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Solvate ionic liquid electrolyte with 1,1,2,2-tetrafluoroethyl 2,2,2-trifluoroethyl ether as a support solvent for advanced lithium-sulfur batteries

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1,1,2,2-tetrafluoroethyl 2,2,2-trifluoroethyl ether (TFTFE) was added to solvate ionic liquid (SIL) based on glyme-lithium salt as a support solvent. The fluorinated ether improves cycle and rate capability of Li-S cells. The key role of TFTFE played in the cell system with SIL is an ionic conduction-enhancing ingredient, especially for high-rate cycle environment.

The issues of energy shortage and environment pollution propel the development of electric vehicles. To cater the strict requests for vehicle-loaded power, all kinds of advanced energy storage devices have been studied extensively. Among these, lithium sulfur (Li-S) battery has attracted worldwide attentions by virtue of its theoretical energy density of up to 2600 Wh kg\(^{-1}\),\(^{1,2}\) which is 10 times higher than that of conventional lithium-ion batteries (LIB). Besides, sulfur has the advantages of non-toxicity and abundance in nature, whereas LIB cathode materials typically contain rare metals.

However, a critical problem originated from redox conversion process of the Li-S batteries is the dissolution of reaction intermediate polysulfides (PS) in the electrolyte.\(^3\) The dissolved PS tends to generate repeating shuttle between the cathode and anode,\(^4\) resulting in low coulombic efficiency and fast self-discharge. Furthermore, the PS can be electrochemically and chemically reduced on Li metal, causing such problems as (a) consuming active species, (b) corroding Li anode, and (c) polarizing Li anode once insoluble products are formed and deposited on the Li surface.\(^5\) Hence the restrictions towards PS are very necessary for boosting cell performance. Optimizing electrolyte composition is often attempted for this purpose, e.g., altering solvent type, controlling electrolyte amount or introducing functional additives, etc.\(^6-8\)

Recently, solvate ionic liquid (SIL)\(^9\) begins to enter the research scope of the Li-S batteries owing to its distinctive structure and properties. The typical case of SIL is the equimolar mixtures of tetraglyme (G4) and certain Li salts (LiX).\(^10\) The formation of complex Li(G4)\(_X\) will weaken the donor ability of G4 solvent because all of the lone pairs of the ether oxygen atoms are donated to the Li\(^+\) [as we know, the coordination number of Li\(^+\) is 4~5].\(^11\) Thus the PS is poorly solvated in the SIL and quite low solubility of PS can be obtained easily in SIL,\(^12\) which reflects the superiority of SIL applying in the Li-S batteries compared to other electrolyte systems. Research results show that SIL electrolyte allow the cell to have a stable charge-discharge cycles and a coulombic efficiency of greater than 99%.\(^12\) However, the cell capacity is still a bit low over the whole cycling period. Besides, the high viscosity of the SIL gives rise to certain polarization, which is harmful to the potential plateau and rate capability of the cell. Interestingly, It is reported that organo-fluorine compound is capable of enhancing the energy and power density once it was added into the SIL,\(^12\) which utilizes the complementary and synergistic actions between SIL and fluorinated ether.

In the study, we aims to select another novel fluorinated ether derivative named 1,1,2,2-tetrafluoroethyl 2,2,2-trifluoroethyl ether (TFTFE) as the support solvent of SIL. Significant improvements of TFTFE-contained electrolyte on electrochemical performances of the Li-S cell are demonstrated here, and the key role of TFTFE in the cell system with SIL is discussed. Several electrolytes using in this experiment were prepared as follows: Lithium bis(trifluoromethane sulfonimide) (LiTFSI, Aldrich) and G4 (Adamas) were mixed at equimolar ratio and magnetically stirred at 50 ºC overnight in an argon-filled glove box, forming Li(G4)\(_X\)TFSI (LiTFSI:G4=1:1, molar ratio). Then the stoichiometric TFTFE (Adamas) was further added into above Li(G4)\(_X\)TFSI to obtain a series of solution mixtures Li(G4)\(_X\)TFSI-xTFT (LiTFSI:G4:TFTFE=1:1:x, molar ratio, x=1~6).

In general, the required properties of a support solvent for SIL electrolyte Li(G4)\(_X\)TFSI in Li-S cells include:\(^11\)
(a) Chemical stability against PS;
(b) Reductive stability against Li metal;
(c) Miscibility with Li(G4)\(_X\)TFSI;
(d) Better mobility than Li(G4)\(_X\)TFSI;
Electrolyte without any PS presents colourless and transparent. However, the colour of Li(G4)1TFSI once adding Li2S becomes yellow and deepens gradually with time. In principle, the lone pairs of the ether oxygen are all donated to Li+ in Li(G4)1TFSI, and the stable Li(G4)4+ complex ion can be formed due to strong ion-dipole interaction between Li+ and G4. Hence PS dissolves hardly in the SIL. The above colour change suggests that the solubility of PS still exists to some extent for Li(G4)1TFSI. When using TFTFE as support solvent, the Li(G4)1TFSI-xTF solution seems lighter than Li(G4)1TFSI at the same standing steps. Especially the colour of Li(G4)1TFSI-xTF is close to colourless and nearly unchanged after standing for 6 days. It suggests that the dissolution of PS is further decreased in the TFTFE-contained electrolyte. Moreover, the dissolution quantity of polysulfide decreases gradually as TFTFE content in the electrolyte raises (see ESI, Fig.S1 and Fig.S2†), which means TFTFE favours the improvement of transport property on the basis of SIL.

The fluorinated ether has very low donor ability because it is always too fluorinated to participate in Li+ solvation. In order to realize the solubility of PS in various electrolytes, S and Li2S with a molar ratio of 7:1 were mixed and added in each electrolyte (the theoretical content of Li2S was controlled to be 0.25 mol L−1). As the solubility of PS in the electrolyte has been characterized extensively by observing the colour of the electrolyte containing PS, the pictures of various solutions after different standing time are recorded and compared in Fig.1a. Generally, the normal electrolyte without any PS presents colourless and transparent. However, the colour of Li(G4)1TFSI once adding Li2S becomes yellow and deepens gradually with time. In principle, the lone pairs of the ether oxygen are all donated to Li+ in Li(G4)1TFSI, and the stable Li(G4)4+ complex ion can be formed due to strong ion-dipole interaction between Li+ and G4. Hence PS dissolves hardly in the SIL. The above colour change suggests that the solubility of PS still exists to some extent for Li(G4)1TFSI. When using TFTFE as support solvent, the Li(G4)1TFSI-xTF solution seems lighter than Li(G4)1TFSI at the same standing steps. Especially the colour of Li(G4)1TFSI-xTF is close to colourless and nearly unchanged after standing for 6 days. It suggests that the dissolution of PS is further decreased in the TFTFE-contained electrolyte. Moreover, the dissolution quantity of polysulfide decreases gradually as TFTFE content in the electrolyte raises (see ESI, Fig.S1 and Fig.S2†). Therefore, more TFTFE contributes to weaker dissociation of PS compared to Li(G4)1TFSI.

The low donor ability implies that TFTFE is hard to overwhelm G4 in Li+ solvation as well. This speculation can be verified from linear sweep voltammetry (LSV) measurements of stainless steel/Li cells loaded various electrolytes (scanning rate: 0.5 mV s−1). As shown in Fig.1b, the anodic peaks of equimolar complex Li(G4)1TFSI is near 5 V vs. Li/Li+, exhibiting high oxidative stability of the SILs. After adding TFTFE, the LSV curves of Li(G4)1TFSI-xTF move towards low-potential direction slightly. The free ether (G4, in this case), which are not involved in the complex with Li+, will be decomposed irreversibly at higher than 4 V vs. Li/Li+. The oxidative limits of Li(G4)1TFSI-xTF is very close to that of Li(G4)1TFSI, revealing that the majority of complex cations Li(G4)4+ still exist steadily and free G4 is scarce in the TFTFE-contained system. In other words, the distinctive solvate structure of SIL can be reserved although TFTFE was introduced into the electrolyte.

It can be seen from the above results that TFTFE meets all the demands for support solvent of SIL and can cooperate ideally with it. Next the electrochemical performances of Li-S cells with various electrolytes were investigated. Sulfur-carbon composite (S-C, 79.1% sulfur, see ESI, Fig.S3†) was prepared according to the method described previously. Sulfur cathode consisted of 80 wt% S-C composite, 10 wt% carbon black (Super P, Timcal) and 10 wt% poly(vinylidene fluoride) (PVDF, 6020 Sofel). The sulfur loading on each cathode was ~1.2 mg cm−2. Coin cells were assembled in the glove box by using above sulfur cathode, Li foil as anode and Advancet G55 as separator. The electrolyte amount in each cell was controlled to be ~18 mL g−1 (the ratio of electrolyte volume to sulfur content in the cathode).

Firstly, the cyclic voltammetry (CV) for the cell with Li(G4)1TFSI and Li(G4)1TFSI-xTF are presented in Fig.2a and Fig.2b, respectively. The sweep rate is 0.1 mV s−1. All of the cells show two reduction peaks and two very close oxidation peaks (similar to those cases using G4 in electrolyte). The reduction peaks in cathodic scan stand for the reduction of elemental sulfur to soluble PS and then to the insoluble Li2S/LiS, respectively. And the oxidation peaks in anodic scan represent the formation of PS and the final oxidized active sulfur (Li2S or S), respectively. The CV patterns in the first four cycles almost overlap each other, indicating steady cycle ability of the cells with the two electrolytes. It should be noted that the second reduction peak is located at higher value and the voltage gap between oxidation and reduction peaks is smaller for the cell with Li(G4)1TFSI-xTF compared to that for Li(G4)1TFSI. TFTFE enhances ion conduction of the electrolyte, thus decreases the over-potential and improves reversibility of the cell.

Fig.2c is the initial potential profiles of the Li-S cells with various electrolytes at 0.1 C between 1.5 V and 3 V. Two plateaus can be clearly observed from the discharge curves, corresponding to two-step reaction of sulfur with metallic Li. The low-potential plateau for Li(G4)1TFSI-xTF reaches ~2.1 V, higher than that for Li(G4)1TFSI (~2.0 V). Meanwhile, the gaps between discharge plateau and charge plateau of the cells containing TFTFE is smaller than that using pure SIL. These phenomena are well consistent with above CV results. In addition, initial discharge capacity of the cell increases when the amount of TFTFE in the electrolyte increases. Since adding the fluorinated ether can further limit the dissolution of PS at the discharge stage, more active sulfur can be recovered.
Among them, the cell with Li(G4)TFSI electrolytes are always superior to that using pure SIL at each rate. The cell capacities using TFTFE-contained rates for various electrolytes are presented in Fig. 3a (the charge further investigated. The specific capacities at different discharge electrochemical stability of the cell.

To better understand the function of TFTFE in the cell system, the electrochemical impedance spectroscopy (EIS) of the Li-S cells with various electrolytes was examined. The frequency range of the measurement was $10^5$~$0.1$ Hz, with the perturbation amplitude of 5 mV. The impedance plots before cycle are composed of a semicircle in medium-to-high frequency and an inclined line in the low frequency (Fig.4a). The former is attributed to the interface charge-transfer resistance ($R_o$), and the latter corresponds to Warburg impedance ($W_o$, associated with Li$^+$ diffusion in the active material).

While the discharge plateau for Li(G4)TFSI-4TF also overtops Li(G4)TFSI at initial cycle (see ESI, Fig.S5†), demonstrating less over-potentials in the former. The plateau potential ascends step by step and then maintains stable during subsequent cycles in the case of Li(G4)TFSI-4TF (Fig.3c), which reveals the achievement of a stable electrochemical environment needs a procedure, like other electrolytes using abundant fluorinated ether.\textsuperscript{20} While the discharge plateau for Li(G4)TFSI is stable all the time (Fig.3d). Therefore, the polarization gap between two electrolytes is further enlarged at latter cycles.

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The fitted resistance ($R_o$), including the electrolyte and electrode resistances.\textsuperscript{24} After 50 cycles, the impedance responses are divided into two obvious semicircles (Fig.4b). The additional semicircle in the high frequency is related to solid-electrolyte interface (SEI) film formed during the charge–discharge process ($R_i$).\textsuperscript{25,26} The fitted resistance data according to the corresponding equivalent circuit are shown in Table 1.

The $R_o$ for the cell with fluorinated ether is obviously smaller than the one without it, which is another convincing evidence of TFTFE on promoting ion transport of the electrolyte. The decline in $R_i$ for Li(G4)TFSI-4TF compared to Li(G4)TFSI suggests that the

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Fig. 2 Cyclic voltammogram of the Li-S cell with (a) Li(G4)TFSI and (b) Li(G4)TFSI-4TF at a sweep rate of 0.1 mV s$^{-1}$; (c) initial potential profiles and (d) cycle performances of the cells with various electrolytes at 0.1 C.
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