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**Boosting High-Performance in Lithium-Sulfur Batteries
via Dilute Electrolyte**

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ABSTRACT

Polysulfide shuttle effects, active material losses, formation of resistive surface layers and continuous electrolyte consumption create a major barrier for the lightweight and low-cost lithium-sulfur (Li-S) battery adoption. Tuning electrolyte composition by using additives and most importantly by substantially increasing electrolyte molarity was previously shown to be one of the most effective strategies. Contrarily, little attention has been paid to dilute and super-diluted LiTFSI/DME/DOL/LiNO₃ based-electrolytes, which have been thought to aggravate the polysulfide dissolution and shuttle effects. Here we challenge this conventional wisdom and demonstrate outstanding capabilities of a dilute (0.1 mol L⁻¹ of LiTFSI in DME/DOL with 1 wt.% LiNO₃) electrolyte to enable better electrode wetting, greatly improved high-rate capability and stable cycle performance for high sulfur loading cathodes and low electrolyte/sulfur ratio in Li-S cells. Overall, the presented study shines light on the extraordinary ability of such electrolyte systems to suppress short-chain polysulfide dissolution and polysulfide shuttle effects.

Keywords: Li-S; Super-Diluted; Electrolyte; Sulfur Cathode; Battery

INTRODUCTION

As the world faces a rapidly growing demand to move to renewable energy sources and to drastically reduce carbon emissions, battery technologies need to offer improved energy storage for electric cars, busses and trucks, drones, electric planes and the grid.¹⁻⁴ For large-scale transportation and many mobile applications, fabrication of lightweight and stable batteries is particularly important, while reducing cathode toxicity remains imperative for low environmental impact.^{2,5} The lithium-sulfur (Li-S) battery system offers a combination of a very low weight, low toxicity, low cost, and high specific energy. With one of the highest theoretical capacities (1675 mAh/g) of any conversion-type cathode, the pursuit of long-lasting and stable Li-S batteries remains a global research focus for the last decade.^{2, 3, 6-8}

In the Li-S conversion chemistry studies, the most commonly used electrolyte comprises ~1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt solution in distilled dimethoxyethane (DME):1,3-dioxolane (DIOX) (1:1, v:v) solvent with 1~2 wt % of LiNO₃ additive.⁹⁻¹¹ The reduction of S typically proceeds through a formation of a series of polysulfide species, which are for the most part soluble in common organic solvents and electrolytes. Successful commercialization of Li-S batteries is severely hindered by polysulfide shuttle effects and strict requirements of low electrolyte/sulfur (E/S: $\mu\text{L}/\text{mg}$) ratio and high S mass loading cathodes in commercial cells.¹²⁻¹⁴ The polysulfide dissolution and the migration of redox - active species cause the loss of active S and thus reversible capacity, self-discharge, low Coulombic efficiency (CE) and unfavorable layer formation on both S cathode and Li anode that induces resistance growth. The lack of a passivating surface layer results in the electrolyte being continuously consumed until it is exhausted to the battery death. To achieve high energy densities of Li-S batteries, the simultaneous employment of rather low E/S ratio and high S mass loading cathode become essential.¹³⁻¹⁵ Such requirements further increase the demands for improved cathode stability against shuttle effects, better electrolyte wetting, faster reaction kinetics and even more stable surface layers to achieve long cycle life and reasonable charging rates.

In previous studies, composite particle design^{2,16-22} and electrolyte modification^{7,23-25} have been the most effective complementary strategies to overcome known challenges. Porous carbons and polar inorganic compounds with different nano-architectures have been widely employed as S or Li₂S hosts.^{21,26-33} Optimizations of both liquid and solid electrolytes have proved to be particularly effective in enhancing the cyclability of a broad range of S/Li₂S cathodes.^{23,34-37}

So far, organic liquid electrolytes and their fundamental studies dominate the mainstream due to their high ionic conductivity. To protect active material from shuttle effects, functional additives (or Li salts) have been reported to induce *in-situ* formation of solid electrolyte interphase to enhance stability and performance of S/Li₂S cathodes.^{25,38-41} In addition, -NH or NH₄⁺ based additives in electrolytes have been reported to adjust the solubility Li₂S or Li₂S₂, aiming

to improve the conversion reaction kinetics.^{42,43} For preventing the polysulfide shuttle in Li-S cells, a novel electrolyte solution of 0.2 mol L⁻¹ containing low-ion-pairing salt (Li[Al(Ohfp)₄]) and a triflamide solvent (N,N-dimethyl triflimide, DMT) have been developed.⁴⁴ In addition, 0.2 mol L⁻¹ solution of novel salt Li[B(OTf)₄] in standard solvents (DME/DOL) has been investigated in Li-S cells.⁴⁵ Since 2013, ultra-saturated salt-solvent mixtures have become a popular avenue to combat the polysulfide dissolution due to smaller fraction of solvent molecules not participating in Li⁺ and TFSI⁻ solvation and available for solvating the polysulfides.⁴⁶⁻⁴⁹ However, such electrolytes typically display high viscosity, low Li⁺ mobility, poor wetting on S cathodes, resulting in low capacity utilization, low rate capability and reduced practically attainable energy density, particularly for low E/S ratio and high mass loading cathodes.^{9, 50} In contrast, one literature at very recent showed that 0.1 M~0.5M LiTFSI with 0.4M LiNO₃ in DME/DOL demonstrated better rate capability and smaller voltage hysteresis, but worse cycle stability in Li-S cells than those in 1M standard electrolytes.⁹ Overall, especially for the standard electrolyte system of LiTFSI/LiNO₃/DME/DOL, little attention has been paid to dilute and ultra-dilute electrolytes, which have been thought to aggravate the polysulfide dissolution and shuttle effects because according to a solution theory a higher fraction of free solvents for solvation should result in stronger and faster solvency.

Here we challenge this conventional wisdom and demonstrate outstanding capabilities of dilute (0.1 mol L⁻¹) electrolytes to enable better electrode wetting, greatly improved high-rate capability and stable cycle performance for high active mass loading S cathodes and low E/S ratio in Li-S cells. We prepare such dilute (0.1M) electrolyte using LiTFSI salt and solvents (DME/DOL, 1:1) with 1 wt.% LiNO₃ and yet attain rather unique and unexpected properties. Using a powerful combination of post-mortem analyses and numerical simulations we explain our discovery of abnormal reductions in short-chain polysulfide dissolution and migration of soluble sulfur species in dilute electrolytes. As additional benefits, the dilute electrolytes are less expensive, lighter, less viscous than both standard 1M and high-M electrolytes, which may open new avenues for the exploration and overcoming challenges of other battery systems.

RESULTS AND DISCUSSION

Carbon capsule-sulfur (CC-S) composites were selected as cathode material in our studies. More details including BET surface area, element mapping, S content and phase are discussed in the supporting information (Fig.S1-S4). Note that S in such electrodes exhibits a direct contact with liquid electrolytes and thus should form polysulfides during cycling and induce polysulfide dissolution and shuttle.^{30,51} The impact of electrolyte molarity was studied using coin cells with Li metal anode and LiTFSI salt concentrations ranging from ultra-concentrated (up to 5M) to regular (1M) to dilute (0.1M) compositions in DME/DOL with 1 wt.% LiNO₃. Rate tests conducted at various current densities (from 0.1C to 2C) on medium loading (2 mg_S·cm⁻²) cathodes allowed us to evaluate changes in the ionic polarization as a function of electrolyte composition (Fig. 1).

The shape of the discharge / charge profiles reveal the voltage curves typical for Li-S chemistry with two plateaus corresponding to S₈→Li₂S₄ (the 1st, shorter, higher voltage plateau) and Li₂S₄→Li₂S (the 2nd, longer, lower voltage plateau).⁵² In a standard 1M electrolyte, the S cathodes displayed high capacity (1265 mAh·g⁻¹) and high 2nd galvanostatic discharge voltage plateau (~2.1 V vs. Li/Li⁺; voltage hysteresis ~0.15 V) at a slow rate of C/10, gradually reducing to ~50% of the initial capacity (650 mAh·g⁻¹ at 2C) and ~1.8 V vs. Li/Li⁺ (voltage hysteresis of ~0.65 V) at 2C (Fig. 1a), indicating a limited rate performance, as may be expected for relatively thick and unprotected from dissolution/shuttle effects CC-S cathodes. Increasing electrolyte concentration to 2M (Fig. 1b), 3M (Fig. S5) and finally to 5M (Fig. 1c) noticeably reduced capacity utilization and increased voltage hysteresis at high rates. In fact, cells with concentrated electrolytes showed very low specific capacity (100-300 mAh·g⁻¹) at 1C and even smaller (50-100 mAh·g⁻¹) at 2C (Fig. 1b-2c). We could not even distinguish two discharge plateaus in such cells at 1C-2C rates, indicating rather poor reaction kinetics in concentrated electrolytes. Quite remarkably, reducing LiTFSI salt concentration to 0.1M resulted in both high accessible capacity and dramatically improved rate performance (~75% of the initial capacity or 956 mAh·g⁻¹ at 1C and 828 mAh·g⁻¹ at 2C) with noticeably smaller distortions of the voltage curves and smaller voltage hysteresis growth with

increasing rates (voltage hysteresis of only $\sim 0.4\text{V}$ at 2C) when compared to cells with 1M , 2M , 3M and 5M electrolytes (Fig. 1a-1e).

Besides sufficiently high rates, here again, low molarity electrolytes showed superior performance (Fig. 1e-1f). When cells were cycled at moderate $\text{C}/2$ rate for 200 cycles, both 1M and 2M electrolytes resulted in a visible capacity degradation to $\sim 65\%$ within 200 cycles, providing a discharge capacity of just $\sim 600\text{ mAh g}^{-1}$ at the 200^{th} cycle. In concentrated electrolytes of 3M and 5M , the cells demonstrated rather low capacity utilization ($100\text{--}200\text{ mAh}\cdot\text{g}^{-1}$) at $\text{C}/2$ due to limited reaction kinetics. However, in 0.1M electrolyte, the cell showed outstanding capacity stability, displaying $\sim 95\%$ capacity retention after 200 cycles ($\sim 970\text{ mAh g}^{-1}$ at the 200^{th} cycle), and suggesting that polysulfide shuttle and irreversible Li_2S deposition on the Li anode and resistance growth was miraculously minimized. As shown in Fig. S6, compared to 1M electrolyte, the cell using dilute (0.1M) electrolyte displays higher CE within 200 cycles. In order to further investigate the difference in the cycling stability behavior, the changes in the voltage profiles within 200 cycles are shown in Fig. 1g-1i and S5. Clearly, there are very minimal changes in the profiles of the cell with 0.1M electrolyte during 200 cycles (Fig. 1g). In contrast, the cell with 1M or 2M electrolyte shows significant changes in the voltage profile and a noticeably higher voltage hysteresis, indicating the serious polysulfide shuttle effects in common $1\sim 2\text{M}$ electrolytes (Fig. 1h and S7a). While using more concentrated 3M and 5M electrolytes, the cells demonstrate rather low capacity, and disappearing of 2^{nd} discharge plateaus because of huge voltage hysteresis beyond working voltage window (Fig. 1i and S7b).

Post-mortem analysis of the electrodes revealed a dramatic impact of salt concentration on the morphologies of both Li anodes and CC-S cathodes. Compared to the SEM images of a fresh CC-S cathode in Fig. S8a, the surface of cycled CC-S electrode in 1M electrolyte becomes rough and fully covered by a thick surface layer containing re-precipitated particles (Fig. 2a), as could be expected from prior-art studies.^{25,39} In addition, the cycled Li metal anode in 1M electrolyte show a rough and highly uneven surface covered with nonuniform solid electrolyte interphase (SEI) layer (Fig. S8c) comprising precipitated Li_2S

nanoparticles and large Li metal grains emerging through the SEI/Li₂S layer (Fig. 2c). The dissolved and re-precipitated polysulfides are known to be associated with the formation of Li₂S in the anode (Fig. 2c), the losses of active material and capacity decay (Fig. 1f) as well as the increased cell resistance (Fig. 2e).^{7, 52} In sharp contrast, the CC-S cathode cycled in 0.1M electrolyte shows only marginal surface changes and absence of unfavorable particles (or layer) after cycling (Fig. 2b and S8b), in agreement with the previously discussed cycling stability results (Fig. 1f). Meanwhile, the Li foil cycled in a 0.1M electrolyte exhibits a very smooth surface morphology with homogeneous large Li grains and thin and dense SEI layer without any visible precipitates and vertical dendrites (Fig. 2d and S8d), confirming that the polysulfide shuttle effects have been successfully suppressed. These findings are also consistent with no visible increase of charge-transfer resistance in the 0.1M electrolyte cell (Fig. 2f). The cycled electrolytes of both 0.1M and 1M were collected to identify possible color changes (Fig. S9). As expected, the color of cycled 1M benchmark electrolyte turned into visible yellow that is much deeper than the color of cycled 0.1M electrolyte, also indicating that the polysulfide shuttle and S loss were noticeably reduced in the 0.1M electrolyte.

Other important considerations for practical cells are attaining favorable cell characteristics for low E/S ratio and high S loadings. As such, several cells with different S mass loadings and E/S ratios were tested in dilute (0.1M) electrolyte (Fig. S10). Using an average E/S ratio of 15 $\mu\text{L}\cdot\text{mg}^{-1}$ and active mass loading of 3.8 $\text{mg}\cdot\text{cm}^{-2}$, the cells showed promising capacity utilizations with a discharge capacity of 1038, 920 and 779 $\text{mAh}\cdot\text{g}^{-1}$ at 0.1C, 0.2C and 0.5C rates, respectively (Fig. S10a). When cycled at 0.5C for over 300 cycles, the cell showed a capacity retention of 92% (718 $\text{mAh}\cdot\text{g}^{-1}$ at 300th cycle) (Fig. S10b). Increasing the active mass loading to 5.2 mg/cm^2 and reducing the E/S ratio to 8 $\mu\text{L}\cdot\text{mg}^{-1}$ (Fig. S10c and d) resulted in discharge capacities of 896, 830 and 716 $\text{mAh}\cdot\text{g}^{-1}$ at 0.1C, 0.2C and 0.5C, respectively, and a capacity retention of

97% within 100 cycles at 0.5C. Compared to previous studies on fully unprotected S cathodes with high loadings,^{13, 53} the rate capability at 0.5C, small voltage hysteresis and cycle stability produced by the high active mass loading (up to 5.2 mg/cm²) and moderate E/S ratio (down to 8 $\mu\text{L}\cdot\text{mg}^{-1}$) in the dilute (0.1M) electrolyte are clearly very promising.

In order to reveal the underlying mechanism(s) for superior performance of dilute electrolytes in Li-S batteries, we analyzed physical properties, interactions with polysulfides and conducted molecular dynamics (MD) simulations. When compared to standard (1M) and concentrated (2M, 3M, 5M, 7M) electrolytes (some of which are often called “solvent-in-salt” electrolytes), an dilute (0.1M) electrolyte utilizes much less salt and offers a smaller density (Fig. 3a and c), which are beneficial for achieving low cost and higher specific energy in Li-S batteries. Through the ionic conductivity studies of 0.1, 1, 3, 5, and 7 M electrolytes, electrolytes with different molarities indeed display different ionic conductivities that are affected by both ion concentration and ionic mobility. As shown in Fig.3b, the ionic conductivity of 0.1M electrolyte (1.78 mS/cm) is lower than that of 1M (12.16 mS/cm). Since the rate performance of cell is determining by Li⁺ solvation/dissociation and the subsequent Li⁺ migration,⁵⁴ both the electrolyte viscosity and wettability of the electrode by the electrolyte are important factors for cell manufacturing rate and cell cycling rate. We investigated the impact of salt concentration on electrolyte viscosity and the CC-S cathode wetting (Fig. 3d and e). The dilute (0.1M) electrolyte enables extremely small viscosity (~ 0.6 cP or mPa·s), which correlates with high Li ion mobility (see Table S2). The wetting of the CC-S cathode by this (0.1M) electrolyte is also excellent (Fig. 3d) with the contact angle of mere 15.8° at 0.06 sec, while standard 1M and moderately concentrated 3M electrolytes display contact angles of 24.1° and 72.1°, respectively. The good wetting, low viscosity and high Li ion mobility of this dilute electrolyte may explain fast the Li⁺ transport at the solid-liquid interface

and higher capacity utilization and lower voltage hysteresis at high C rates (Fig. 2).

MD simulations of short-chain polysulfide Li_2S_2 placed in a dilute (0.1M) electrolyte show a very strong aggregation of Li_2S_2 (Fig. 4a and Fig.S11), suggesting a very low Li_2S_2 polysulfide solubility.¹¹ LiTFSI is fully dissociated in low LiTFSI concentrations, with TFSI⁻ anions being well dispersed (Fig. 4a) while the Li⁺ cations being strongly bound to the $\text{S}_2^{(2-)}$ anions (Fig. S12a), thus bridging the Li_2S_2 into a well-defined domain (Fig. 4a) that indicates a strong phase separation of short-chain polysulfide in the electrolyte. Increasing the LiTFSI salt concentration from 0.1 M to 1M increases Li-TFSI aggregation (see higher peak for Li-O(TFSI) in Fig. S12). As a result, the TFSI⁻ anions become more frequently binding to Li⁺ and thus screening the desired Li⁺ and polysulfide interactions. This screening prevents bridging and agglomeration of the Li_2S_2 into separate domains and result in the Li_2S_2 becoming much more evenly distributed in the simulation box (Fig. 4b) with a much weaker intermolecular S...S peak for short-chain polysulfides (Fig. 4d). Further increase of the LiTFSI salt concentration to 3M makes less solvent available to solvate both Li_2S_2 and LiTFSI, resulting in an expected (from prior art studies) increased aggregation of sulfide anions (reduced polysulfide Li_2S_2 dissolution) and the increased S...S first peak compared to 1M LiTFSI electrolyte (Fig. 4c and 4d). However, the value of this peak for 3M electrolyte remains significantly smaller than that for 0.1M electrolyte, highlighting superior performance of 0.1M electrolyte in terms of increased short-chain polysulfide agglomeration and thus reduced S loss and shuttle effects during 2nd discharge voltage plateau (solid to solid conversion reaction). The 1M LiTFSI is the most vulnerable to polysulfide shuttle effects due to a combination of two factors: (i) sufficient screening of Li_2S_2 by TFSI⁻ anions and (ii) availability of free solvent to solvate ions. Interestingly, aggregation of long-chain Li_2S_4 was less dependent on the LiTFSI concentration as shown in Fig.S13, showing similar solubility of long-chain

polysulfides in both 0.1M and 1M electrolytes. According to previous reports, the formation of liquid long-chain polysulfides (S_8^{2-} , S_6^{2-} and S_4^{2-}) can effectively increase the active sulfur utilization via enhancing the reaction kinetics of solid–liquid and liquid-solid sulfur conversion (offering more and short pathways for ion and electron transports).^{11, 55-57} Therefore, no significant difference of long-chain polysulfides dissolution can explain the similar capacity utilizations at small C rates (0.1C-0.5C) in both 0.1M and 1M electrolytes in Fig.1a and d. As another explanation, fundamentally the lattice energy of the salt Li_2S_2 is higher than that of Li_2S_4 , Li_2S_6 and Li_2S_8 (larger anion size). Thus, the long-chain polysulfides (Li_2S_x , $x=4,6,8$) have higher solubilities in DOL/DME. Yet, the situation changes if one compares the solvating properties of the 0.1 and 1.0 M LiTFSI electrolytes. Although the solvents are same (DOL/DME), the ionic strength of the solution, which corresponds to the capacity to dissolve smaller ions with higher lattice energies, increases from 0.1 to 1.0 M. This easily explains the reduced solubility of the smaller Li_2S_2 compound in the lower ionic strength electrolyte (0.1 M). In addition, this explanation is in agreement with the entire MD-simulation.

Moreover, despite lower viscosity for 0.1M LiTFSI + 0.5M Li_2S_2 electrolyte compared to 1M LiTFSI + 0.44M Li_2S_2 electrolyte the $S_2^{(2-)}$ self-diffusion coefficient is factor of two lower for the more dilute electrolyte due to much stronger aggregation of Li_2S_2 in the former resulting in reduced mobility of $S_2^{(2-)}$. When both Li_2S_2 and Li_2S_4 species are present in electrolyte simultaneously the Li_2S_4 species bind to Li_2S_2 and their aggregates as shown in Fig. 4(e-f) resulting in lower mobility of S_4^- when Li_2S_2 aggregates are present, i. e. in dilute electrolytes.

In Fig. 5, the lithium polysulfide dissolution experiments were conducted in pure solvent, dilute (0.1M), standard (1M) and concentrated (3M) electrolytes to see the color changes with time (which are indicative of the formation, dissolution and diffusion of mixed long-chain polysulfides). Similar to previous

results (Fig. 4) and prior art studies,⁴⁷ the lithium polysulfide formation, dissolution and diffusion into the bulk of the electrolyte are somewhat limited in concentrated electrolytes (3M electrolyte in Fig. 5) when compares with 1M electrolyte. When do the comparison among the results in pure solvents, 0.1M and 1M solutions, the observed deep yellow color indicates the rapid formation of long-chain polysulfides (might be the mixture of S_8^{2-} , S_6^{2-} and S_4^{2-}) at room temperature, and demonstrates the strong solvency of long-chain lithium polysulfides in three solutions. However, in the pure solvent and 0.1M solutions the dissolved S species diffuse even more slowly not only when compared with 1M, but also with 3M electrolytes (Fig. 5), which means the polysulfide shuttles effects are largely reduced in the 0.1M electrolyte. More LiTFSI salt in 1M electrolyte aggravates the diffusion of polysulfides. This unexpected behavior (suppressed polysulfide diffusion/shuttle) is correlated with a significantly more pronounced aggregation of Li_2S_2 and their mixtures with Li_2S_4 observed in MD simulations of dilute electrolytes (Fig. 4). Slower polysulfides diffusion lead to better cycle stability (Fig. 1f and g), smooth surface morphology of cycled electrodes (Fig. 2b and d) and no change of charge-transfer resistance during cycling (Fig. 2f) in the 0.1M electrolyte.

In summary, we have demonstrated an unexpected ability of the dilute electrolyte (0.1 mol L^{-1} of LiTFSI in DME/DOL with 1 wt.% $LiNO_3$) to offer outstanding performance in high-energy Li-S batteries. Due to very low viscosity, excellent wetting on sulfur cathodes and dramatically reduced short-chain polysulfide dissolution and polysulfides shuttle effects, the carbon-sulfur cathodes displayed much higher rate capability and better cell stability (in terms of both capacity retention and the lack of growth in charge transfer resistance) in the 0.1M electrolyte than in standard 1M or concentrated electrolytes for medium ($2 \text{ mg}_S \cdot \text{cm}^{-2}$) and high-loading ($3.8\text{-}5.2 \text{ mg}_S \cdot \text{cm}^{-2}$) electrodes. Post-mortem analyses and lithium polysulfide dissolution experiments confirmed significantly reduced shuttle of long-chain polysulfides in 0.1M electrolyte. MD

simulations shine more light on the superior performance of dilute LiTFSI-based electrolytes: at low salt concentrations (0.1M LiTFSI) Li^+ cations bridge Li_2S_2 into large phase-separated domains preventing short-chain polysulfide dissolution into the bulk of the electrolyte; aggregations of Li_2S_4 via participation in the Li_2S_2 aggregates (forming Li_2S_2 - Li_2S_4 clusters) lead to slowing down of not only Li_2S_2 diffusion but also Li_2S_4 diffusion at 0.1M (vs. 1M LiTFSI). Therefore, dilute electrolytes may become more suitable for the next-generation Li-S batteries and possibly other conversion-type cathode chemistries. We call for future studies of dilute and ultra-dilute electrolytes on high sulfur loadings and low E/S ratios to be carried out in Li-S pouch cells.

ASSOCIATED CONTENT

The Supporting Information is available free of charge. It mainly includes the experimental details, characterizations, details of simulation, and electrochemical characterizations.

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Notes

The authors declare no competing interests.

Author Contributions

F.W., Y.Y., and G.Y. conceived the idea. F.W. and F.C. carried out the materials synthesis, characterization, electrochemical studies and wrote the original draft. M.S. synthesized the carbon capsule nanopowder. O.B. did the simulation part. All the authors discussed the results and contributed to the writing of manuscript.

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Figures

Figure 1. Electrochemical characterizations of CC-S cathode in electrolytes with various salt concentrations: voltage profiles of CC-S cathode at different C rates in (a) 1M, (b) 2M, (c) 5M and (d) 0.1M electrolytes; (e) discharge capacity at different C-rates of the CC-S sample in electrolytes with different concentrations; (f) cycling performance at C/2 of the CC-S cathode in produced electrolytes from 0.1M to 5M, displaying higher rate and more stable cycling performance in dilute (0.1M) electrolyte; Changes in charge–discharge profiles at 0.5C in (g) 0.1M, (h) 1M and (i) 5M electrolytes. All electrolytes comprised 1 wt.% LiNO₃ additives.

Figure 2. Post-mortem analysis of cycled electrodes and EIS changes revealed a drastic effect of ultra-dilute electrolyte in Li–S batteries: SEM images of (a) CC-S cathode and (c) Li anode after 200cycles in 1M electrolyte as a benchmark; SEM images of cycled (b) CC-S cathode and (d) Li anode after 200cycles in 0.1M electrolyte; the EIS changes of cells within 100 cycles in both (e) 1M and (f) 0.1M electrolytes. Nearly no changes in the cathode, a dense-smooth surface morphology with large grains and no visible Li dendrites on the Li anode, and nearly no charge-transfer resistance increase in the 0.1M electrolyte.

Figure 3. Comparison studies of physical properties among ultra-dilute, standard and concentrated electrolytes: (a) the digital photos of 2ml pure solvent and different volumes of Li salt corresponding to different electrolyte concentrations for 2ml liquid in the electrolyte; (b) ionic conductivity of 0.1, 1, 2, 3, and 5 M electrolytes (note good agreement with MD predictions shown in Table S2); (c) density and (d) viscosity of electrolytes with different molarities; (e) digital photographs of the different molarity electrolyte droplet contact angles on CC-S cathode, showing much less salt, lower density, lower viscosity and better wetting properties of a dilute (0.1M) electrolyte.

Figure 4. Snapshots of MD simulations boxes highlighting (a-c) S_2 anions and (e) S_2 and S_4 anions (shown in yellow), solvent and TFSI $^-$ are shown as a wire frame; (d) intermolecular radial distribution functions (RDFs) of S-S from S_2 anions corresponding to (a-c), (f) the Li_2S_2 - Li_2S_4 clusters from simulations (e).

Figure 5. Lithium polysulfide dissolution experiments: the color changes of four samples with different salt (LiTFSI) concentrations containing the same amount of Li_2S and S mixtures ($\text{Li}_2\text{S}:\text{S}=1:3$ mol/mol) were recorded by digital camera with time (without any shaking). The mass of powder was calculated by an ideal formation of $0.2 \text{ mol L}^{-1} \text{ Li}_2\text{S}_4$ in 3 ml of liquid. The produced samples are: pure solvent (0M), 0.1 mol LiTFSI per 1 mol solvent (here we call it 0.1M), 1 mol LiTFSI per 1 solvent (1M), and 3 mol LiTFSI per 1 mol solvent (3M), respectively.

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