elevated S_4^{2-} and S_8 concentrations compared with the OE cathode, suggesting accumulation of PS species near the cathode resulting from restricted dissolution into the bulk electrolyte. This local enrichment does not translate into greater total sulfur loss because long-range PS transport, the key shuttle mechanism, is effectively inhibited.

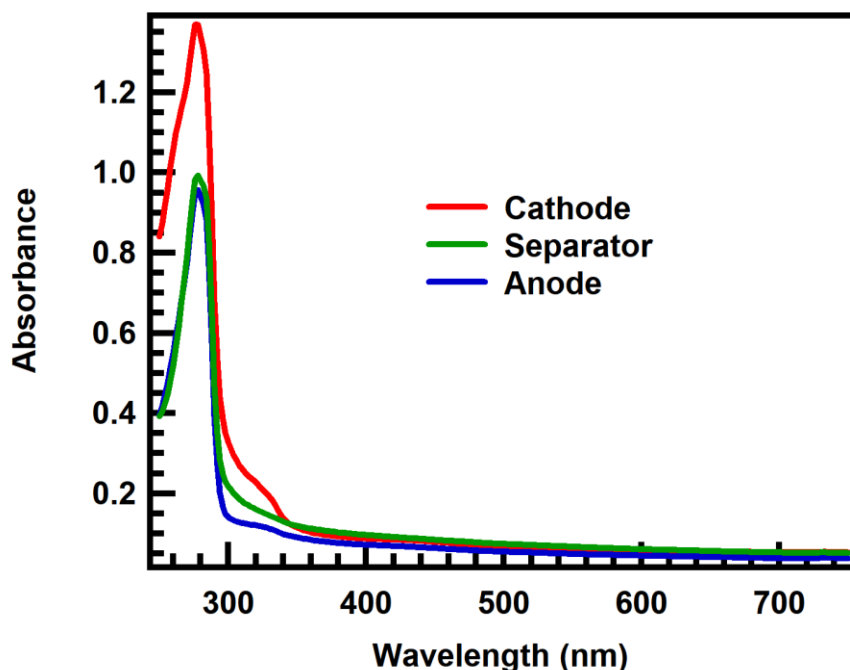


Figure 9. UV-Vis spectra of DOL soaks from post-cycled (3 cycles) cell components in ME: cathode (red), separator (green), and anode (blue). PS concentrations in the separator and anode soaks are the lowest among all three electrolyte systems, consistent with effective localization of PS species near the cathode.

UV-Vis spectra and quantitative data for ME cells are shown in Figure 9 and Tables S9-S11. PS species are detected in all three component soaks, confirming that dissolution is not fully eliminated in any system studied. However, the total PS concentrations in the ME separator and anode soaks are the lowest among all three electrolyte systems. The ME cathode soak exhibits elevated S_8 and S_4^{2-} relative to ILE, suggesting that PS species form near the cathode but are effectively prevented from migrating across the cell. This ‘localization’ behavior, PS generation without extensive transport, is a hallmark of effective PS suppression strategies and is consistent with the superior structural preservation and capacity retention observed for ME-cycled cathodes. Figure S11 summarizes the polysulfide species concentration (μM) in DOL soaks of the anode (A), separator (S), and cathode (C) for OE, ILE, and ME cells after 3 cycles. Figure 10 shows the UV-Vis spectra of the three neat electrolytes alongside the pure DOL solvent. This comparison confirms that the electrolyte components themselves do not contribute spurious absorbance in the PS detection windows, validating the spectroscopic approach.

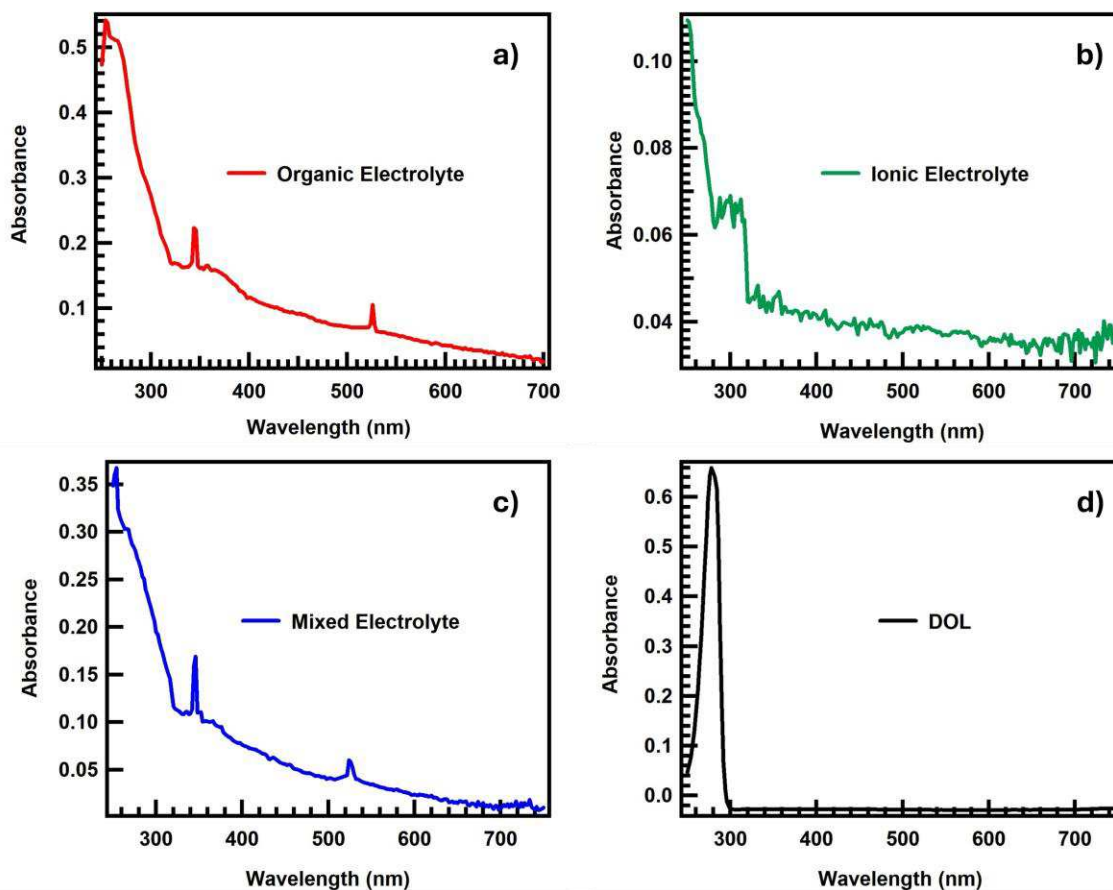


Figure 10. UV-Vis spectra of pure electrolytes and DOL solvent: (a) OE, (b) ILE, (c) ME, and (d) DOL. None of the electrolyte components contribute spurious absorbance in the PS detection wavelength windows (260-650 nm), validating the spectroscopic quantification approach.

The cumulative sulfur loss calculations (Table 1) reveal a clear, monotonic trend across electrolyte systems. The OE incurs the highest sulfur loss (19.52-19.53%), the ILE shows intermediate loss (15.30-15.33%), and the ME the lowest (13.14-13.16%), representing a 22% and 33% reduction relative to OE for the ILE and ME, respectively (Figure 11). This ordering is consistent with the Lewis basicity argument: the carbonate-based OE (high donor number) strongly solvates polysulfide anions and promotes their dissolution and long-range transport, while the TFSI⁻-based ionic liquid component in the ILE and ME inhibits this process. The fact that the ME achieves lower sulfur loss than the pure ILE, despite incorporating a 50 vol% OE component, is noteworthy and warrants further investigation. One plausible explanation is that the OE modifies the ionic liquid solvation shell structure in a manner that reduces PS solubility beyond what simple mixing rules would predict. Alternatively, the ME may form a more passivating cathode-electrolyte interphase that physically restricts PS egress from the electrode surface. Spectroscopic and interfacial characterization studies (e.g., X-ray photoelectron spectroscopy, cryo-electron microscopy) are underway to distinguish between these mechanistic possibilities.

Table 1. Quantitative summary of total sulfur lost to polysulfide dissolution after 3 formation cycles for each electrolyte system, and reduction relative to OE.

Electrolyte	Total %S Lost (3 cycles)	Reduction vs. OE
Organic (OE)	19.52-19.53%	Reference
Ionic Liquid (ILE)	15.30-15.33%	-22%
Mixed (ME)	13.14-13.16%	-33%

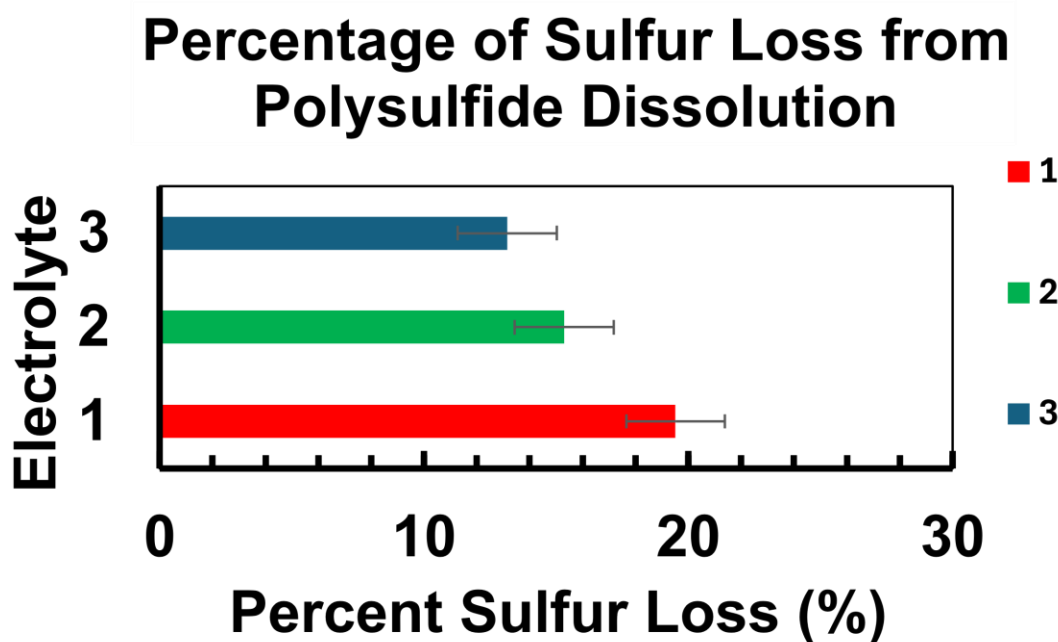


Figure 11. Bar chart summarizing percentage sulfur loss due to polysulfide dissolution for the three electrolyte systems after 3 formation cycles: OE (Electrolyte 1), ILE (Electrolyte 2), and ME (Electrolyte 3). Error bars represent the range across replicate Beer-Lambert calculations using the upper and lower bounds of the $S_3^{\bullet-}$ molar absorptivity.

Overall, the UV-Vis data provide a quantitative, component-resolved comparison of PS dissolution across OE, ILE, and ME systems in Li/FeS₂ cells, and establish the ME as the most effective PS-suppressing electrolyte among those studied, a result not predictable from the properties of the individual components.

4. Conclusions

We have systematically compared the electrochemical performance and polysulfide dissolution behavior of Li/FeS₂ coin half-cells assembled with three electrolyte systems: a conventional organic electrolyte (OE: 1.0 M LiPF₆ in EC:DMC), an ionic liquid electrolyte (ILE: 1.0 M LiTFSI in 9 M Pyr₁₄FSI), and a 1:1 v/v hybrid (ME). Phase-pure pyrite cathodes were confirmed by XRD and Raman spectroscopy prior to cycling. Post-cycling XRD demonstrates that the ME-cycled

cathode retains the most intact pyrite structure, consistent with reduced irreversible conversion and attenuated PS dissolution.

Cyclic voltammetry reveals that the ME produces the most reproducible redox features across successive cycles, while the ILE displays the most well-resolved peaks, attributable to slower, more reversible kinetics under low-donor conditions. GCD measurements confirm that the ILE initially retains capacity better than OE during formation, likely through SEI stabilization in the ionic liquid medium, while the ME delivers the smoothest and most ordered voltage profiles across both formation and extended cycling.

Quantitative UV-Vis analysis of post-cycled cell-component DOL soaks provides the first comparative, component-resolved measurement of PS dissolution across these three electrolyte classes. Total sulfur loss follows the order OE (19.52-19.53%) > ILE (15.30-15.33%) > ME (13.14-13.16%), demonstrating a 33% reduction in sulfur loss for the ME relative to OE. The ME achieves lower sulfur loss than the pure ILE despite incorporating a high-donor carbonate component, pointing to synergistic solvation effects or enhanced interfacial passivation in the hybrid system.

These results establish that hybrid ionic liquid-organic electrolyte design simultaneously enhances ionic transport and suppresses polysulfide shuttling in Li/FeS₂ cells, a combination that neither pure electrolyte achieves independently. This work provides a quantitative foundation for optimizing electrolyte composition in FeS₂-based secondary lithium batteries and motivates further studies of interfacial chemistry (XPS, cryo-TEM), rate performance, and long-cycle stability in hybrid electrolyte systems.

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Declarations

Competing interests

The authors declare no competing interests.

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