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Effects of imidazolium salts on discharge performance of rechargeable lithium–sulfur cells containing organic solvent electrolytes

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Abstract

In this study, lithium–sulfur (Li–S) cells using mixed imidazolium salts and lithium salts for the electrolytes are investigated as a means to improve discharge performance and cycle-life characteristics. By introducing 5 or 10 vol.% of imidazolium salt into the electrolytes containing lithium salts, the Li–S cells give a greatly enhanced discharge capacity of >600 mAh g^{-1} up to the 100th charge–discharge cycle. Furthermore, both the discharge capacity and the average discharge voltage at a high discharge rate, as well as the low-temperature performance, are all dramatically improved when compared with those of conventional cells using organic electrolyte solvents and lithium salts.

Keywords: Lithium–sulfur cells; Imidazolium salts; Electrolytes; Discharge capacity; Average discharge voltage; Low-temperature performance

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1. Introduction

The development of portable electronic devices has led to a corresponding increase in the demand for secondary batteries having both a lighter weight and a higher capacity. A lithium–sulfur (Li–S) battery with a positive electrode made of sulfur-based compounds is one of the most promising approaches to satisfying these demands. An ambient-temperature lithium–sulfur cell has attracted the attention of many research and development groups due to its inherently high specific energy [1–12]. The cell contains a sulfur cathode, a lithium metal anode and an electrolyte consisting of organic solvents and lithium salts. In terms of specific energy, lithium–sulfur batteries are the most attractive candidates among the batteries under development because lithium has a specific capacity of 3830 mAh g^{-1}, and sulfur has a specific capacity of 1675 mAh g^{-1}, assuming that sulfur is fully reduced to sulfide ion (S^{2-}) during discharge. Furthermore, the sulfur-based compounds are environmentally friendly and less costly than other materials.

The Li–S cells operate via a redox reaction mechanism that is distinctly different from that of the commercial lithium-ion cells, in which the redox reaction mechanism is based on an intercalation–de-intercalation of Li-ions. In Li–S cells, the lithium metal is oxidized and the elemental sulfur reacts with the Li ions during the discharge process, i.e.,

$$\mathrm{Li} \rightarrow \mathrm{Li}^+ + e^- \qquad (1)$$

$$S_8 + 16\mathrm{Li}^+ + e^- \rightarrow 8\mathrm{Li}_2S \qquad (2)$$

The reverse reaction occurs during the charge process. The electrochemical redox reaction of sulfur in an organic electrolyte is very complicated and the reaction mechanism is still controversial [13,14]. For example, many intermediates such as Li_2S_8, Li_2S_4, Li_2S_2, and Li_2S, exist during the redox process.

Although Li–S cells have many advantages, they also suffer from the serious problem of low sulfur utilization, that resuls in low discharge capacity. The sulfur utilization is referred to as a ratio of the amount of sulfur involved in the

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electrochemical redox reaction of the battery to the amount of the total injected sulfur. The sulfur utilization is limited by the insulating nature of sulfur and Li_2S. Accordingly, unless the electrolyte is suitable, the electrochemically reduced products of the sulfur (e.g., Li_2S_2 or Li_2S) are precipitated, and thus do not participate in further electrochemical reactions.

Recently, Chu [15] showed that Li–S cells have a high capacity during the first discharge cycle at a high temperature. On the other hand, Li–S cells show a poor cycle-life due to the loss of active material by a diffusion of soluble polysulfide into the electrolyte solution. Cycle-life performance is also strongly influenced by degradation and non-stability of the lithium metal electrode. Two types of liquid electrolyte solvents are most widely used. One is a primary solvent with the general formula $R_1(CH_2CH_2O)_nR_2$, where n ranges between 2 and 10, R_1 and R_2 are different or identical alkyl or alkoxy groups, and the other is a secondary solvent with a donor number of 15 or more [16]. A multi-component organic solvent has been studied to obtain high discharge capacity and high discharge voltage [11]. Despite this form of approach towards the development of an optimum electrolyte, lithium–sulfur batteries have failed to obtain a satisfactory capacity, a good rate capability, and acceptable cycle-life characteristics.

According to current research, an electrolyte of salts and a solvent based on a cyclic or non-cyclic carbonate are anticipated to provide lithium-ion batteries with a high ionic conductivity and a high oxidation potential. In these batteries, lithium salts such as $LiClO_4$, $LiBF_4$ or $LiPF_6$ are generally used. Recently, however, lithium salts with of triflate, imide or methide-based anions have been considered as a means to improve cell performance [17]. The aforementioned carbonate electrolyte enables lithium ion batteries to deliver a good performance, but causes adverse effects when used in lithium–sulfur batteries. The latter behaviour is due to the electrochemical or chemical reaction of the polysulfide being very unstable in a carbonate-based electrolyte, To be suitable for lithium–sulfur batteries the electrolyte must meet the following criteria: (i) chemical stability (i.e., no reactivity) with polysulfide; (ii) high solubility of polysulfide; (iii) low reactivity with lithium metal.

Attention has also been drawn to imidazolium cation-based salts with that take the form of liquid phase at room temperature. These belong to a class of ‘ionic liquids’ and are cation-based non-aqueous electrolyte salts which are capable of being applied to electrical storage devices such as a super-capacitors and batteries [18]. As disclosed in a US patent [19], a non-aqueous electrolyte containing a liquid salt such as 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIPF_6$) is useful in a carbon-based electrochemical double-layer capacitors as it has a high concentration (>1 M), high thermal stability (>100 °C), and a large capacitance (>100 F g^{-1}).

Furthermore, an electrolyte solution in which liquid-phase salts are mixed with various carbonate-based organic solvents for application in lithium-ion batteries has been reported [19,20]. The electrolyte shows improved characteristics such as high ion conductivity (>60 mS cm^{-1}), a wide window of electrochemical stability (>4 V at 20 $\mu A\ cm^{-2}$), and high salt concentration (>3 M). When electrochemical capacitors or batteries have used electrolytes including the above-mentioned liquid-phase salts, the capacitance and the specific energy, respectively, have been improved [21].

Despite the fact that battery performance depends on the type and composition of the salt and organic solvent used in the electrolyte, none of the above-mentioned patents and articles has disclosed an optimum species and composition of the salts and organic solvents for lithium–sulfur batteries. In particular, the use of imidazolium salts have not been developed. Accordingly, this study examines the effect of adding imidazolium salts (1-ethyl-3-methyl-imidazolium bis(perfluoroethyl sulfonyl) imide (EMIBeti), 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BMIPF_6$)) to the electrolyte. In order to evaluate the resulting cell performance, the discharge capacity, the charge–discharge cycle characteristics, the high-rate capability, and the behaviour at low temperature have been investigated.

2. Experimental

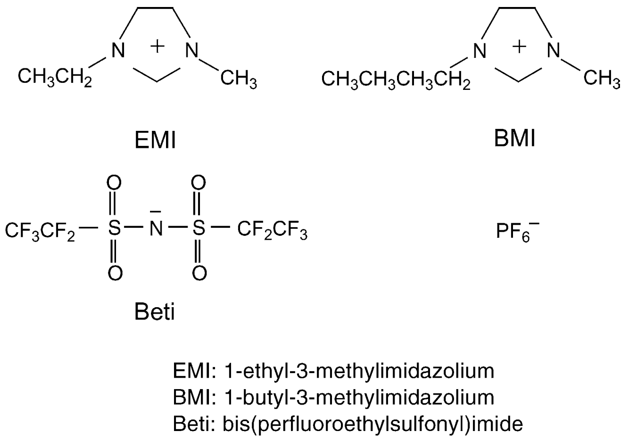
2.1. Preparation of Li–S cells containing organic electrolytes

67.5 wt.% elemental sulfur, 11.4 wt.% Ketjen black as a conductive material, and 21.1 wt.% polyethylene oxide as a binder were mixed in an acetonitrile solvent to form a slurry for the positive electrode of a lithium–sulfur cell. The resulting slurry was coated on a carbon-coated aluminium current-collector.

The slurrly-coated current-collector was dried in a vacuum oven at 60 °C for over 12 h. From this, a positive electrode with a current density of 2 mAh cm^{-2} dimensions of 25 mm × 50 mm was prepared. The negative electrode was a lithium metal foil with a thickness of 200 μm. The positive electrode, the vacuum dried separator, and the negative electrode were laminated and placed in a pouch into which the electrolyte was infected, namely, 0.5 M $LiSO_3CF_3$ (LiTf: lithium triflate) or 0.5 M $LiPF_6$ in a dimethoxyethane (DME)/dioxolane (DOX) (8/2, v/v) solvent. To this electrolyte, EMIBeti or $BMIPF_6$ (Covalent Associates, Inc.) was introduced. The imidazolium salts are cation or anion species, as shown in Scheme 1. Finally, the pouch was sealed to form the test cell.

2.2. Evaluation of cycle-life characteristics of Li–S cells

The cycle-life characteristics of the test cells were evaluated at a room temperature. The discharging and charging behaviour was examined with a Maccor battery tester. The



Scheme 1. Chemical structure of imidazolium salts.

cell was initially discharged for one cycle at a current density of 1.0 mA cm^{-2}, since the test cell was in a fully-charged state immediately after assembly. This current density is equivalent to the 0.5*C* rate when based on the theoretical capacity of sulfur. Charge and discharge tests were then carried out between 1.5 and 2.8 V versus Li/Li$^+$ at a constant current of 1.0 mA cm^{-2} (0.5*C* rate) for 100 cycles.

2.3. Evaluation of discharging characteristics of Li–S cells

Evolution of the charge and discharge characteristics was performed via the same procedure as that used for cycle-life studies, except that the charge and discharge tests were carried out between 1.8 and 2.8 V versus Li/Li$^+$ and discharge current densities of 1.0 and 2.0 mA cm^{-2} were employed. The specific energy (mWh g^{-1}) was calculated by measuring the average discharge voltage and discharge capacity. The average discharge voltage is defined as the value where 50% of the total discharge capacity has been delivered, as shown later in Fig. 3. The specific energy was determined by multiplying the average discharge voltage by the discharge capacity.

2.4. Evaluation of cell performance at low temperature

The low-temperature performance of the cell was evaluated at −10 and −20 °C. The cell was initially discharged for one cycle at 1.0 mA cm^{-2}. This discharge capacity was defined as the standard value at room temperature. Thereafter, the charge process was performed at 1.0 mA cm^{-2} at room temperature, followed by transferring the test cells to a low temperature of −10 or −20 °C, leaving them for 2 h, and then discharging at 1.0 mA cm^{-2}. The cell performance is reported as the ratio (as a percentage) of the resulting discharge capacity at low temperature to the standard discharge capacity.

3. Results and discussion

On discharging (i.e., electrochemical reduction), the sulfur–sulfur bonds in the positive active material of the Li–S cell are cleaved and this results, in a decrease in the oxidation number of the sulfur. On recharging (i.e., electrochemical oxidation), the sulfur–sulfur bonds are reformed, and thus increase the oxidation number of the sulfur. The electrical energy is stored in the battery as chemical energy during the charging process and is converted into electrical energy during discharge.

To examine the effect of imidazolium salts on the discharge performance of Li–S cells, the salts were introduced to a 0.5 M LiTf in DME/DOX (8/2, v/v) solution. The discharge capacity versus cycle number relationship for cells containing different amounts of EMIBeti is given in Fig. 1. Each test cell shows a gradual increase in capacity up to around the 10th cycle. This probably can be explained by the fact that the electrochemical redox reaction of sulfur has an activation step due to a gradual phase change from a solid state to the dissolved polysulfide state.

On the first cycle, a test cell without EMIBeti salt exhibits a discharge capacity of 850 mAh g^{-1}-sulfur. This value is about 50% of the theoretical capacity, and is quite similar to that repeated elsewhere [15]. During the early stages of cycling, the discharge capacities of cells containing 5 or 10 vol.% EMIBeti salt are slightly lower than that of the cell without EMIBeti. On the other hand, the capacity of the cell without EMIBeti rapidly decreased after the 30th cycle, whereas the capacities of the cells with 5 or 10% EMIBeti slowly decreased at approximately the same rate up to the 100th cycle. Thus, the stability of the discharge capacity is greatly improved by the addition of 5 or 10% EMIBeti.

The origin of the improvement in cell performance cannot be easily explained because charge–discharge cycle characteristics are dependent on many factors (e.g., interaction between polysulfide and imidazolium salts, chemical and physical stability of the sulfur and lithium electrode, ion conduc-

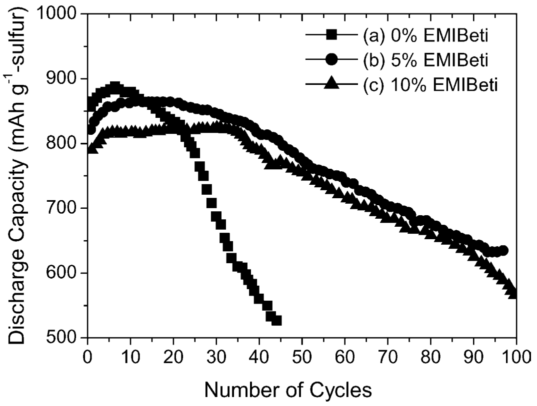


Fig. 1. Discharge capacity vs. cycle number for Li–S cells using organic electrolytes with salts of: (a) 0.5 M $LiSO_3CF_3$; (b) 0.5 M $LiSO_3CF_3$ + 5% EMIBeti; (c) 0.5 M $LiSO_3CF_3$ + 10% EMIBeti.

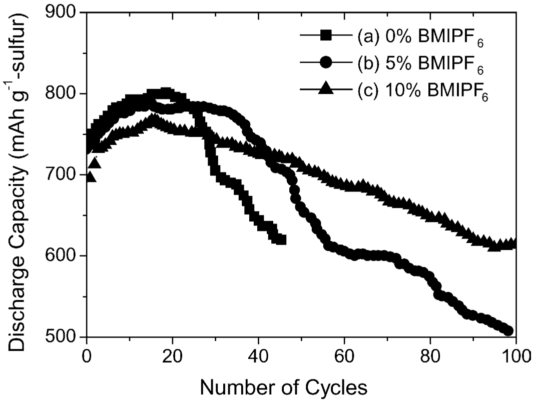


Fig. 2. Discharge capacity vs. cycle number for Li–S cells using organic electrolytes with salts of: (a) 0.5 M $LiPF_6$; (b) 0.5 M $LiPF_6$ + 5% BMI PF_6; (c) 0.5 M $LiPF_6$ + 10% BMI PF_6.

tivity of the electrolyte, electrochemical reaction kinetics). One of the primary reasons may be enhancement in the electrochemical reaction of the polysulfide by the large volume size of the imidazolium cations. This size effect can influence both ion conductivity and electrochemical stability [20,22]. Another possibility is related to the stability of the lithium surface during the redox reaction. It has been previously reported that salts having an imide-type anion (e.g., TFSI (bis(trifluoromethylsulfonyl)imide), Beti) give better cycle-life than triflate anions [23].

The discharge capacities of test cells containing 0.5 M $LiPF_6$ mixed with a $BMIPF_6$ salt are presented in Fig. 2. Up to the 100th cycle, the cells containing 5 or 10 vol.% $BMIPF_6$ salt show less decline in capacity than the cell without $BMIPF_6$ salt. The capacity of the latter decreases rapidly after the 30th cycle. Furthermore, the discharge capacity of the cell containing 10% $BMIPF_6$ at the 100th cycle is higher than that of the cell with 5% $BMIPF_6$. Thus, the stability of the discharge capacity is improved by the addition of 10% $BMIPF_6$.

To evaluate the dependence of discharge performance on discharge rate, tests were performed at discharge rates of 1.0 and 2.0 mA cm^{-2}. The corresponding data for the 15th cycle, at which the cell performance reaches a steady state after the activation step of the electrochemical reaction of the sulfur, are given in Figs. 3 and 4. These are quite typical curves for Li–S cells, which have a voltage plateau at about 2.0 V. The average discharge voltage and specific density of cells with 5 or 10% EMIBeti are superior to those of the cell without EMIBeti salt. The improved values of both parameters are further enhanced with increase in the discharge rate, i.e., 2.0 mA cm^{-2} (1.0*C*-rate). Therefore, cells containing imidazolium salts appears to have a better rate capability.

Furthermore, changes in the discharge characteristics with different electrolytes are more prominent at the higher discharge rate. At 1.0 mA cm^{-2}, the specific density of the cell containing 10% EMIBeti is similar to that of the cell with 5% EMIBeti, whereas at 2.0 mA cm^{-2} the specific density of the cell with 10% EMIBeti is clearly superior.

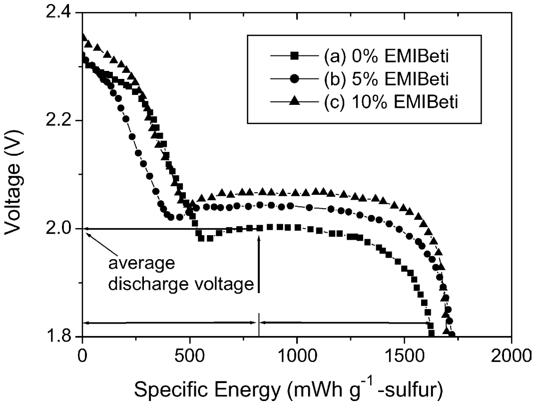


Fig. 3. Specific energy vs. voltage for Li–S cells on 15th cycle at discharge rate of 1.0 mA cm^{-2} using organic electrolytes with salts of: (a) 0.5 M $LiSO_3CF_3$; (b) 0.5 M $LiSO_3CF_3$ + 5% EMIBeti; (c) 0.5 M $LiSO_3CF_3$ + 10% EMIBeti.

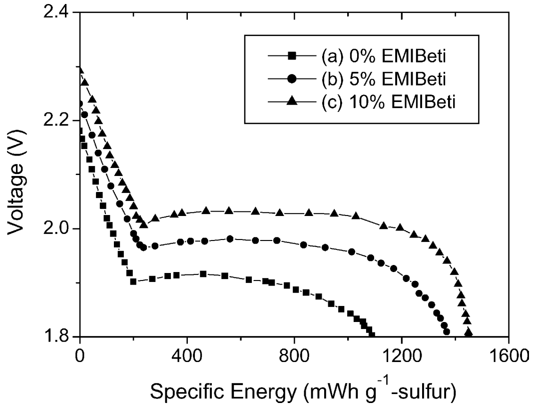


Fig. 4. Specific energy vs. voltage for Li–S cells on 15th cycle at discharge rate of 2.0 mA cm^{-2} using organic electrolytes with salts of: (a) 0.5 M $LiSO_3CF_3$; (b) 0.5 M $LiSO_3CF_3$ + 5% EMIBeti; (c) 0.5 M $LiSO_3CF_3$ + 10% EMIBeti.

The discharge capacities of Li–S cells on the 15th cycle are presented as a function of EMIBeti salt content in Fig. 5. At discharge rates of 0.5 and 1.0*C*, the cell with 5 wt.% salt content delivers greater capacity. Above 10 wt.% content, the

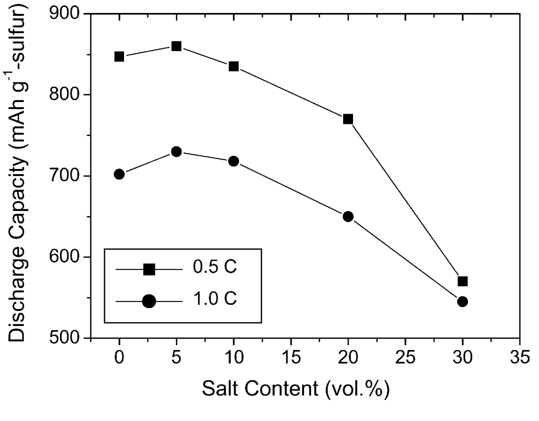


Fig. 5. Discharge capacity vs. content of EMIBeti salt for Li–S cells on 15th cycle using organic electrolytes and at different discharge rates.

Table 1
Ratio (%) of discharge capacity of Li–S cells with different salt compositions at −10 and −20 °C to discharge capacity measured at room temperature

Temperature (°C)	0.5 M $LiCF_3SO_3$	0.5 M $LiCF_3SO_3$ + 5% EMIBeti	0.5 M $LiCF_3SO_3$ + 10% EMIBeti	0.5 M $LiCF_3SO_3$ + 20% EMIBeti
−10	74	80	83	81
−20	58	67	70	43

cells show decreased capacity with increasing salt content. This behaviour can be explained by the slow and irreversible electrochemical redox reaction of polysulfide. The redox reaction is dependent on the ionic conductivity and viscosity of the electrolyte solution. In this case, the ion conductivity is changed only slightly by a change in the salt content [3]. By contrast, the viscosity is increased proportionally with the salt content. As a result, the viscosity is a more critical factor for obtaining a high discharge capacity. Consequently, a salt content of 5 or 10 wt.% is required for a high discharge capacity.

The average discharge voltage as a function of EMIBeti salt content at different discharge rates is presented in Fig. 6. The average discharge voltage gradually increases with increase in salt content up to 20 vol.%, but decreases at 30 vol.%. The average discharge voltage is probably inversely proportional to the internal resistance of the test cells, which is decreased by introducing the imidazolium salts. The influence of EMIBeti content on the average discharge voltage is rather small compared with the influence on capacity.

Data from discharge tests performed at −10 and −20 °C are summarized in Table 1. A cell without EMIBeti yields 74 and 58% of the standard discharge capacity at −10 and −20 °C, respectively. By contrast, a cell with 5% EMIBeti show better performance, namely, a capacity of 80 and 67% at −10 and −20 °C, respectively. On increasing the salt content to 10%, the capacity value is slightly increased. These improved discharge capacities can be attributed to the superior ionic conductivity of the electrolyte on introducing the imidazolium salt. A cell with 20% EMIBeti experiences a rather large decrease in capacity to 44% at −20 °C. This can be related to the phase change of the EMIBeti itself from a liquid to a solid at this temperature, because the salt has a melting point of −12 °C [24].

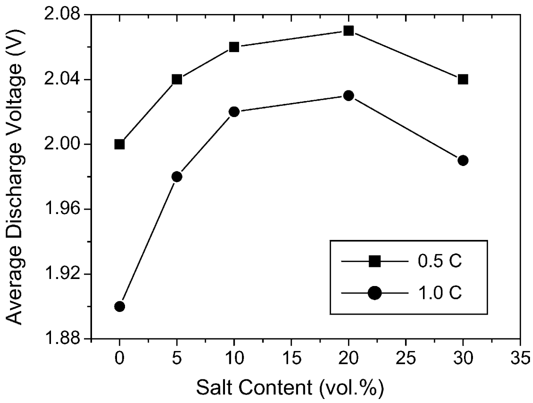


Fig. 6. Average discharge voltage vs. content of EMIBeti salt for Li–S cells on 15th cycle using organic electrolytes and at different discharge rates.

4. Conclusions

The efficacy of adding imidazolium salts to an electrolyte in order to improve the performance of Li–S cells has been investigated. The discharge capacity after the 100th cycle is >600 mAh g^{-1}, in the presence of 5 or 10% EMIBeti. This performance is superior to that of conventional cells without EMIBeti that suffer a drastically decreased discharge capacity of 550 mAh g^{-1} on the 40th cycle. The improved charge–discharge cycle characteristics can be related to enhancement of the electrochemical reaction of the polysulfide by the imidazolium cation and improved stability of the surface morphology of the lithium negative electrode.

For discharge performance at a high rate, the addition of EMIBeti salt causes a prominent enhancement of both the discharge capacity and the average discharge voltage. Cells containing 10% EMIBeti salt display the best discharge capacity. Cell performance at −10 and −20 °C is also improved by introducing EMIBeti salt with 10% EMIBeti, for example, the discharge capacity ratio at −20 °C is increased from 58 to 70%.

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