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Spatial and Kinetic Regulation of Sulfur Electrochemistry on Semi-Immobilized Redox Mediators in Working Batteries

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Abstract: Use of redox mediators (RMs) is an effective strategy to enhance reaction kinetics of multi-electron sulfur electrochemistry. However, the soluble small-molecule RMs usually aggravate the internal shuttle and thus further reduce the battery efficiency and cyclability. A semi-immobilization strategy is now proposed for RM design to effectively regulate the sulfur electrochemistry while circumvent the inherent shuttle issue in a working battery. Small imide molecules as the model RMs were co-polymerized with moderate-chained polyether, rendering a semi-immobilized RM (PIPE) that is spatially restrained yet kinetically active. A small amount of PIPE (5% in cathode) extended the cyclability of sulfur cathode from 37 to 190 cycles with 80% capacity retention at 0.5 C. The semi-immobilization strategy helps to understand RM-assisted sulfur electrochemistry in alkali metal batteries and enlightens the chemical design of active additives for advanced electrochemical energy storage devices.

Introduction

The rechargeable lithium–sulfur battery (Li-S battery) built upon a lithium metal anode and a sulfur-based cathode is considered as one of the most promising systems for the highenergy-density energy storage.^[1] The sulfur cathode possesses a very high theoretical capacity of 1672 mAh g⁻¹. Compared with transition-metal-based cathode materials, sulfur is of greater abundance, lower cost, and more environmentally benign.^[2] However, there are huge obstacles on the way toward practical applications owing to the coupled reaction-transport complexities and intrinsic poor kinetics of the multi-electrochemical kinetics of Li-S couples are expected to be regulated to fully demonstrate the potential of sulfur cathodes in a working battery.^[4]

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To manipulate the analogous multi-electron and multiphase chemistry in lithium-air batteries,^[5] dye-sensitized solar cells,^[6] and the flow batteries,^[7] redox mediators (RMs) that are redox-active within the working potential ranges have been designed and introduced. They act as a mobile electron carrier and enable long-range electron transfer to in-solution species beyond those at the electrochemical interfaces.^[8] A RM with appropriate redox potentials to match either the Li_2S /polysulfide (2.0–2.1 V vs. Li/Li^+) or the polysulfide/S₈ (2.2-2.4 V vs. Li/Li⁺) redox pairs is expected to maintain the longevity of rechargeable Li-S batteries.^[9] Inorganic RMs such as iodine/iodide and the metallocene derivates have been proved effective in oxidizing the dead Li₂S.^[10] Meanwhile, organic RMs hold advantages of tunable redox potentials and electrochemical stabilities. Various molecules such as conjugated quinones,^[11] Schiff bases,^[12] disulfide organics,^[8] metallocene, and imides^[13] have been successfully adopted.

However, most of the above-mentioned RMs are small molecules that are soluble and mobile in liquid electrolytes, leading to multiple side effects. The dissolved RMs diffuse across the separators and accept/donate electrons on each electrode, inducing inherent internal shuttle just as lithium polysulfides. These RMs also react with lithium metal electrode and cause anodic corrosion. However, as a dilemma, the mobility is an indispensable property for RMs to transport the electrons between inactivate isolated sulfur species and the conductive surfaces. Considering the spatial separation between two electrodes in a working battery, it is ideal if a RM can be designed with high accessibility to the sulfur cathode, while naturally constrained from the lithium anode. Employing a RM-impermeable membrane as the separator is a viable route yet this membrane usually sacrifices the Li⁺ transport coefficient.^[14] Designing intrinsically shuttle-free RMs has been thus far regarded as a promising alternative strategy.

Herein, a semi-immobilization strategy is proposed to achieve a high-effective and shuttle-free RM for Li-S battery with small overpotential and rapid redox reactions. Redox-active imide monomers are co-polymerized with soft poly(-ethylene oxide)-poly(propylene oxide) (polyether) chains, rendering a copolymer RM (referred as PIPE) that fully inherits the semi-constrained features of polyether.^[15] Imide is selected as the model small-molecule RM due to its appropriate redox potential window (for pyromellitic dimide, 1.8–2.5 V vs. Li/Li⁺).^[16] The redox-active imide segments in the RM swing in a small distance; while the entire large polymeric molecules hardly diffuse across the separator to lithium metal

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Figure 1. Working mechanism of semi-immobilized RM. Illustration of how PIPE serves as a RM to regulate the electron transfer reaction between sulfur, polysulfides, and sulfides on conductive surfaces. The large molecular amount of PIPE also prevents its motion to the lithium anode.

anode due to the low mobility. Consequently, the RM is mobile over the cathode while free of the shuttle effect in a working cell. (Figure 1)

Results and Discussion

Co-polymerization was adopted to construct the shuttlefree RM PIPE from equivalent pyromellitic dianhydride (PMDA) and polyether diamine (PEDA) (Figure 2a).^[17] After ether extraction of solvents and followed by desiccation, the product PIPE shows as a dark-yellow sticky soft solid in Figure 2b.

The abundant imide units in PIPE was detected by FTIR spectroscopy (Figure 2c). Characteristic peaks at 1770, 1720, 731, and 1356 cm⁻¹ correspond to of C=O symmetric stretch, C=O asymmetric stretch, C=O bending, and C-N stretch, respectively. Only a very weak N-H signal at 3480 cm⁻¹ corresponding to the residual amino terminals. The vanished amino hydrogen signal of PEDA after synthesis was further



Figure 2. Characterization of PIPE. a) Illustration of PIPE synthesis. b) The digital image of as-prepared PIPE, which is a dark-yellow soft sticky solid, compared with the ingredient liquid PEDA. c) The Fourier transform infrared (FTIR) spectra of PIPE.

detected by the hydrogen nuclear magnetic resonance (¹H NMR), confirming the adequately conversion of PEDA (Supporting Information, Figure S1). The complete condensation and dehydration indicate a sufficiently long polymer chain, which guarantees the inhibited motion of the whole polymer to the anode side. As measured by gel permeation chromatography (GPC), the average molecular weight is 1.01×10^4 , which is in between poly(ethylene glycol) dimethyl ether (PEGDME) and high-weight polyether (Supporting Information, Figure S2). The latter two have been employed in Li-S batteries with distinct solubility and mobility in etherbased electrolytes: PEGDME is highly soluble while segments in ultra-long or cross-linking polyether can hardly be mobile.^[18] The moderate molecular weight of PIPE further supports its semi-constrained feature. Considering that the molecular weights of dianhydride and polyether chains are 218 and about 400 respectively, a typical PIPE molecule on average contains 17 active imide units with a stretched chain length of 50 to 100 nm. These numbers reveal the high density of redox-active centers and the large-molecule feature that restrains the molecular motions. We further simulated the interaction between imide groups and carbon and obtained a moderate binding energy of -0.88 eV, further proving the additional π - π interaction that contributes to the immobilization (Supporting Information, Figure S3). We also synthesized fully insoluble PIPE by decreasing the chain length from 8-10 ethoxy groups between two imide segments to 4-5, revealing the importance of having an appropriate length of the ethoxy chains in enabling the partial dissolution of PIPE in ether-based electrolytes (Supporting Information, Figure S4).

To serve as a RM in Li-S batteries, PIPE must have an appropriate redox potential window and fast redox kinetics. Due to the intrinsic reactivity of carbonyl groups in the imide segments and the fact that each conjugated segment contains four carbonyl groups, PIPE should in principle exhibits twoelectron reaction mechanism that is similar to that for pyromellitic dimide (Figure 3 a).^[9,19] Using cyclic voltammetry, we identified two single-electron-transfer steps with corresponding reduction peaks from neutral to mono-anion (r₁PIPE) at 2.46 and 2.33 V, and from r₁PIPE to dianion-



Figure 3. Characterization of the redox mechanism. a) Illustration of two-electron redox mechanism of conjugated imide segments in PIPE. b) Cyclic voltammetry (CV) of PIPE in ether-based electrolyte vs. Li/Li⁺ electrode, where the single-electron redox peaks are marked. The indices correspond to those in (a). c)–h) Model reactions of PIPE and reduced PIPE with various sulfur species.

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(r₂PIPE) at 2.01 and 1.9 V vs. Li/Li⁺ (Figure 3b). The peak splitting is proposed to be attributed to the different residues of $-CH_2-$ and $-CH(CH_3)-$ from PEDA that are bonded to the nitrogen atoms in the imide. Specifically, the hyperconjugation and inductive effect of $-CH(CH_3)-$ was proposed to raise the redox potential, corresponding to the subsidiary peaks r_{1a} and r_{2a} . These peaks are almost within the entire charge/discharge potential windows of sulfur in ether-based electrolytes, which are usually at 2.3–2.4 (polysulfide/S₈) and 2.0–2.1 V (Li₂S/polysulfide) vs. Li/Li⁺, respectively. From a thermodynamic point of view, PIPE at different redox stages should be able to react with various sulfur species possessing different equilibrium potentials.

To demonstrate the above thermodynamic arguments and probe the redox kinetics of PIPE, a series of visualized model experiments were conducted (Figure 3c-h). S₈, Li₂S₈, Li₂S₄, and Li₂S solutions or dispersions were prepared, respectively to refer to the fully oxidized, high-order intermediate, loworder intermediate, and fully reduced states of sulfur cathode during charge/discharge cycles, respectively (Supporting Information, Figure S5). PIPE or the reduced state of PIPE (electrochemically synthesized r₁PIPE and r₂PIPE) was added to the solutions. After the addition of PIPE, the color of Li_2S_8 suddenly faded, indicating the rapid kinetics of Li_2S_8 oxidation to sulfur by PIPE. The reducing kinetics by r₂PIPE is comparably fast. The r₂PIPE with azure blue color immediately turned green after being dropped into to Li_2S_4 solution, of which the color came from the oxidization of r_2 PIPE to r_1 PIPE. The color change attributed to the reaction between PIPE species and solid sulfur species (sulfur/Li₂S) is also obvious. PIPE fast reduced to blue r₂PIPE with exceed Li₂S, and r₂PIPE oxidized to r₁PIPE with dark green color after stirring with exceed S₈ powder (Figure 3g; Supporting Information, Figure S6). The above experiments show the facile chemical reactions between PIPE/r2PIPE and polysulfides despite the spatial confinement of small-molecule imide units within a polymer chain. The motion of polymer chains in the electrolyte enables its accessibility to polysulfides or even immobile solid phases of sulfur/Li2S.

To isolate the shuttle behaviors of PIPE and sulfur, sulfurfree PIPE/carbon paper cathode was evaluated. During 100 cycles at a current density of 0.057 mA cm⁻², an average high Coulombic efficiency over 99.5% was achieved and maintained over cycling, displaying no obvious shuttle effect (Supporting Information, Figure S7). Compared to the physical-barrier strategy,^[14] engineering intrinsically semi-immobilized RMs does not sacrifice the Li⁺ ion transport property and thus allows a small voltage hysteresis and high energy efficiency of 91.5% (Supporting Information, Figure S7b), confirming the high reversibility of imide groups as extrinsic RMs of lithium polysulfides.

The redox properties of PIPE within the working potential windows of Li-S batteries allow PIPE to participate in the complete electrochemical cycle of sulfur. To evaluate the effect of PIPE in transforming sulfur, multiple electrochemical measurements were carried out. Firstly, sulfur-free carbon paper cathode with or without PIPE was applied to potentiostatically electrodepositing Li_2S from a Li_2S_8 electrolyte (Figure 4a). PIPE-containing cell exhibited a nucleation



Figure 4. Sulfur transformation regulated by PIPE. a) The deposition of $Li_2S_{(2)}$ from Li_2S_4 at 2.0 V, battery with PIPE exhibits a better nucleation. b) The reviving test of batteries discharged to 1.7 V. c) Charge and discharge curves of the large Li_2S particles (ca. 200 µm) on the carbon paper, Li_2S can be utilized only with the help of PIPE. d) The model test for the immigration of sulfur species in Li_2S batteries with or without PIPE. e)–j) SEM images of the two carbon paper layers corresponding to d) after 5 charging and discharging cycles. e)–g) Li_2S dispersion on 5th cycled CP cathode with PIPE are uniformly dispread, while h)–j) Li_2S on the w/o PIPE cathode remains a large-particle morphology and mostly staying at the original side, corresponding to the extremely poor capacity. g),j) exhibit the current collector side layer of the double layer cathode and e),f),h),i) show the opposite layer.

peak stronger in intensity and earlier in onset compared to that of control cells without PIPE or with PEDA (Supporting Information, Figure S8), demonstrating the faster deposition rates and higher nucleation density with PIPE. Moreover, the potentiostatic deposition at more negative potential of 1.7 V shows circa 2 times higher discharge capacity with PIPE (Supporting Information, Figure S9), which can be attributed to thicker Li_2S deposits on the carbon paper featuring the typical three-dimensional growth.^[20]

Secondly, the second voltage plateau that contributes the most capacity is usually terminated owing to the exhaustion of electrochemical active interface and the consequent large overpotential needed to drive the polysulfide-to-Li₂S conversion.^[21] It is then crucial to elongate the second plateau and fully utilize active materials. When introduced PIPE, a fully discharged cell was revived and further released a capacity of 140 mAh g^{-1} at 0.1 C. Subtracted by the contribution from PIPE (equivalent to 8.6 mAh g_s^{-1}), the revived capacity with PIPE, corresponding to $\approx 30\%$ of the capacity of the terminated low voltage plateau, is still much higher than 11% of the revived low-plateau capacity in the control battery during the resting time after injected with a blank electrolyte (Figure 4b; Supporting Information, Figure S10). This comparison verifies the ability of PIPE to activate residual polysulfides in the working electrolyte.

The semi-immobilized imide RM in PIPE can not only activate unused mobile polysulfides but also revive the capacity of isolated immobile phases of sulfur/Li₂S. To demonstrate this point, a special double layered carbon paper cathode was applied, in which the layer (layer B in Figure 4d) toward the anode was loaded with bulk Li₂S particles while both layers were controlled to be modified with PIPE or

unmodified (layer A and B in Figure 4d). The cathode modified with PIPE can be effectively charged to 600 mAh g^{-1} without showing the typical high initial charge barrier, in sharp contrast to the inactive performance without PIPE (Figure 4c).^[22] The active materials in cathode after five cycles were located by scanning electron microscope (SEM).^[23] In the absence of PIPE, bulk Li₂S remains on the layer B with 200 to 400 µm in diameter. With PIPE, however, bulk Li₂S is not observed. Concurrently, the layer A of non-PIPE cell is similar to the pristine carbon paper, while uniform deposition of Li₂S on the layer A is detected in the PIPE cell (Figure 4e-h). These experiments unambiguously demonstrate the ability of semi-immobilized PIPE to motion in the range of cathode through lyophilic polyether chains and then to revive the deactivated phases through chemical reactions with the imide groups. The activation of isolated solid phases is in accordance with the model experiments (Figure 3g).

The practical application of PIPE as a semi-immobilized RM in Li-S batteries was evaluated with typical carbon/sulfur cathodes. To ensure a constant sulfur loading, PIPE is applied by substituting half of the poly(vinylidene fluoride) (PVDF) binder.^[24] Videlicet, only a 5% amount of PIPE was added in the cathode. For comparison, pure poly(ethyl oxide) (PEO, $M_w = 1 \times 10^4$) without the redox-active imide unit was also evaluated. As shown in the CV (Supporting Information, Figure S11), all reduction peaks of PIPE-containing cells are positively shifted by more than 50 mV and all oxidation peaks are negatively shifted by about 100 mV, showing that PIPE effectively reduces the polarization. In terms of the cyclability, the PIPE-containing cells exhibited a significant enhancement in comparison to the pristine battery with an initial capacity of 1220 mAh g^{-1} at 0.5 C (1 C = 1672 mA g^{-1}), which is close to that with PVDF and PEO (Figure 5a). However, the PIPE cell preserved 80% of its initial capacity after 190 cycles, which is 142 and 153 more than the PEO and PVDF cell, respectively, revealing the significantly improved cyclability. Through the comparison between PEO and PIPE, such



Figure 5. Electrochemical properties of Li-S batteries equipped with organic RMs. a) The cycle performances for 300 charging and discharging cycles at 0.5 C of PIPE contained battery, in comparison with those without PIPE. b) The charge and discharge profiles of lithium sulfur batteries with and without PIPE at 0.2 C and 2 C. c) Cycle performance of PIPE including a high-loading practical Li-S battery with a sulfur loading of 3.2 mg_s cm⁻².

an improvement is mainly attributed to the RM activity of incorporated imide units in the polyether chain as the capacity contribution from imide itself is negligible (0.3% of the total theoretical capacity). Generally, a low cyclic fading rate of 0.083% for 300 cycles and an average Coulombic efficiency (CE) of 98.4% were enabled by PIPE, much better than the value 94.9% by small PEG-imide-PEG molecule RM without immobilization (Supporting Information, Figure S12). It should be noted that due to the semiimmobilized strategy, the PIPE cell only attains the advantages of imide as the RM but prevents the internal shuttle of imide and its side reactions with lithium anode. The smooth anode surface can be therefore observed (Supporting Information, Figure S13). On the contrary, oligomeric PEDA displayed fast capacity fading and CE waving after 40 cycles, indicating the vigorous anodic failure caused by the migration of soluble and terminal-reactive PEDA to the anode (Supporting Information, Figure S14).

The regulated sulfur electrochemistry by PIPE also allows an enhancement in the rate performance (Supporting Information, Figure S15). The strong enhancement in high rate capability is mainly ascribed to the better kinetics through the regulation of PIPE, as revealed by the voltage–capacity profiles (Figure 5b).^[25] The increase in capacity at 0.2 C by PIPE mainly originates from the prolonged stage below 2.1 V, in accordance with the capacity reviving test (Figure 4b). Such an increase becomes more obvious at high rate.

To fully exert PIPE as a RM in practical Li-S batteries, the sulfur loading was increased to $3.2 \text{ mg}_{\text{s}} \text{ cm}^{-2}$ and a high and stable capacity of 860 mAh g⁻¹ at 0.1 C was still obtained after 50 cycles (Figure 5 c). This performance is comparable to recent reports (Supporting Information, Table S1).^[26] As the importance of electrolyte-to-sulfur (E/S) mass ratio is gathering more and more attention,^[27] PIPE cells with various E/S ratios from 4 to 10 were evaluated (Supporting Information, Figure S16 and S17). It is clearly shown that at low E/S ratios of 4, even higher capacities can be obtained than cells with E/S ratios of 5, 8, and 10. Our trial in electrolyte-starve Li-S cells further demonstrates the promise of designing and applying intrinsically active semi-immobilized RMs for practical working Li-S batteries.

Generally, the semi-immobilized design of RM to enable the kinetic and spatial mediation follows the concept of longrange regulation. Different from independent small RM molecules, active sites chained on PIPE are restrained by the whole polymer of several to tens of nanometers. The longrange polymer chain regulates the mobility and interfacial affinity of imide sites and polyether segment, enabling the semi-immobilization between insoluble bulk solid and fully diffusive small molecules. For one thing, polyether chain induces the nano-scaled mobility of neighboring imide sites. Considering the matched size of sulfur nucleation with PIPE in sulfur cathode, imide sites within PIPE could symmetrically interact with sulfur interface to mediate the redox reaction in Li-S batteries. For another the polymeric structure restricted the long-range diffusion between electrode, preventing the additional shuttle effect of Li-S batteries.

Conclusion

We propose a semi-immobilization strategy to design efficient RMs for Li-S batteries with high sulfur utilization and long cycling life. The imide segments exhibit desirable redox properties in regulating the sulfur electrochemistry within the working potential range while their embedment in soft, lyophilic, and moderate-weight polymer chains allow local motions to fully access isolated active phase and also circumvent the inherent shuttle effect of small-molecule RMs. With a tiny amount (5%) of semi-immobilized PIPE RM in the sulfur cathode, the electrochemical performance of Li-S batteries can be significantly improved. Our strategy brings out an emerging paradigm to efficiently and durably regulate the sulfur electrochemistry in working batteries and is expected to motivate the design of novel RMs for abundant chemistries and applications.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cathode electrochemistry · kinetics regulation · lithium–sulfur batteries · redox mediators · sulfur redox reactions

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