A low cost composite quasi-solid electrolyte of LATP, TEGDME, and LiTFSI for rechargeable lithium batteries*

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(Received 15 March 2017; revised manuscript received 5 April 2017; published online 10 May 2017)

The composite quasi solid state electrolytes (CQSE) is firstly synthesized with quasi solid state electrolytes (QSE) and lithium-ion-conducting material $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP), and the QSE consists of [LiG4][TFSI] with fumed silica nanoparticles. Compared with LATP, CQSE greatly improves the interface conductance of solid electrolytes. In addition,it has lower liquid volume relative to QSE. Although the liquid volume fraction of CQSE is droped to 60%, its conductivity can also reach 1.39×10^{-4} S/cm at 20 °C. Linear sweep voltammetry (LSV) is conducted on each composite electrolyte. The results show the possibility that CQSE has superior electrochemical stability up to 5.0 V versus Li/Li^+. TG curves also show that composite electrolytes have higher thermal stability. In addition, the performance of Li/QSE/$LiMn_2O_4$ and Li/CQSE/$LiMn_2O_4$ batteries is evaluated and shows good electrochemical characteristics at 60 °C.

Keywords: quasi solid state electrolytes, $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$, conductivities

PACS: 82.47.Aa, 65.40.gk, 82.45.Gj **DOI:** 10.1088/1674-1056/26/6/068201

1. Introduction

Recently, lithium ion batteries (LIBs) with higher energy densities and longer cycle lives are attracted a significant attention, due to the fast-growing market of electric vehicles (EVs) and electrical energy storage systems.[1–3] Because lithium metal anode has extremely high theoretical specific capacity (3860 mAh/g), low density (0.59 g/cm^3) and the lowest negative standard electrode potential (−3.040 V versus the standard hydrogen electrode), rechargeable metallic lithium batteries can improve the battery energy density up to 300 Wh/kg ∼ 500 Wh/kg. Before its commercialization, there are many obstacles which need to be overcame, such as non-uniform deposition, large volume expansion and lithium dendrite.[1,2] High voltage and capacity cathodes are another way to acquire higher energy densities, for instance $LiNi_{0.5}Mn_{1.5}O_4$ and Li_2MnO_3.[4] However, conventional organic liquid electrolytes have high chemical activity and narrow electrochemical window, which cannot meet the new requirements.[5] Solid electrolytes have a wide electrochemical window in the range of 0 V to 10 V and are non-flammable characteristics to greatly enhance the safety of the battery and pack, such as $Li_7La_3Zr_2O_{12}$,[6] $La_{0.62}Li_{0.16}TiO_3$, $Li_{1.4}Al_{0.4}(Ge_{0.6}Ti_{0.33})_{1.6}(PO_4)_3$,[7] $Li_{1.4}A_{10.4}Ti_{1.6}(PO_4)_3$,[8] PEO,[9,10] PEC,[11] and PVC.[12] Due to the stability between solid electrolytes and metal lithium anode or the high-voltage cathode,[13,14] solid state batteries are considered as a possible solution to simultaneously achieving high energy density and longer cycle lives. But it is difficult to achieve a good contact between the solid electrolytes and cathode materials[15] or between the solid electrolytes and solid electrolytes.[16,17] In order to resolve such issues, many attentions have been paid on quasi-solid-state electrolytes (QSE).[18,19] These materials are prepared by utilizing the strong interaction on the surface of oxide nanoparticles to solidifying lithium-ion-conductive ionic liquids (IL) or nonaqueous electrolytes. Due to ionic liquids' superior properties,QSE retains the excellent performance of the ionic liquid, such as flame resistance, very low vapor pressure, and high ion conductivity. However, the expensive costs of ionic liquids hinder its large-scale application. The solvate ionic liquids behave like RTILs and have high lithium ion conductivity,[20] such as the equimolar complex of triethylene glycol dimethyl ether (triglyme, G3) or tetraethylene glycol dimethyl ether (tetraglyme, G4) with Li-salts ([LiG3][TFSI] or [LiG4][TFSI]). The QSE consists a different ratio of solvate ionic liquids (SIL) and oxide mixtures.[21] The states of SIL-oxide mixtures depend on the mixing ratios. For instance, the content of fumed silica nanoparticles increases that changes the state from gels to quasi-solids and reduces the conductivity at the same time.

*Project supported by the National Natural Science Foundation of China (Grant Nos. 52315206 and 51502334), the Funds from the Ministry of Science and Technology of China (Grant No. 2016YFB0100100), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA09010000), and the Foundation from Beijing Municipal Science & Technology Commission (Grant No. D171100005517001).

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Lithium ion transport mechanism shows in Fig. 1(a), the oxide particles are coated a layer of IL and the lithium ions migrate along these surfaces which is shown the red line in Fig. 1(a). Because the oxides are not lithium ion conductor, the larger volume of IL is needed to maintain high conductivity and excellent battery performance in QSE.[19]

On the other hand, the lithium ion conductor of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ is one of the promising solid electrolytes for solid batteries because of its rich raw materials and high ionic conductivity. But its disadvantage is high reduction potential about 2.4 V and low grain boundary conductivity of 10^{-5} S/cm $\sim 10^{-7}$ S/cm.[22]

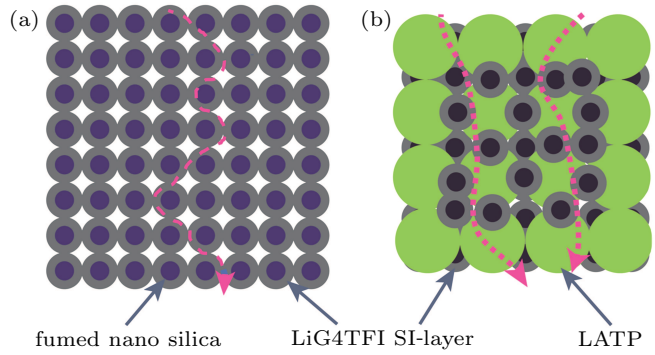


Fig. 1. (color online) Conceptual diagrams of fumed nano silica (clear-cut blue inner circles) and [LiG4][TFSI] (vaguely-outlined gray outer circles) composite material, LATP solid electrolyte (green circles), red dashed line represents a lithium-ion conduction path in QSE (a) and CQSE (b), respectively.

2. Experiment

The fumed nano silica (particle diameter: 7 nm) and tetraethylene glycol dimethyl ether (G4; purity: 99%) were purchased from Sigma–Aldrich Co. The LiTFSI powders were purchased from Alfa. $LiMn_2O_4$ for the cathode were prepared from previous reports.[23] Polyterafluoroethylene (PTFE) was also provided by Sigma–Aldrich Co.

The nominal chemical formula of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ was synthesized by the solid state reaction of stoi-chiometric amounts of Li_2CO_3, $Al(OH_3)$, TiO_2, and $NH_4H_2PO_4$ and a 5-wt% excess of Li_2CO_3 for compensating volatilization Li components during synthesis. The test of ICP shows that the real ratios of Li:Al:Ti:P is 1.44:0.39:1.59:3. After the LATP powers are shaped to pellets of 13-mm diameter, it is calcined at 850 °C for 2 h.

Firstly, the ionic liquid of [LiG4][TFSI] was prepared by mixing lithium bis(trifluoromethanesulfonyl)amide powders(LiTFSI) and tetraethylene glycol dimethyl ether (G4) according to equimolar and stirring for 24 hours at 45 °C in the glove box. Next, the [LiG4][TFSI] solution was mixed with fumed nano silica at a volume fraction $\xi = 50$, 60, 70, and 80 vol% in methanol by stirring for 3 h. Then mixtures were dried for 12 h at 60 °C on a hot plate to remove methanol and form QSE. Secondly, the CQSE was prepared by mixing LATP and QSE which volume fraction is fixed at 80 vol% in methanol by stirring for 3 h and then dried for 12 h at 60 °C. Last, the preparation process of CQSE membrane is admixing CQSE and PTFE at a weight ratio of 94 : 6. Then the mixtures were rolled to free standing membrane. The procedure is the same with QSE membrane.

The lithium-ion conductivities of each QSE membrane and CQSE membrane were obtained from AC impedance spectrum, which was recorded in a Swagelok-type airtight cell. In the Swagelok cell, the membrane was sandwiched between two stainless steel sheet (SSS). The diameters of membrane and stainless steel sheet used in Swagelok cell were about 12 mm and 10 mm, respectively. The measurements were performed by using an impedance analyzer (IM6ex) with a perturbation of 20 mV in the frequency range 2 Hz$\sim$ 3 MHz. Ionic conductivity was calculated using the following equation with the measured resistance value R (in unit Ω).

$$\sigma = \frac{d}{(R \times S)}, \tag{1}$$

where d (in unit cm) and S (in unit cm^2) are the thickness and effective area of the pellet or membrane.

Linear sweep voltammetry (LSV) was conducted on each composite electrolyte from 2 V to 5.5 V versus Li/Li$^+$ at a scan rate of 0.1 mV/s by using a potentiostat (Solartron 1480). To evaluate the electrochemical performance, Li/QSE/Li and Li/CQSE/Li batteries are assembled.

The x-ray diffraction (XRD) patterns of the products are collected on a Bruker ASX D8 advanced x-ray diffractometer equipped with the Cu Kα radiation at a rate of 1°/min.

TG measurements were conducted on Netzsch STA 449C differential scanning calorimeter in the air at a scanning rate of 5 °C/min from room temperature to 375 °C.

A scanning electron microscope (SEM, SU-6600, HITACHI) and an energy dispersive x-ray spectrometer (EDX, Incas-act, Oxford Instruments) were used to characterize the QSE and CQSE.

A composite-solid-state cell was assembled using the 2032-type coin cell configuration with $LiMn_2O_4$ and Li (99.9%, China Energy Lithium Co.) as the cathode active material and anode, respectively. The cathode components were $LiMn_2O_4$, CQSE or QSE, acetylene black and PTFE at a weight ratio of 30:60:5:5. Then the cathode mixtures were rolled onto the aluminum foil and dried at 60 °C under vacuum for 6 h. Single-layer quasi-all-solid-state lithium secondary batteries were prepared by directly stacking cathode composite, CQSE sheet with a diameter of 16 mm and a Li metal anode with a diameter of 10 mm without any further treatment in an argon atmosphere glove box. The charge/discharge cycling performances were measured at 60 °C by a Land BT2000 Battery Test System (Wuhan, China) in the voltage range of 3 V$\sim$ 4.3 V with current rate of 0.1 C.

3. Results and discussion

Figure 2(a) shows the XRD pattern of as prepared LATP. Although 25% of Ti^{+4} ion is replaced by Al^{+3} ion, the XRD diffraction can be indexed as pure NASICON structure [$LiTi_2(PO_4)_3$](ICSD95979), which is similar with those reported before.[24] Sharp diffraction peaks of the NASICON structure indicate a good crystallinity after crystallization at 950 °C for 3 h. The scanning electron micrograph of the as synthetic powers is shown in Fig. 2(b). It can be seen that the size of LATP is 2 μm∼ 3 μm. The pellet was shaped to 13-mm diameter and calcined at 850 °C for 2 h. AC impedance measurement is performed using an Au/LATP/Au electrode. A typical impedance plot is obtained at 20 °C for LATP electrolyte pellet which is shown in Fig. (2(c). The appearance of the tail at low frequencies cased by Li ion blocking. The impedance plot could be well resolved into bulk, grain-boundary, and electrode resistances. Due to the low bulk resistance, the radius of the semicircle represents grain boundary resistance (R_{gb}). According to Eq. (1) (pellet 0.2874 cm in thickness, 1.1 cm in diameter, and 3154 Ω for R_{gb}), the total conductivity is 8.28×10^{-5} S·cm^{-1}. In order to reduce this resistance, glass-ceramics and elements substitution are introduced to improve its interface.[24,25]

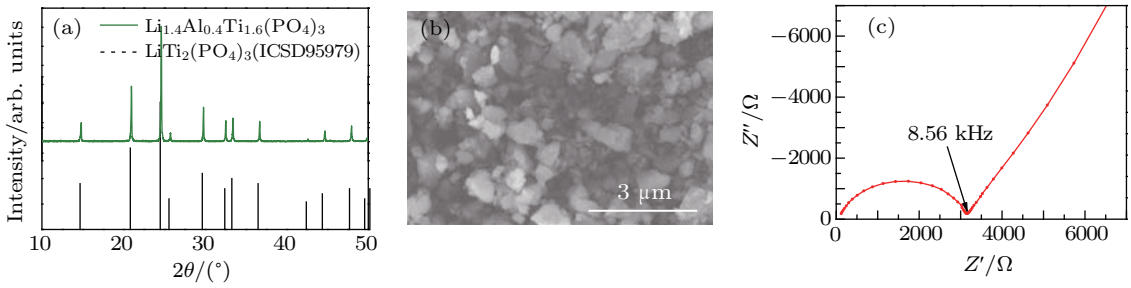


Fig. 2. (color online) (a) XRD patterns of the pristine LATP, (b) SEM image of LATP powders, (c) Nyquist plot for the LATP pellet at 20 °C.

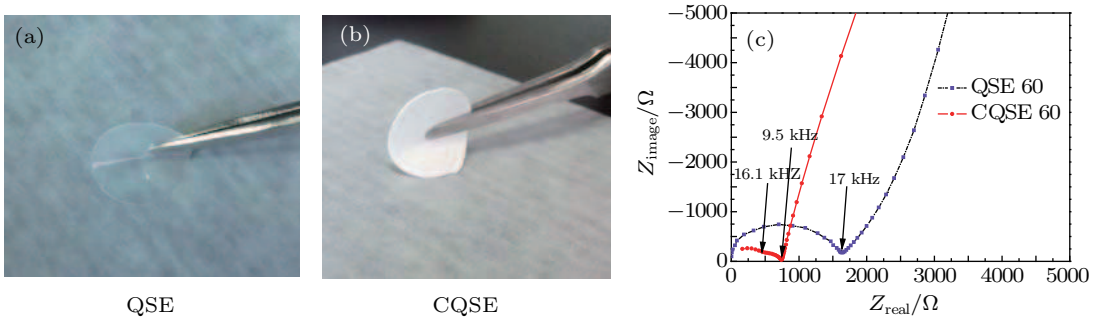


Fig. 3. (color online) Photos of QSE (a) and CQSE (b) membrane with 60 vol% [LiG4][TFSI]; (c) Nyquist plot of CQSE and QSE membrane with 60-vol% [LiG4][TFSI] at 20 °C.

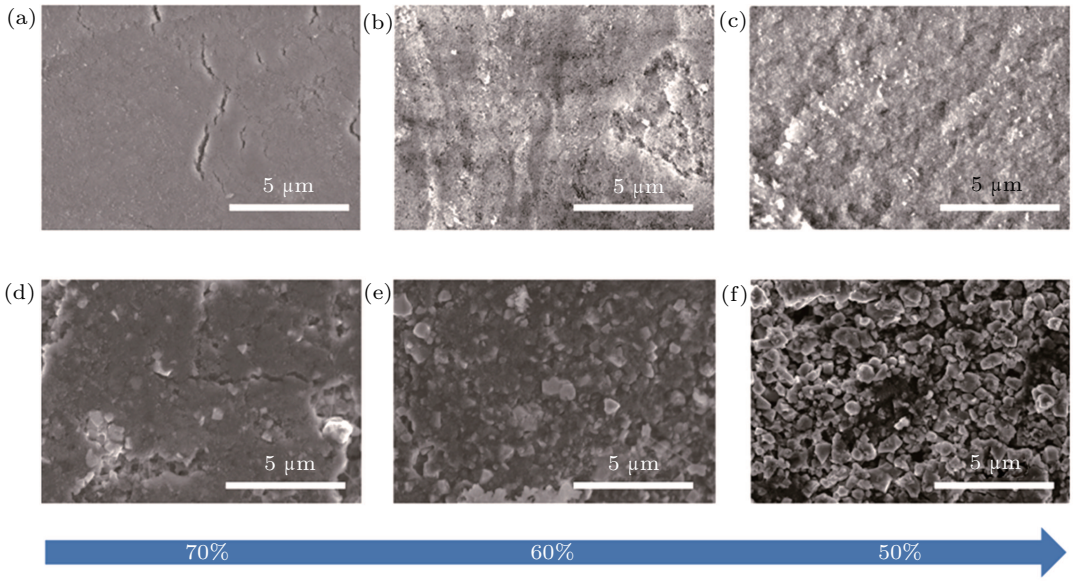


Fig. 4. (color online) SEM images of QSE membrane with 70 (a), 60 (b), 50 (c) vol% of [LiG4][TFSI] and CQSE membrane with 70 (c), 60 (d), 50 (e) vol% [LiG4][TFSI].

Table 1. Component content of different electrolytes.

	QSE 70	CQSE 70	QSE 60	CQSE 60	QSE 50	CQSE 50
Volume of [LiG4][TFSI]	70	70	60	60	50	50
Weight of [LiG4][TFSI]	60	57	49	44	39	34
Weight of G4	26	25	21	19	17	15

The QSE and CQSE were prepared in free standing with a common process which was described by experiment part. All those membranes have a mechanical flexibility compared to LATP pellet from Figs. 3(a) and 3(b), which is very important for assembling solid-state electricity and maintaining electrical contact during cycling. Electrical conductivity measurements were performed using Li ion blocking stainless steel electrodes. The impedance plot of the CQSE and QSE membranes is demonstrated in Fig. 3(c) at 20 °C. The spectrum of the CQSE is composed of two semicircles in the high frequency range (16 kHz) and the low frequency range (9 kHz), which is corresponding to the QSE and grain boundary resistance of LATP by the frequency response in Fig. 2(c). Figure 3(c) also shows that the grain boundary resistance significantly reduces by QSE filled in the particle gap compared to Fig. 2(c).

Figure 4 shows SEM images of QSE membranes with 70 (a), 60 (b), 50 (c) vol% of [LiG4][TFSI] which are denoted by QSE 70, QSE 60, QSE 50. Similarly, CQSE membranes with 70 (d), 60 (e), 50 (f) vol% of [LiG4][TFSI] are denoted by CQSE 70, CQSE 60, CQSE 50. It is clear that the contact between nano-particles becomes loosely with reduction of the [LiG4][TFSI]'s volume fraction in QSE membranes as shown in Figs. 4(a)–4(c). For CQSE membranes, all the LATP particles are uniformly surrounded by QSE in Figs. 4(d) and 4(e), which is supported the original intention of our experimental design. In the composite structure, lithium ion can easily transport from different LATP particles which an improve its interfaces. However, when the volume of [LiG4][TFSI] reduces to 50%, the connections between LATP and QSE are very loosely and that will hinder the transportation of lithium ion. According to the density of [LiG4][TFSI] (1.4 g/cm^3),[26] the component contents of QSE and CQSE were calculated and the results are listed in Table 1. It clearly shows that CQSE reduces the weight of G4 in comparison with QSE with the same volume of [LiG4][TFSI], which means it is highly safer than QSE.

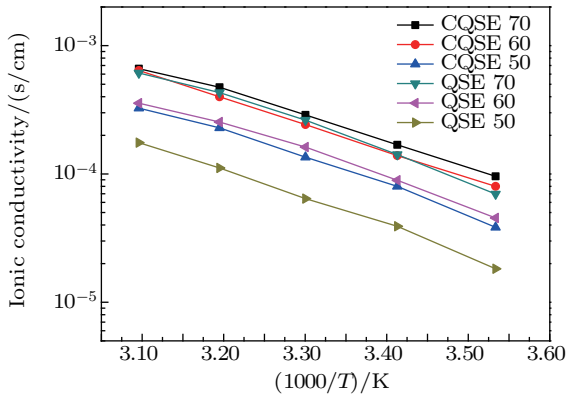


Fig. 5. (color online) The variations of the ionic conductivities for CQSE and QSE membranes with 70, 60, 50 vol% of [LiG4][TFSI] in the temperature range of 10 °C∼ 50 °C.

Table 2. The conductivities of different components ($\times 10^{-4}$ S/cm).

Temperature/°C	QSE 70	CQSE 70	QSE 60	CQSE 60	QSE 50	CQSE 50
10	0.698	0.957	0.454	0.800	0.182	0.384
20	1.41	1.69	0.892	1.39	0.391	0.801
30	2.63	2.88	1.62	2.42	0.64	1.35
40	4.30	4.74	2.54	3.99	1.11	2.29
50	6.12	6.61	3.56	6.41	1.75	3.26

Figure 5 shows the Arrhenius plots for the ionic conductivities of the CQSE and QSE membranes with various [LiG4][TFSI] contents. The activation energies of the various [LiG4][TFSI] membranes are calculated by using the equation $\sigma = A\exp(-E_a/KT)$, where σ, A, k, and E_a represent ionic conductivity, pre-exponential constant, Boltzmann constant, and activation energy for lithium ion conduction, respectively. It is clearly shown in Fig. 5 that the ionic conductivities of QSE are lower than CQSE with the same volume of [LiG4][TFSI]. Although the addition of LATP reduces the liquid content of QSE, the composite electrolytes still keep high conductivity.

The activation energies of the composite membranes are calculated to be in the range of 0.26 eV∼ 0.34 eV in the lower temperature region (10 °C∼ 40 °C). The ionic conductivities of CQSE 50 dramatically drop compared to CQSE 60, which may be caused by poor connectivity between different LATP particles as shown in Fig. 4(f).

In order to clearly show the conductivities of different components, all the data are listed in Table 2. The ionic con-

ductivities of CQSE 60 and QSE 60 is 1.39×10^{-4} S/cm and 0.892×10^{-5} S/cm at 20 °C, respectively.

Linear sweep voltammetry (LSV) was conducted to investigate the electrochemical stabilities of the composite quasi-solid state electrolytes. As presented in Fig. 6, all the CQSEs are found to be electrochemically more stable in the cathodic sweep direction than the QSE-only membrane, which was caused by wide electrochemical window of LATP and the lower content of [LiG4][TFSI]. Beyond the 5.0-V region, the composite membranes start to decompose due to oxidation. However, the oxidation peak currents of QSE are observed less than 5 V. The lower liquid content exhibits much better oxidation stability in CQSE components. Thus, these composite membranes exhibit a trend that has a superior electrochemical stability up to 5.0 V versus Li/Li$^+$, which means that they have the potential as new solid electrolytes for high voltage positive cathode batteries.

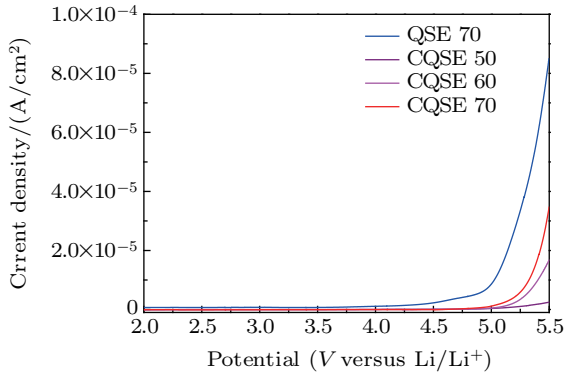


Fig. 6. (color online) Linear sweep voltammetry for the QSE and CQSE from 2 V to 5.5 V versus Li/Li$^+$ at a scan rate of 0.1 mV/s.

The safety problem of liquid lithium ion batteries is derived from the use of volatile and flammable organic solvents in the battery, which is very dangerous with an improper use, such as overcharge. Reducing the electrolyte content is one of the ways to enhance battery safety, but it will increase the battery resistance. Surprisingly, CQSE can keep the high conductivities and improve the thermal stability. Figure 7 shows the TG curves of CQSE and QSE with a heating rate of 5 °C/min from room temperature to 375 °C in air. The TG curves show that the weight of CQSE decreases more slowly than QSEs. It clearly shows that the loss of QSE 70 reaches 4.15 wt% at 150 °C in Table 3, while the CQSE 70's only reduces by 1.95%, which means that CQSE's battery has better safety performance at high temperature.

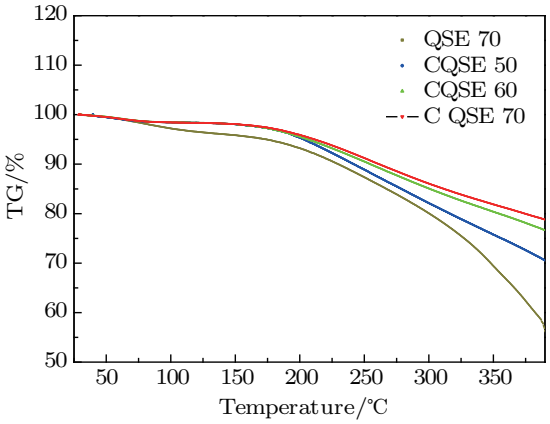


Fig. 7. (color online) Weight loss for the QSE 70, CQSE 70, CQSE 60, and CQSE 50 at a scanning rate of 5 °C/min from room temperature to 375 °C.

Table 3. The weight loss of different components.

Temperature/°C	QSE 70	CQSE 70	QSE 60	QSE 50
50	0.54	0.53	0.43	0.41
100	2.76	1.56	1.55	1.54
150	4.15	1.95	1.94	1.89
200	6.78	4.68	4.45	4.08
250	12.75	11.12	9.48	8.76
300	19.97	17.87	14.95	13.93

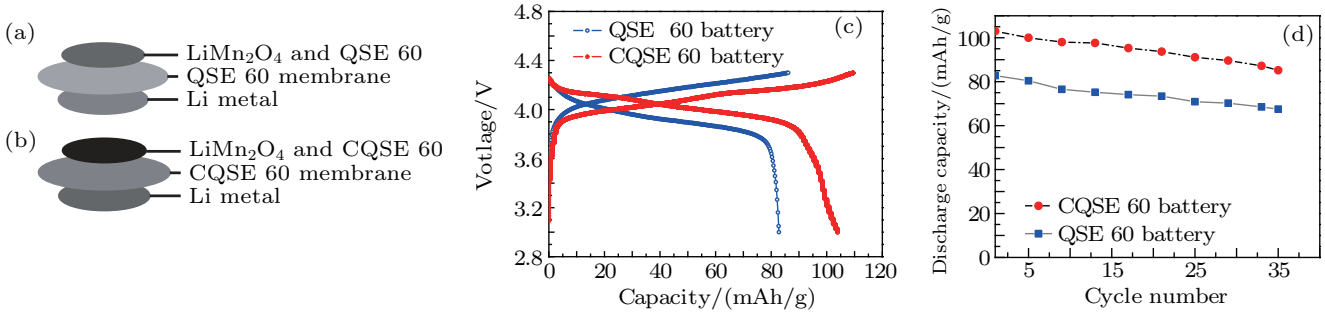


Fig. 8. (color online) The model of QSE (a) and CQSE (b) battery, the first charge–discharge profiles (c) and discharge capacity (d) of the $LiMn_2O_4$/Li cells with CQSE 60 and QSE 60 at 60 °C.

The QSE battery and CQSE battery (coin cell 2032 type) consisting of a $LiMn_2O_4$ cathode, a CQSE, and QSE membrane and a Li metal anode is assembled. These structures are shown in Figs. 8(a) and 8(b), respectively. Its charge and discharge behaviors were also investigated at 60 °C. The initial charge and discharge capacities of CQSE battery were found to be 109 mAh·g^{-1} and 103 mAh·g^{-1} at 0.2 °C (initial Coulombic efficiency 94.5%), as shown in Fig. 8(c). In contrast, QSE battery exhibited the charge–discharge capacities of only 86 mAh·g^{-1} and 82.8 mAh·g^{-1} at the same current den-

sity. The behaviors of the charge and discharge characteristics in the 1st cycle confirm that the polarization of CQSE battery exhibits smaller than QSE battery's. The capacity of quasi-solid-state battery decreases along with the cycle as shown in Fig. 8(d), which may be caused by the ionic liquid reductive decomposition at the lithium anode and a high voltage oxidation between cathode /electrolyte interface at 60 °C.

4. Conclusion

In summary, the CQSE composed of QSE and inorganic LATP in various ratios are firstly synthesized and characterized. The ionic conductivities of the CQSE membranes are higher than that of QSE membranes with the same volume of [LiG4][TFSI]. Although the liquid volume fraction of CQSE is dropped to 60%, its conductivity can also reach 1.39×10^{-4} S/cm at 20 °C. LSV results also show that the electrochemical stability of the CQSE membranes improves in cathodic directions. TG curves show that CQSE can improve the performance of high-temperature battery. The QSE can easily fill the space between the LATP and cathode at room temperature, which will reduce the interface resistance and improve the conductivity. The quasi-solid state batteries of Li/QSE/$LiMn_2O_4$ and Li/CQSE/$LiMn_2O_4$ batteries are evaluated at 60 °C and show good electrochemical performance. The capacity attenuation may be caused by the consumption of [LiG4][TFSI] which may not be stale with lithium anode and cathode at 60 °C.

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