Improving the over-all performance of Li-S batteries via electrolyte optimization with consideration of loading condition

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Abstract

Lithium sulfur (Li-S) batteries are very promising electrochemical storage system due to their high gravimetric energy density and low cost. Enormous efforts have been put on Li-S battery to achieve its commercialization. The function of electrolyte is a key issue in achieving the high performance of Li-S system, and several additives have been tried. But very few works have been working on the electrolyte optimization method with the consideration of over-all performance, including cycling stability, rate

capability, especially self-discharge prevention ability, and the consideration of loading condition. In this work, we focus on the incorporation of room temperature ionic liquid (IL) as co-solvent, and the effect of IL in mitigating the polysulfide dissolution via systematical mechanism study of self-discharge phenomena. Moreover, the optimization of IL incorporation ratio is discussed for the sake of the better over-all electrochemical performance of Li-S cell by considering cycling stability, rate performance and self-discharge prevention ability, which is found to vary with loading condition. The improved understanding of the effect of IL on battery performance will help the development of electrolyte for Li-S batteries.

1. Introduction

Li-S batteries have become one of the most promising candidates for next generation energy storage systems, due to their high theoretical capacity, low cost and environmental friendly properties[1-4]. They have been listed as the “closest to market” energy storage system among all in the recent *Nature* news[5]. However, the practical application of Li-S batteries has been hindered by several shortcomings, including the poor cycling stability, low coulombic efficiency and the severe self-discharge during battery storage, etc., compared to other system[6-10]. Most of these problems stem from the polysulfide dissolution in Li-S batteries during cycling[11, 12]. Severe shuttle effect is resulted, along with active material loss and high self-discharge capacity loss. Several issues need to be addressed to further improve the performance of Li-S batteries, including the design of sulfur cathodes with polysulfide retention strategies[9], the design of new electrolyte with reduced polysulfide solubility, and other Li-electrode protection methods, etc. The novel ideas in electrode structure design include retaining the sulfur species inside the encapsulate structure[13-16], improving the affinity between the electrode surface and the dissolved polysulfide via the functionality of the binders[16-20] or chemical modification of electrode[15, 21, 22]. Specially designed or commercialized conductive binders are also incorporated to improve the conductivity and sulfur utilization of the Li-S electrode[20]. The majority of electrolyte design focused on the incorporation of co-solvent to reduce the dissolution capability of polysulfide, such as room-temperature ionic liquid (IL) [12, 23-25] and other organic co-solvent [6, 26].

The design of a variety of room temperature ILs has been performed in the Li-S batteries, because of their low flammability, negligible volatility, high thermal stability, acceptable conductivity, and a wide electrochemical potential window[27, 28]. Different ILs have been tried out by Park et al., with good analysis of the saturation solubility of Li_2S_x ($x=1-8$) in a series of ILs[23]. Other efforts have been put on using IL as co-solvent with organic solvent to achieve faster Li^+ ion transport property as well as the suppression of polysulfide dissolution[28-31]. Also, Zheng et al. has proposed that the improvement of performance is mainly attributed to IL-enhanced passivation film on the lithium anode surface[25]. In the

practical regime, high sulfur loading of the electrode is a key parameter to achieve the high energy density and low cost requirement[32]. The self-discharge process is controlled by the solubility of polysulfide in the electrolyte, the diffusion rate of polysulfide in the electrolyte, and passivation of SEI at Li electrode surface[33]. Although self-discharge performance is a critical property for energy storage system, it has just arouse people's attention very recently [19, 34-37] and the research of self-discharge phenomena is specially needed with systemic study of electrolyte composition.

Huge efforts have been put in the cell-level application of Li-S batteries with novel electrode design to further increase the sulfur loading of the electrode [21, 38-40], while very few have been put on the study of electrolyte composition with consideration of loading condition Li-S system, except for a few works focused on optimization of the electrolyte with the sulfur ratio[3, 41, 42]. The incorporation of IL or other organic solvents usually aims at reducing the polysulfide dissolution in electrolyte design. However, in Li-S system with higher loading, larger amount polysulfide dissolution is required in the limited volume of electrolyte for the reaction, and higher demand for ion transport capability is required. Therefore, the research in balancing between the reduction of polysulfide dissolution and improvement of ion transport capability is in urgent need.

The low Li^+ ion transport ability is commonly known as a limiting factor for the application of IL for electrolyte. The incorporation of organic solvent into IL electrolyte can dilution the high viscosity and the solvate IL can still serve as supporting Li- salts in the electrolyte[43, 44]. In this work, electrolyte design for Li-S batteries is performed by incorporating room-temperature IL as co-solvent, and the systematical optimization of the composition is performed with balancing between the solubility of polysulfide and the conductivity of Li^+ ion in the electrolyte. The improvement in over-all performance is evaluated with consideration of four critical aspects: cycling stability, rate capability, self-discharge prevention ability, as well as loading condition. Self-discharge performance is a most direct reflection of the reduction of polysulfide dissolution, a systematic study of self-discharge phenomena is performed with consideration of electrolyte composition. The self-discharge performance is systematical studied at different state of

charge (SOC) for the Li-S system, considering that the different solubility of polysulfide species (Li_2S_x , $x=1-8$) at each SOC may lead to performance changes. Furthermore, in order to minimize the effect of the SEI-passivation induced difference on Li electrode surface as discussed in Zheng et al.'s work[25], we specially perform the self-discharge test on fresh electrodes. For the over-all performance improvement with the series IL-electrolyte design, the electrochemical impedance spectroscopy (EIS), cycling test, and rate capability test are performed. It is found that the over-all performance needs to be optimized with the consideration of the reaction resistance, ion diffusion ability, and polysulfide solubility, etc. Also, when taking loading condition into consideration, a much less IL ratio is optimized in the electrolyte for higher sulfur loading Li-S batteries. Therefore, a general idea about the IL-electrolyte optimization method in Li-S batteries with consideration of over-all battery performance is conceived in this work, with loading condition of sulfur electrode specially addressed.

2. Material and methods

2.1 Materials

The micrometric sulfur powder is purchased from Mallinckrodt Company, and acetylene black (AB) is purchased from Denka Japan. The binders in this work is poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate (PEDOT/PSS), purchased from Sigma-Aldrich Inc. The electrolyte for cell testing is composed of 1 M bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in solvent composed of 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME 1:1 in volume) and IL with various ratios, and 1 wt% LiNO_3 (approximately 0.4M LiTFSI in electrolyte with pure IL). Also, polyethyleneglycol dimethyl ether (PEGDME) is used as solvent for comparison. The molecular weight of PEGDME is around 500 Dalton. The IL is 1-butyl-1-methyl-pyrrolidinium-bis(trifluoromethanesulfonyl)imide in this work, bought from Iolitec Inc.. All the other chemicals for the electrolyte are purchased from Sigma-Aldrich Inc.

2.2 Cathode fabrication

The micrometric sulfur powder is used as active material in this work. The PEDOT/PSS is first diluted in de-ionized water to achieve a 5 wt% ratio of PEDOT. Sulfur powder and AB are added into the binder-solvent solution. The weight ratio of these three components is: 50% sulfur, 10% PEDOT, 40% AB. The mixture is mixed by ball-milling method for overnight to obtain uniform slurry. The laminate is then made by coating the slurry on a 30- μm -thick battery-grade aluminum current collector with a Mitutoyo doctor blade and an Elcometer motorized film applicator. After the laminate is fully dried, it is further dried in a vacuum oven at 50 °C for overnight. Sulfur mass loading of electrode is about 0.4 mg cm^{-2} and 1.5 mg cm^{-2} .

2.3 Cell assembly and testing

Li-S batteries are tested with 2325-type coin cells (National Research Council Canada). The cells are assembled in an argon-filled glove box with oxygen content less than 0.1 ppm. The size of the sulfur electrode is 1/2-inch OD, and the size of the lithium metal counter electrode is 11/16-inch OD. The Li foil is purchased from FMC-Lithium Co.. The separator used is polypropylene film (Celgar 2400). Galvanostatic cycling tests are performed on a Maccor series 4000 cell tester (Maccor, Inc.). The cell voltage window is 1.5–2.6 V. 50 μL electrolyte is added for the low loading cell (0.4 mg cm^{-2}) and 70 μL electrolyte is added for the higher loading cell (1.5 mg cm^{-2}).

Two sets of self-discharge test procedures are designed for the fresh electrode and cycled electrode respectively. The “fresh electrode self-discharge test” is taken by doing the 60 hour self-discharge rest at 70% state of charge (SOC) in the first discharge process for a fresh cell. The “cycled electrode self-discharge test” is taken after 10 cycles at C/10 to get a relatively stable performance. Then the self-discharge test is performed by charging the cells to their fully charged state and then discharge to different SOC before performing the self-discharge test for 60 hours. The SOC state for self-discharge test is 100%SOC, 90%SOC, 50%SOC and 30%SOC, respectively. The discharge to precise SOC is controlled by the galvanostatic discharge time measured from the previous cycle. All cells are tested in the thermo chamber at 30°C. All experiments set-up has 2-3 samples for confirmation. The rate test for cells with

different IL-electrolyte is performed at C/10, C/5, C/3, C/2, 1C, 3C, 6C and C/10, with 5 cycles at each rate. The EIS is tested at 50% depth of discharge in the frequency 10 mHz~ 100 KHz.

3. Results and Discussion

3.1 The effect of IL-electrolyte on Self-discharge Performance in Li-S cell

Good self-discharge prevention ability is one of the most critical properties for all energy storage system, but the systematic mechanism study of self-discharge is scarcely mentioned in previous Li-S works. In Li-S batteries, the self-discharge phenomena takes place when polysulfide species are dissolved in the electrolyte, diffuse to the counter electrode and then react with Li metal. It is expected that the self-discharge capacity loss could be decreased when the polysulfide dissolution and transport ability in the electrolyte is reduced, or a physical barrier could be built at the Li-anode surface (e.g. SEI layer). The effect of IL-electrolyte on self-discharge performance is systematical studied at a series of SOC (100%SOC, 90%SOC, 50%SOC and 30%SOC) in the Li-S system, considering that the different solubility of polysulfide species (Li_2S_x , $x=1-8$) at each SOC may lead to performance changes. A series of IL-electrolyte is designed in this work which is composed of DOL/DME with different ratios of IL as co-solvents. Volume ratios between DOL/DME and IL are set to 1:0, 3:1, 1:1, 1:3, 0:1 and named as 0% IL, 25% IL, 50% IL, 75% IL and 100% IL, respectively. A high viscous PEGDME is used as solvent for reference. Commercialized PEDOT/PSS as conductive binder with micrometric sulfur is specially selected for this work, which has demonstrate good performance with all commercial materials and easy processing method[20].

Self-discharge test procedures are designed for the fresh electrode and cycled electrode respectively. For fresh electrode, the protocol is taken by setting a 60 hour rest at 70% state of charge (SOC) in the first discharge of a fresh electrode, as illustrated in Fig. 1(a), named as “fresh electrode self-discharge test”. The 70% SOC corresponds to the end of the first plateau, where the cell has the largest amount polysulfide dissolution before precipitation takes place. The sulfur composition here is a mixture

polysulfide of different chain lengths, with an average Li to S ratio around 2:4 (nominally Li_2S_4)[45]. The design of “fresh electrode self-discharge test” aims to minimize the effect of the SEI-passivation-induced difference on Li electrode surface during the self-discharge test. Although the SEI might still form from the reaction between the polysulfide/electrolyte and the Li metal during the short-time discharge from 100%SOC to 70%SOC, but since the continuous dissolution of Li exists on the fresh surface during discharge and the surface is kept refreshed; we suspect that the influence from electrolyte is minimal compared to the reaction between polysulfide and Li metal during 60-hour long reaction time. Therefore, the effect of self-discharge is firstly discussed in the “fresh electrode self-discharge test” with elimination of SEI-passivation-induced difference. The self-discharge capacity loss factor for the fresh electrode ($Q_{sd-fresh}$) is quantified by comparing the test cell with another cell that has the same cell configuration but without rest step during discharge.

$$Q_{sd-fresh} = 1 - \frac{C_a}{C_c}$$

C_a is the sum of discharge capacity of the cell with rest step; C_c is the discharge capacity of another cell without rest step during discharge.

For the cycled electrode, the test is performed after 10 cycles, named as “cycled electrode self-discharge test”. All cells are charged to their fully charged states, and then discharged to different SOC (100%SOC, 90%SOC, 50%SOC and 30%SOC) before the 60-hour self-discharge rest. The factor of self-discharge capacity loss ($Q_{sd-cycled}$) and the irreversible capacity loss (Q_{ir}) the cycled electrode are quantified. The self-discharge loss factor $Q_{sd-cycled}$, which shows the capability loss ratio during the self-discharge test, is calculated as:

$$Q_{sd-cycled} = 1 - \frac{C_a}{C_b}$$

C_a is the sum of discharge capacity before and after the 60 hours rest; C_b is the discharge capacity in the cycle prior to the self-discharge test.

The irreversible capacity loss factor Q_{ir} which shows the ratio of capacity that couldn't be recovered after self-discharge rest is calculated as:

$$Q_{ir} = 1 - \frac{C_f}{C_b}$$

C_f is the discharge capacity in the following cycle after the self-discharge test; C_b is the discharge capacity in the cycle prior to the self-discharge test.

The self-discharge capacity loss ratios $Q_{sd-fresh}$ during fresh electrode self-discharge test are plotted in the column chart in Fig. 1(b) with the series IL-electrolytes. We can see that with increasing ratio of IL in the electrolytes, from 0%IL up to 75%IL, the $Q_{sd-fresh}$ of the Li-S cells gradually decrease. Since the difference in the SEI at Li surface among cells with different electrolytes is minimal in fresh electrode, the decrease of self-discharge loss may mainly result from the reduction of the polysulfide dissolution and/or transport ability by the increase ratio of IL in the electrolyte. To demonstrate the reduction effect of polysulfide dissolution by IL incorporation, visualized experiment is performed in Fig. 2 by dissolving the same amount of polysulfide (Li_2S_6) in to 100%IL, 50%IL, 0%IL respectively. The dissolution ability of polysulfide decrease significantly with increasing ratio of IL, and solid phase species is observed in an electrolyte with higher IL ratio. The ability of polysulfide dissolution is determined by the solvation of Li^+ ions in polysulfide with electrolyte molecules[23]. Since the molecules solvation ability of Li^+ in the IL-electrolyte, selected in this work, is lower than the organic solvents, such as DOL/DME and PEGDME, a reduced solubility of polysulfide can be achieved in electrolytes with the presence of IL. The polysulfide solubility decreases with higher IL ratio in the electrolytes. Furthermore, a larger $Q_{sd-fresh}$ is observed in the high viscous PEGDME compared to 50%IL and 75%IL. The viscosity of PEGDME (8.9cP)[46] is similar with the 50% IL (7.41cP)[25], which indicates they have similar polysulfide transport/diffuse ability. If the transport ability plays a more important role, the PEGDME should not have that large self-

discharge loss in comparison. Hence, we believed the self-discharge loss is reduced by the less dissolution of polysulfide with higher ratio of IL in the electrolyte. Also, this dissolution difference will lead to variation in the total capacities, which are indicated by C_c and C_b in all three expressions. This capacity difference may process influence on the self-discharge data to some extent, which is mainly taken into consideration by the denominators C_c and C_b . But the influence is too large when the variation is huge, as in the case of self-discharge data of 100%IL. It does not follow the same trend with others in Fig. 1(b). This is because that although the discharged capacity loss during the 60-h rest is only 55.46 mAh/g for 100% IL (364.86 mAh/g for 0% IL), the denominator C_c of total discharge capacity without rest step is less than 400 mAh/g for 100% IL (more than 1100 mAh/g for 0% IL). Therefore a large relative ratio of self-discharge capacity is obtained for 100%IL[28].

The systematical study the self-discharge phenomenon is further performed at different SOC (100%SOC, 90%SOC, 50%SOC and 30%SOC) with cycled electrodes, and the self-discharge prevention effect among different IL-electrolytes is performed. The self-discharge capacity loss factor (Q_{sd}) and the irreversible capacity loss factor (Q_{ir}) are plotted in the column charts in Fig. 3. There are several phenomena worth discussing in these charts. First, at each SOC, the self-discharge capacity loss and the irreversible capacity loss of the cycled cells with each IL-electrolyte follow the similar trend as the fresh electrode self-discharge test in Fig. 1(b). The cells with the 0%IL and 25%IL show largest self-discharge loss, followed by PEGDME; and the 50%IL and 75%IL show much smaller self-discharge loss. This is the result of the reduced polysulfide dissolution ability with increasing IL ratio in electrolytes, from 0%IL to 75%IL. With the increasing of IL ratio in the electrolytes, gradually stronger “solvent effect” and the reduction in polysulfide dissolution are resulted [43, 44]. Less side reactions with lithium and less shuttle effect can exist when the polysulfide is in the solvated state than the dissolved state [44]. Therefore, more stabilized polysulfide can be achieved by the solvent molecules in the electrolytes in high ratio IL-electrolytes and a much improved self-discharge performance is resulted. Also, the 75%IL show much less self-discharge capacity loss in self-discharge test of the cycled electrode than the test for the fresh

electrode. This is because in cycled self-discharge test, a much more stable passivation layer is formed on the lithium metal surface in 75%IL compared to others during the initial 10 cycles, the inhibition of the redox shuttle is resulted, and a much improved self-discharge prevention capability is observed [43]. Second, when comparing the capacity loss of self-discharge test for fresh electrode (70%SOC) and the test for cycled electrode (90%SOC), we can find that the self-discharge capacity loss ratio is very similar for each electrolyte. Third, for each IL-electrolyte, the self-discharge loss decreases with lower SOC, except for 50%IL and 75%IL. This is because that the majority of polysulfide species changes in Li-S cell at different SOC and the dissolution ability of polysulfide varies according to the changes of the chain length of polysulfide[23, 24, 44]. At 50%SOC and 30%SOC, the polysulfide gradually precipitated as solid phase because of the smaller solubility of the shorter chain polysulfide (Li_2S_x , $x=1-4$). From higher SOC to 50%SOC and 30%SOC, the short chain polysulfide gradually precipitated as $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}_2$ on the cathode surface, and the remaining amount of polysulfide in the electrolyte decrease. Therefore, a much smaller self-discharge loss is observed at these two SOC. Fourth, an interesting phenomenon of capacity recovery is observed with some of the electrolyte (50%IL, 75%IL and PEGDME) at 50% SOC or 30%SOC. This capacity recovery may come from the re-activation of some isolated solid phase lithium sulfide (Li_2S). When viscosity of the electrolyte is high, some of the polysulfide and sulfur ($\text{Li}_2\text{S}/\text{S}_8$) has more chance of being electronically isolated in the electrode and being kept away from sufficient charge/discharge reaction. Especially in the case of solvate ILs, when the solubility of polysulfide are low, the polysulfide are supposed to remain trapped and predominantly react in solid-state [44]. The isolation of active material is part of the reason for the capacity decay and insufficient sulfur usage in Li-S batteries. During the 60-hour self-discharge rest, the soluble polysulfide has enough time to penetrate and react with the isolated $\text{Li}_2\text{S}/\text{S}_8$ and the sulfur species with higher solubility is achieved. Therefore, capacity recovery is observed in the self-discharge process. This phenomenon is more dominate when the viscosity of the electrolyte is high (75%IL than 50%IL and PEGDME). Fifth, comparing Fig. 3(a) and (b), it is found that irreversible capacity loss contributed to most of the self-discharge capacity, which means that the elimination of self-discharge via electrolyte design can greatly prohibit the active material loss.

In all, the 75%IL shows the best self-discharge prevention ability among all IL-electrolytes followed by 50%IL. Detailed mechanism study of the self-discharge performance is performed, which stresses the reduction of polysulfide dissolution by IL. Some capacity recovery is observed during the self-discharge process with 75%IL and 50%IL. It gives further evidence of the improvement in incorporating the IL in Li-S electrolyte, and necessity in the electrolyte optimization to achieve good over-all performance.

3.2 Cycling Performance and Rate-capability of Li-S cell with IL-electrolyte

In the previous section, the effect of electrolyte in improving self-discharge performance is discussed and the optimized composition ratio of IL in the electrolyte is achieved. Further efforts are performed in IL-electrolyte optimization with consideration of the over-all performance, including cycling and rate performance. Fig. 4(a) is the cycling performance of Li-S cells with different IL-electrolytes. Among all, the cell with 0%IL shows the highest discharge capacity (1400 mAh g^{-1}) in the first cycle, but its capacity shows rapidest decay in the following cycles. The cell with 75%IL shows the most stable performance with capacity of 1000 mAh g^{-1} after 50 cycles. The cell with 50%IL shows the second best cycling stability, and the 25%IL shows much faster capacity decay, similar as 0%IL. The difference in reaction kinetics among different electrolytes can be further analyzed through voltage profiles, shown in Fig. 4(b). Smaller over-potential is observed in the electrolyte with less IL addition (0%IL, 25%IL and 50%IL). This may partially result from the weaker “solvent effect” with less IL at the present, which is caused by the difference in polysulfide solubility [43, 44]. Faster reaction kinetics takes place in cells with 0%IL than 25%IL and 50%IL. The electrochemical impedance spectroscopy (EIS) is also conducted for the cells with different electrolytes to examine reaction kinetics. As shown in Fig. S1, the impedance study clearly shows that the reaction resistance increase with IL ratio and is consistence with the voltage profile analysis.

The increase in IL ratio can greatly improve the cycling stability via suppress of polysulfide dissolution; the increase in viscosity and decrease in ion conductivity may affect the reaction kinetics and the rate

performance, as plotted in Fig. 5. As measured in the previous study[25], the viscosities of IL-electrolyte increase with the increase of IL ratio, which are 1.56 cp, 3.07 cp, 7.41 cp, 25.3 cp, 118.6 cp for 0%IL, 25%IL, 50%IL, 75%IL and 100%IL; and the conductivities are 13.21, 13.82, 10.40, 4.98, 1.56 mS cm⁻¹, respectively. Excellent rate performance is achieved in x%IL (x= 25-75) with capacity around 800 mAh g⁻¹ at C/2 and 600 mAh g⁻¹ at 1C. But the 75%IL can provide efficient reaction when the cycling rate increases further to 3C and 6C. This further demonstrates that the conductivity is one of the most deciding factors for the reaction kinetics. The reaction kinetics for 0%IL is fast as well, but much faster capacity decay is observed in both Fig. 4(a) and (b), which is the result of high polysulfide dissolution.

The PEGDME shows a faster decay and a poor rate performance with less than 400 mAh g⁻¹ at C/2. This indicates that in PEGDME, due to the high viscosity and slow ion transportation, the Li-ion diffusion and migration is not fast enough to facilitate the reaction at rate higher than C/2. However, as checked from reference data source, the viscosity of PEGDME is very near to the 50%IL, while 50%IL can perform well even at 6C. Therefore the high viscosity does not necessarily lead to the poor rate performance. With the co-solvent of x%IL (x=25-75), although a high viscosity is inevitable, the high demand for Li-ion transportation can be compensated through the good ionic transport property, so the good rate performance can be ensured. The overall trend of capacity loss in Fig. 5a is very similar as the trend in Fig. 4 with minor departure. And the minor difference may result from the high rate test, during which some of the systems can't provide efficient charge transport to support the high rate reaction kinetic and the higher capacity loss is resulted. This phenomenon is very prominence in the case of Li-S cell with PEGDME electrolyte. The cells cycled at 1C can also be used to well demonstrate the high rate performance of the electrolytes of x%IL (x=0-75) compared to PEGDME, shown in Fig. 5(b). The cycling became stable after the initial drop due to the high rate cycling.

Therefore, although the best cycling performance at lower C-rate and self-discharge prevention ability is obtained with 75%IL, the optimization of the IL-electrolyte composition under certain circumstance

should be trade-off regarding to the long term cycling performance and the cycling rate required. In the circumstance of extreme high rate (higher than 1C) is required, the 50%IL will be better choice.

3.3 Further Optimization of IL-electrolyte with Loading Consideration

High sulfur loading design of the electrode has drew most attention in current Li-S battery researches, but the electrolyte design for Li-S system with consideration of loading condition has been scarcely mentioned. The incorporation of IL or other organic solvents usually aims at reducing the polysulfide dissolution. However, in Li-S system with higher loading, larger amount polysulfide dissolution in the limited volume of electrolyte and faster reaction kinetics are required for the reaction, therefore the balancing between this polysulfide dissolution reduction and ion transport capability need to be re-evaluated. In this work, the discussion of IL-electrolyte is performed with 1.5mg cm^{-2} sulfur loading of Li-S batteries, three times of the loading of the previous section. In the Li-S cells with higher sulfur loading, higher requirement exists for reaction kinetics, such as the ion transport capability, etc. In Fig. 6, cells with 0%IL and 25%IL show the highest specific capacity of over 1000 mAh g^{-1} in the first two cycles, while cells with 50%IL and 75%IL show lower initial capacity. In the long term cycling, the cell with 50%IL shows the best cycling stability followed by cell with 25%IL. The specific capacity for cell with 75%IL is relatively low. This trend is different from the previous case with the low loading (Fig. 4), in which 75%IL shows the best performance. With increased sulfur loading, the current density is higher at a given C-rates for Li-S cells and the charge transport capability of the electrolyte will become the limit for the cell performance. The optimized composition should be somewhere between 25% IL and 50 %IL for the cells with higher loading. Therefore, the optimal performance needed to make a good trade-off between ionic conductivity of electrolyte and solubility of polysulfide.

In this way, the optimal IL-electrolyte is a complicated balance not only on the polysulfide dissolution, ion transportation, but also on sulfur loading condition of the electrode and the kinetics requirement of the cell operation. This work provides insights into the effect of the IL as Li-S co-solvent, and guides the development of electrolyte for Li-S batteries.

4. Conclusion

In this work, the IL is incorporated as co-solvent in electrolyte to achieve good overall performance of the Li-S batteries, including the self-discharge prevention ability, the cycling stability and the rate capability, with the consideration of loading condition. The addition of IL in electrolyte can greatly improve the stabilization of the polysulfide via solvent effect; the side reactions and shuttle effect in Li-S cells are reduced. The reduction of polysulfide dissolution and the improved stabilization in high IL ratio electrolyte leads to improvements in self-discharge prevention ability, and noticeable capacity recovery is observed in high IL ratio electrolyte in self-discharge test at low SOC. With consideration of over-all performance, an optimized IL-electrolyte composition is achieved to maximize self-discharge elimination performance, cycling performance and rate capability. This optimized composition of IL-electrolyte has been found to highly depend on the application circumstance, such as different rate requirement and the loading requirement, due to trade off between polysulfide solubility, ion transport capability and the reaction kinetics. In this way, this work can provide useful insights into the effect of the IL as co-solvent, and give important guidelines to the development of electrolyte for Li-S batteries.

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Figure captions:

Fig. 1 (a) The schematic diagram of self-discharge test. (b) The self-discharge capacity loss ratio during the fresh electrode self-discharge tests.

Fig. 2 The photo images of the Li_2S_6 dissolved in (a)100%IL, (b)50%IL, (c)0%IL; The microscope images of the solution (d)100%IL, (e)50%IL, (f)0%IL.

Fig. 3 The self-discharge capacity loss factor (Q_{sd}) (a) and irreversible capacity loss factor (Q_{ir}) (b) for cells with 0% IL, 25% IL, 50% IL, 75% IL and 100% IL electrolytes at 100%SOC, 90%SOC, 50%SOC and 30%SOC during the self-discharge test for the cycled electrode.

Fig. 4 Cycling performance (a) and voltage profile (b) of the Li-S cells with different electrolytes.

Fig. 5 Rate performance (a) and cycling performance at 1C (b) of the Li-S cells with different electrolytes.

Fig. 6 Cycling performance of higher loading Li-S batteries with the different electrolytes.

Fig. 1

Fig. 2

Fig.3

Fig. 4

Fig. 5

Fig. 6