RAPID COMMUNICATION

Concentrated dual-salt electrolytes for improving the cycling stability of lithium metal anodes*

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Lithium (Li) metal is an ideal anode material for rechargeable Li batteries, due to its high theoretical specific capacity (3860 mAh/g), low density (0.534 g/cm^3), and low negative electrochemical potential (−3.040 V vs. standard hydrogen electrode). In this work, the concentrated electrolytes with dual salts, composed of Li[N(SO_2F)$_2$] (LiFSI) and Li[N(SO_2CF_3)$_2$] (LiTFSI) were studied. In this dual-salt system, the capacity retention can even be maintained at 95.7% after 100 cycles in Li|$LiFePO_4$ cells. A Li|Li cell can be cycled at 0.5 mA/cm^2 for more than 600 h, and a Li|Cu cell can be cycled at 0.5 mA/cm^2 for more than 200 cycles with a high average Coulombi efficiency of 99%. These results show that the concentrated dual-salt electrolytes exhibit superior electrochemical performance and would be a promising candidate for application in rechargeable Li batteries.

Keywords: lithium metal rechargeable batteries, dual-salt electrolyte, concentrated electrolytes

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1. Introduction

Lithium (Li) metal as an anode material for rechargeable Li batteries has captured considerable attention due to its high theoretical specific capacity (3860 mAh/g), low density (0.534 g/cm^3), and low negative electrochemical potential (−3.040 V vs. standard hydrogen electrode).[1–3] For the reason that a Li metal anode can achieve higher energy density than graphite as the anode,[4] especially for Li–air and Li–sulfur batteries,[5] which have been intensively revived in recent years. However, some problems including Li dendrite growth and low Coulombic efficiency (CE) during continuous charge/discharge processes urgently need to be overcome when using a Li metal anode for rechargeable Li batteries.

It has been demonstrated that the electrolyte plays an important role in improving the cycling stability of a Li metal anode.[6] Li metal reacts with nearly all dipolar aprotic organic solvents (e.g., ethers and carbonates), and produces serious side reaction products. It is already known that ethers (e.g., 1,3-dioxolane (DOL), dimethyl ether (DME)) display better compatibility with Li metal, when compared with carbonates (e.g., dimethyl carbonate (DMC), ethylene carbonate (EC), diethyl carbonate (DEC)). Aurbach *et al.*[7] indicated that $LiAsF_6$-DOL electrolyte could improve the cycling efficiency of Li metal and long-term cycle life up to 300 cycles under a small current density of 0.3 mA/cm^2. This would be attributed to good elasticity, stabilized organic polymer film SEI (Solid Electrolyte Interphase) on the surface of Li metal via a reduction of DOL during charge/discharge processes. Hence, Li dendrites could be inhibited and cycling efficiency could be enhanced. However, the electrolyte salt $LiAsF_6$ is toxic, and the solvent DOL is not so stable, which make the battery easy to go to failure eventually.

Recently, we found a new class of 'Solvent-in-Salt' electrolyte with highly concentrated Li[N(SO_2CF_3)$_2$] (LiTFSI) in DOL/DME = 1:1 (by volume) electrolytes,[8] which can improve the cycling stability of Li metal and suppress the shuttle effect in Li–S batteries. Furthermore, a dual-salt electrolyte (Li[N(SO_2F)$_2$] (LiFSI)-LiTFSI/DOL-DME) exhibits an effective protection of a unique SEI layer and remarkably enhanced CE (ca. 99%) as indicated by Yang *et al.*[9] However, only 120 cycles are reported. More recently, Zhou *et al.*[10] reported that a new type of concentrated electrolyte composed of Li[(FSO_2)N(SO_2CF_3)] (LiFTFSI), LiFSI, and ether solvents can improve the cycling stability of Li metal and inhibit Li-metal dendritic growth. These results indicated that concentrated dual-salt electrolytes have a promising application for improving the CE of Li metal and inhibiting dendritic Li growth.

Here, we report the concentrated dual-salt electrolytes composed of LiFSI and LiTFSI for improving the cycling stability of Li metal anodes (see Fig. 1). This system can form

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a compact and thin SEI layer, also it can show outstanding long-term cycling performance and high CE. The superior cycling performances of the concentrated dual-salt electrolytes were also demonstrated, compared with single-salt (LiTFSI) electrolyte.

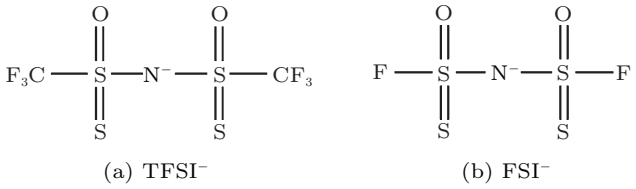


Fig. 1. The representative structure of (a) $TFSI^-$ and (b) FSI^- anions.

2. Experiments

2.1. Preparation of dual-salt electrolytes

All the procedures related to the preparation of solutions and cell assembly were carried out in an argon-filled glove box (H_2O and $O_2 < 1$ ppm). Anhydrous lithium bis (fluorosulfonyl) imide ($LiN(SO_2F)_2$, LiFSI, Suzhou Fluolyte Co., China), lithium bis (trifluoromethanesulphonyl) imide ($LiN(SO_2CF_3)_2$, LiTFSI, TCI, Japan), 1,3-dioxolane (DOL) and dimethoxy ethane (DME) (1:1 V/V, BASF). Firstly, DOL and DME were mixed with a volume ratio of 1:1, then 1M LiFSI + 2M LiTFSI, 2M LiFSI + 1M LiTFSI and 3M LiTFSI were weighted respectively. Finally the salts were dissolved in the mixed solvent and stirred at room temperature for 24 hours. The total mole concentration of dual-salt and single-salt electrolytes were all 3 mol-per 1L.

2.2. Electrochemical measurements

The CR2032 coin cells (Li|Cu, Li|Li, Li|$LiFePO_4$) were assembled in an argon-filled glove box with pure Li foil as the counter electrode, with a certain amount of electrolytes (120 μL) and Celgard 2400 separator. In Li|Cu cells, the constant current density for the Li metal plating/stripping was set at 0.5 and 1.0 mA/cm^2 using a Land BT2000 Battery Test System (Wuhan, China) at room temperature. Li|Li symmetric cells were assembled with Li metal used as the working and counter electrodes. The current density is 0.5 mA/cm^2 and the cell is cycled for over 600 h, which corresponds to 150 charging/discharging cycles. In Li|$LiFePO_4$ cells, the current density was 0.5 mA/cm^2 and the cycling rate was set at 0.1C. The cathode in Li|$LiFePO_4$ cells is a commercial product from Amperex Technology Limited with the active material of 6.71 mg/cm^2.

2.3. Characterizations

The cells were disassembled in an argon filled glove box (H_2O and $O_2 < 1$ ppm) and washed with DOL/DME (1:1 V/V) three times. The washed electrodes were dried in the vacuum chamber of the glove box for at least 6 h before being transferred to the SEM chamber. The specially designed transfer box was used to transfer the sample, which avoids exposure of the sample to the air. The Li anodes and Cu substrates for further characterizations were carried out by a Hitachi S-4800 microscope (SEM). XPS data were obtained using an ESCALab250 electron spectrometer with monochromatic Mg Kα radiation, and specific correction was conducted by using a C 1s binding energy of 284.6 eV.

3. Results and discussion

3.1. Physicochemical properties of electrolytes

The physicochemical properties at room temperature of these three electrolytes are listed in Table 1. The density of these three electrolytes is almost the same, while the ionic conductivity decreases as the viscosity increases. Among which, the system of 2M LiFSI + 1M LiTFSI displays the highest ionic conductivity of 12.2 S·cm^{-1}, which is similar to a conventional $LiPF_6$ electrolyte used in lithium-ion batteries. The glass transition temperature observed shows that all these electrolytes are glass-forming liquids.

Table 1. Physicochemial properties of the dual-salt and single-salt electrolytes.

Sample (25 °C)	1M LiFSI + 2M LiTFSI	2M LiFSI + 1M LiTFSI	3M LiTFSI
ρ/g·cm^{-3}	1.28	1.26	1.29
η/cp	6.99	5.02	5.69
δ/mS·cm^{-1}	3.97	12.2	5.45
T_g/°C	−114.4	−110.4	−114.9

3.2. Li metal deposition morphology on Cu substrates

The morphology of Li initial deposition on a Cu substrate is observed by SEM for the Li|Cu cell at a current density of 0.5 mA/cm^2 at 25 °C, and the deposition capacity is 1 mAh/cm^2. As shown in Figs. 2(a)–2(d), it can be seen that in the Li|Cu cells with the dual-salt electrolytes, the morphology was quite compact. In contrast, the morphology of the cells with single-salt electrolyte is loose, which may result in a serious side reaction between the freshly deposited Li and the electrolyte. As a result, a side reaction may continue to occur during the following charge/discharge process, and more electrolyte would be consumed, which accelerates the failure of the cell. Due to the addition of LiFSI,[11] the dual-salt cells exhibit more compact deposition morphology than the cells with single-salt electrolyte and are more suitable for applications of a long-cycle and high-rate charge/discharge process.

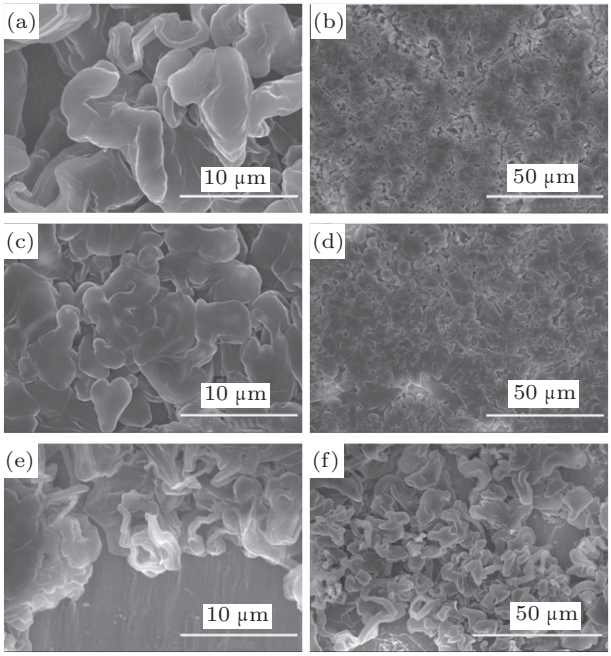


Fig. 2. SEM images of the morphology of Li plating on a Cu substrate after the initial deposition in different electrolytes. (a), (b) 1M LiFSI + 2M LiTFSI. (c), (d) 2M LiFSI + 1M LiTFSI. (e), (f) 3M LiTFSI. The current density was 0.5 mA/cm^2.

3.3. Li|Cu cells

The CE of Li metal anode is an important parameter to evaluate the utilization of metallic Li. CE is defined as the ratio of the amount of Li stripped from the working electrode versus the amount of Li plated on the counter electrode during each cycle.[12] The average CEs of the Li|Cu cells were 98.7% and 98.6% after 200 cycles for the 1M LiFSI + 2M LiTFSI and 2M LiFSI + 1M LiTFSI electrolytes, respectively, at a current density of 0.5 mA/cm^2. In contrast, the 3M LiTFSI electrolyte shows a lower CE of 91.7% and appears fluctuation after 100 cycles (Fig. 3(a)). As shown in Fig. 3(b), at a higher current density of 1 mA/cm^2, the 3M LiTFSI electrolyte shows a much lower CE of less than 90%. However, the CE of cells with the dual-salt electrolyte (1M LiFSI + 2M LiTFSI) is still 94.6% after 100 cycles, and the CE of cells with dual-salt electrolyte (2M LiFSI + 1M LiTFSI) can even reach 97.7% after 200 cycles (Fig. 3(b)). It is obvious that the dual-salt systems show better performance than the single-salt system. This may be attributed to the synergistic effect of LiFSI and LiTFSI, which is beneficial for improving the quality of SEI films in Li|Cu cells.[9]

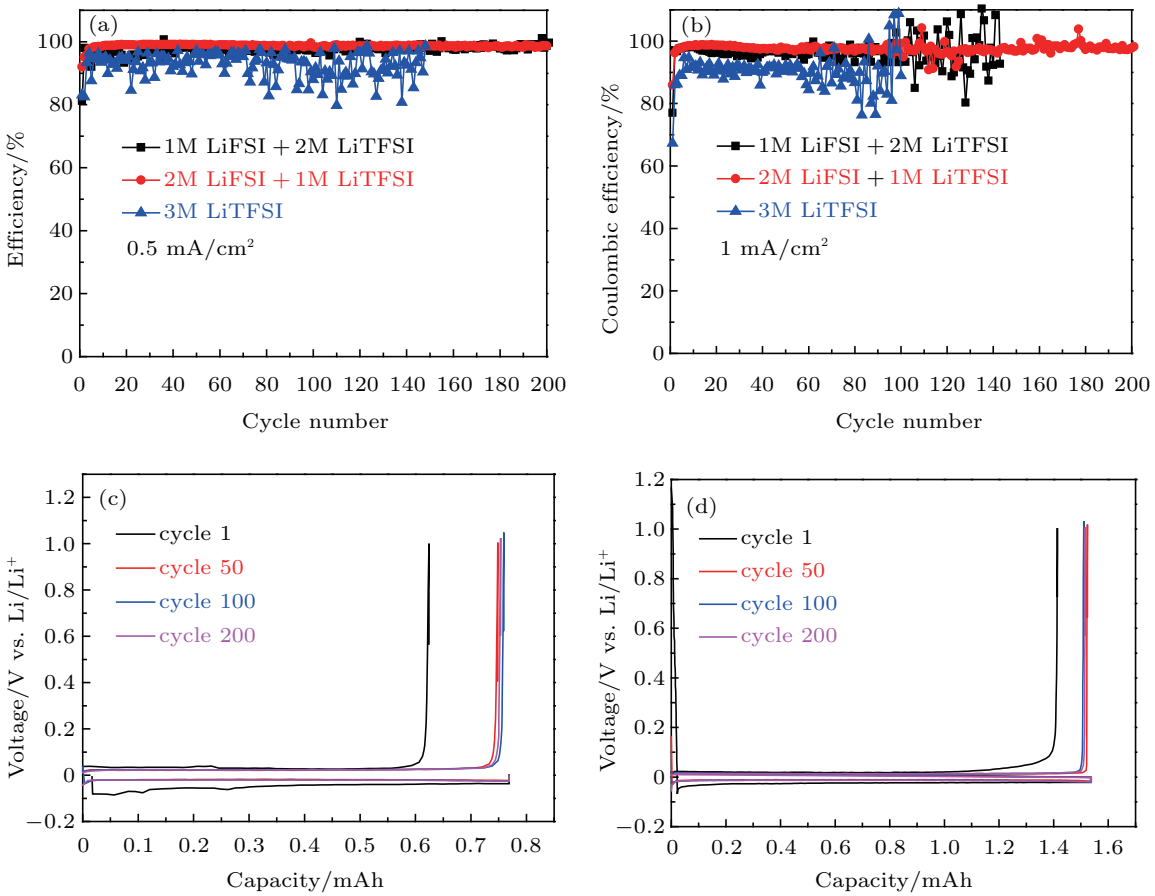


Fig. 3. Electrochemical performance of Li metal plating/stripping on a Cu working electrode at a current density of 0.5 mA/cm^2. (a) CE of Li deposition/stripping in different electrolytes at a current density of 0.5 mA/cm^2. (b) CE of Li deposition/stripping in different electrolytes at a current density of 1 mA/cm^2. (c) Voltage profiles for the Li|Cu cells in 1M LiFSI + 2M LiTFSI at a current density of 0.5 mA/cm^2. (d) Voltage profiles for the Li|Cu cells in 2M LiFSI + 1M LiTFSI at a current density of 0.5 mA/cm^2.

As seen from Fig. 4, 3M LiTFSI electrolyte shows much thicker SEI films, which may be due to the serious side reactions, in comparison with the dual-salt electrolytes. In addition, the voltage profiles of the Li|Cu cells with 1M LiFSI + 2M LiTFSI and 2M LiFSI + 1M LiTFSI cycled at 0.5 mA/cm^2 are observed, as shown in Figs. 3(c) and 3(d), respectively, indicating that both cells are highly stable for more than 200 cycles. Furthermore, a higher CE of the initial cycle is achieved as the concentration of FSI^- increases, suggesting that FSI^- plays a significant role in promoting the utilization of metallic Li.

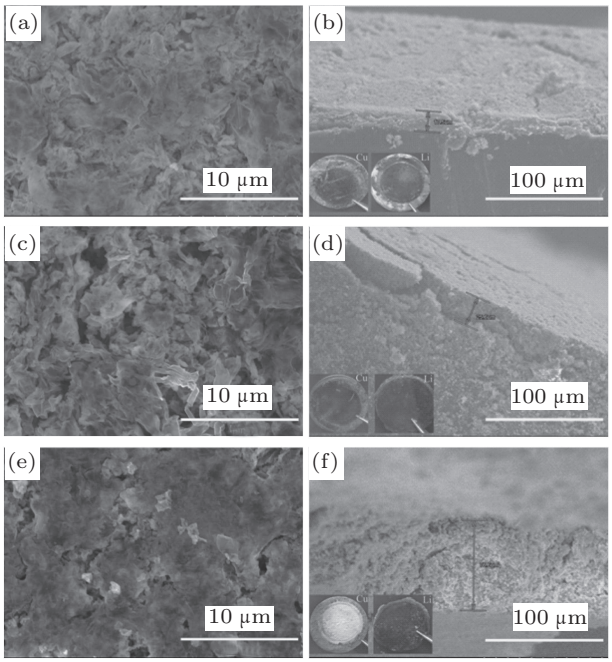


Fig. 4. SEM and optical images of Li and Cu electrodes after 200 cycles in Li|Cu cells. The deposition current density was 0.5 mA/cm^2. (a) 1M LiFSI + 2M LiTFSI. (b) Cross section of 1M LiFSI + 2M LiTFSI. (c) 2M LiFSI + 1M LiTFSI. (d) Cross section of 2M LiFSI + 1M LiTFSI. (e) 3M LiTFSI. (f) Cross section of 3M LiTFSI.

3.4. Formation of a stable SEI layer

The morphologies of the SEI layer formed on the Li anode surface in different electrolytes are investigated by SEM and optical images. Li was deposited at a current density of 0.5 mA/cm^2 in a Li|Cu cell. Figures 4(a) and 4(c) show that the Li metal surface is smooth in the dual-salt electrolytes (e.g., 1M LiFSI + 2M LiTFSI and 2M LiFSI + 1M LiTFSI) after 200 cycles. This may be due to the effect of LiFSI, which can form a uniform inorganic layer on the Li surface with the major composition of LiF.[13–16] Figures 4(b) and 4(d) show the cross section of the cycled Li metal in dual-salt systems, and the thickness of SEI layer is 17 μm and 25 μm, respectively. The optical images of the Cu and Li electrodes after the 200th cycle are also shown in the figure. It can be seen that the SEI layers formed on the Cu and Li electrode surface are dark gray. In contrast, the morphology of the Li metal anode surface in a single-salt electrolyte is worse than that in dual-salt electrolytes (Fig. 4(c)), also there are many large cracks. The thickness of the SEI layer is much thicker (76 μm, as seen in Fig. 4(f)), which may hinder the transport of Li ion in electrode and lead to battery failure eventually.

Furthermore, x-ray photoelectron spectroscopy (XPS) analysis is used to analyze the compositions of the SEI. Figure 5 displays the compositions of metallic Li anodes surface in Li|Cu cells after 100 cycles. The differences of F 1s peaks are obvious between the dual-salt electrolytes (1M LiFSI + 2M LiTFSI and 2M LiFSI + 1M LiTFSI) and single-salt electrolytes (3M LiTFSI). There are two peaks assigned for F in $-CF_3$ and LiF, respectively. In the dual-salt electrolytes, the intensity of LiF peak is much higher than that in the single-salt electrolytes. As mentioned above in Fig. 4, LiF is one of the major inorganic compositions of a SEI layer

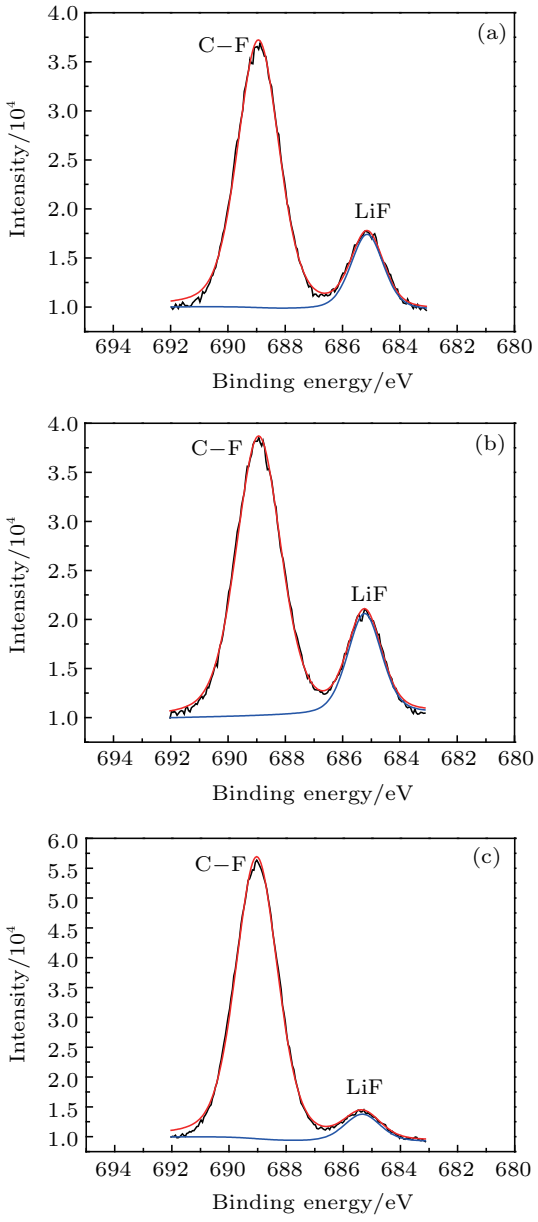


Fig. 5. X-ray photoelectron spectroscopy (XPS) analysis of metallic Li anodes after 100 cycles in Li|Cu cells. (a) 1M LiFSI + 2M LiTFSI. (b) 2M LiFSI + 1M LiTFSI. (c) 3M LiTFSI.

on a Li surface. Compared with the cells with dual-salt electrolyte, there is less amount of LiF and more reduction products of $TFSI^-$ in the cells with single-salt electrolyte, which may result in the formation of a heterogeneous surface film in the single-salt electrolyte. With the addition of LiFSI, it can help to form an even deposition of Li and a stable SEI film on the surface of the Li metal anode.

3.5. Li|Li cells

A symmetric Li|Li cell is assembled to investigate the cycling stability of the Li metal anode in different electrolytes at a current density of 0.5 mA/cm^2. It can be seen that the cell is cycled for over 600 h, which corresponds to 150 charging/discharging cycles (Fig. 6). In the dual-salt systems (1M LiFSI + 2M LiTFSI and 2M LiFSI + 1M LiTFSI), the polarization voltage decreases after cycling for a few hours and is stable at 20 mV in the next 600 h, suggesting that the SEI films formed on Li metal surface are stable.[17,18] In contrast, the cell with single-salt electrolyte (3M LiTFSI) shows serious fluctuation of voltage after 400 h. This is due to a non-uniform current density distribution caused by the heterogeneous surface film, as discussed above, which may lead to the formation of Li dendrite.

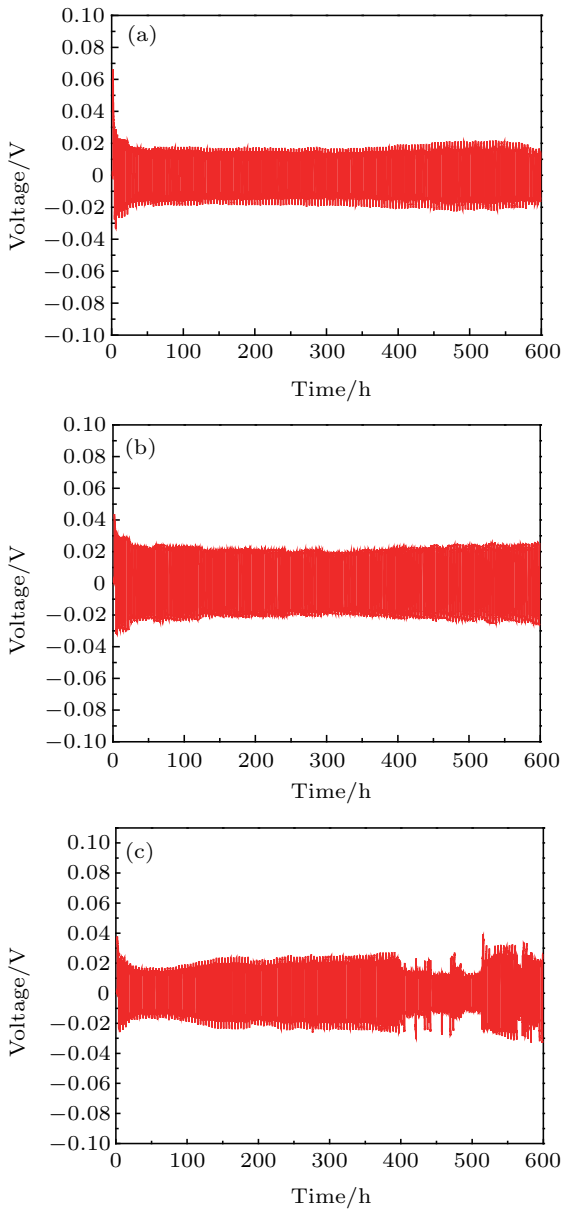


Fig. 6. Cycling performance for the Li|Li symmetric cells in different electrolytes at a current density of 0.5 mA/cm^2. (a) 1M LiFSI + 2M LiTFSI. (b) 2M LiFSI + 1M LiTFSI. (c) 3M LiTFSI.

3.6. Li batteries cycling performance

Li|$LiFePO_4$ cells were also used for better proving the cycling stability of Li metal anodes in the concentrated electrolytes with dual-salt. The cell is charged and discharged at room temperature at the 0.1C rate. Figures 7(a) and 7(b) show

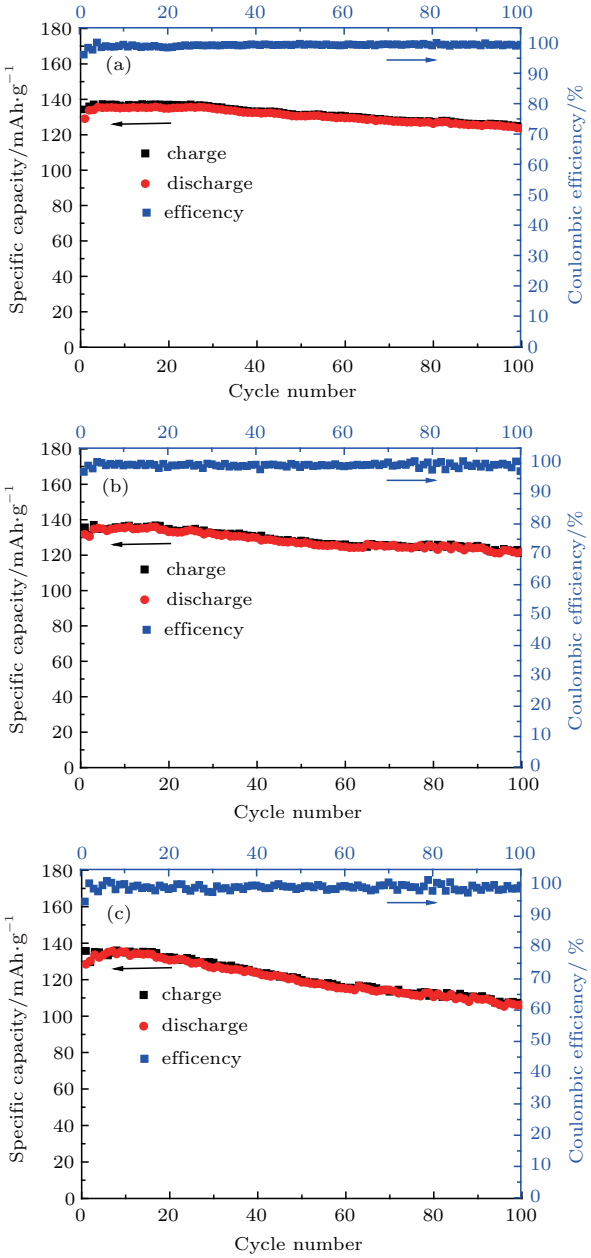


Fig. 7. Cycling performance of Li|$LiFePO_4$ cells in different electrolytes at 0.1 C. (a) 1M LiFSI + 2M LiTFSI. (b) 2M LiFSI + 1M LiTFSI. (c) 3M LiTFSI.

the charge and discharge profiles of the first 100 cycles. The capacity retention can even be maintained at 95.7%, 92.5%, and 81.6% after 100 cycles in 1M LiFSI + 2M LiTFSI, 2M LiFSI + 1M LiTFSI electrolytes, and 3M LiTFSI, respectively. The values of CE of the 100th cycle are 99.4% and 98.6%, respectively. It can be seen that cycle life is improved significantly, also the capacity decreases smoothly in contrast with 3M LiTFSI (Fig. 7(c)), indicating that cells with dual-salt electrolyte generate organic polymer SEI films with good elasticity and stability at the Li metal surface.[19] These results are consistent with Fig. 5. The SEI layer of these two dual-salt electrolytes is more compact than that of the single-salt electrolyte. Therefore, they consume less amount of Li and electrolytes, which could maintain excellent cycle life.

4. Conclusions

The concentrated dual-salt electrolytes (1M LiFSI + 2M LiTFSI and 2M LiFSI + 1M LiTFSI) have been studied. Compared with the single-salt (3M LiTFSI) electrolyte, in the electrolytes with the addition of LiFSI, the SEI layer of these two dual-salt system is more compact and thinner. This is due to the fact that LiFSI can form a uniform inorganic layer on the surface of Li electrode with the major composition of LiF. The cross-sectional SEM images show the thickness of the SEI layer was 17 μm and 25 μm, respectively, in dual-salt electrolyte. A Li|Li cell can be cycled at 0.5 mA/cm^2 for more than 150 cycles, and a Li|Cu cell can be cycled at 0.5 mA/cm^2 for more than 200 cycles with the CE of 98.7% and 98.6%. Also the Li|$LiFePO_4$ cells can operate properly in the dual-salt electrolytes with the capacity retention of 95.7% and 92.5% after 100 cycles. All the above results indicate that concentrated dual-salt electrolytes would be a promising candidate for application in rechargeable Li batteries.

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