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Short communication

Mesoporous silica/ionic liquid quasi-solid-state electrolytes and their application in lithium metal batteries

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H I G H L I G H T S

- Quasi-solid-state electrolyte is prepared by introduction of mesoporous silica host.
- Quasi-solid-state electrolyte has good thermal and electrochemical stability.
- Quasi-solid-state electrolyte allows successful battery operation at 25 °C.

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In this work, the ordered mesoporous silica, SBA-15, is chosen as the matrix for the first time to prepare quasi-solid-state electrolytes (QSSEs) with an ionic liquid, LiTFSI salt and PVdF-HFP. The as-obtained QSSEs are evaluated by electrochemical methods. Lithium metal batteries containing these QSSEs exhibit high discharge capacity and good cycle performance at room temperature, indicating successful battery operation.

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1. Introduction

Lithium metal batteries (LMBs) are considered to be one of the most promising electrochemical storage and power systems due to high theoretical capacity (3860 mAh g⁻¹) of the lithium metal anode [1,2]. However, the practical application of LMBs is retarded by safety issues, which is attributed to uneven lithium deposition and growth of lithium dendrites [3], as well as the properties of volatility, flammability and easy leakage of the conventional organic electrolytes [1]. Therefore, it is essential to develop new classes of safe electrolytes in order to accommodate the

development of lithium metal batteries.

Ionic liquids (ILs) have attracted considerable interest for their desirable properties such as negligible vapor pressure, nonflammability, good thermal stability and electrochemical stability. Recently, quasi-solid-state electrolytes (QSSEs) with ionic liquids immobilized on inorganic materials have been developed, which are capable of combining the advantages of inorganic materials (sufficient mechanical strength and avoiding liquid leakage) with those of ionic liquid electrolytes (good electrochemical performance) [2]. To date, there have been some investigations regarding QSSEs prepared by a sol–gel route [4], which exhibit impressive cell performance [5]. Nevertheless, it should be noted that the sol–gel reaction would yield lots of volatile side products such as water, methanol and formate esters, which results in a relatively long drying period [4,6].

Direct dispersion of oxide nanoparticles in ionic liquid electrolytes is a facile and versatile way to obtain QSSEs [7]. So far, there

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have been reports about the ionic conduction and lithium ion transportation mechanism of these QSSEs [8,9], as well as a few reports about their applications in LMBs [2,10,11]. According to previous works, we could find that host and ionic liquid types, as well as the cathode microstructure have an impact on electrochemical properties. Inspired by above analysis, we suppose that besides above-mentioned factors, the QSSE microstructure may affect electrochemical properties.

The QSSE microstructure is strongly related to its host microstructure. To date, oxide particles which are used as hosts to prepare QSSEs focus on conventional nanoparticles. Compared with conventional nanoparticles, ordered mesoporous materials can afford 3D ion transport pathway due to the uniform pores of narrow size distribution and well-organized array of interconnected straight channels [12], which is beneficial to the transportation of lithium ions. In this paper, the ordered mesoporous silica, SBA-15, is directly introduced for the first time to prepare QSSEs, in which SBA-15, an ionic liquid electrolyte and a small amount of PVdF-HFP are employed as the matrix, ion conducting mediator and pellet-shaping agent, respectively. *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR_{1,201}TFSI) is chosen as the ionic liquid electrolyte solvent for its higher conductivity than standards pyrrolidinium-based ILs [13,14], while lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is chosen as the Li-salt. The thermal and electrochemical properties of the as-obtained QSSEs were characterized, and battery tests on the solid-state Li/QSSE/LiFePO₄ cells at room temperature were also performed.

2. Experimental

The ionic liquid PYR_{1,201}TFSI was synthesized by using a modified route [15]. A lithium salt-ionic liquid solution (Li-IL) of molality 0.6 mol kg⁻¹ was prepared by adding a proper amount of LiTFSI to the ionic liquid. The viscosity was evaluated by using a viscometer (DV-III ULTRA, Brookfield Engineering Laboratories, Inc.).

SBA-15 (XF Nano; pore diameter: 7–9 nm; specific surface area: 550–600 m² g⁻¹), Li-IL and PVdF-HFP (poly (vinylidene fluoride-co-hexafluoro propylene), Aldrich) with a weight ratio of 1:3.5:0.1 were well distributed in acetone respectively and mixed together under stirring. Then the solvent was removed by raising the temperature, and the obtained white powder was pressed into pellets with diameters of 18 mm and thicknesses of about 0.35 mm. The as-prepared QSSE pellets were dried at 105 °C under vacuum for 48 h. A series of component ratios were checked to make sure that the QSSEs contained as much Li-IL as possible while the QSSE pellets could be obtained smoothly. It was found that the optimum weight ratio of SBA-15: Li-IL: PVdF-HFP is 1:3.5:0.1.

The morphology and structure of the QSSE were characterized by field emitting scanning electron microscopy (FE-SEM, Hitachi Co., Ltd., Japan) and high-resolution transmission electron microscopy (HR-TEM, JEM-2010HT).

TGA scan was recorded with a Q5000IR (TA Instruments) in the temperature range between 25 °C and 600 °C at a heating rate of 10 °C min⁻¹ under the nitrogen atmosphere. The ionic conductivity of the QSSEs was tested by impedance spectroscopy measurements with a CHI660D electrochemical workstation. Linear sweep voltammetry (LSV) was performed at 25 °C (scan rate 10 mV s⁻¹) using an SS (stainless steel)/QSSE/Li cell. The charge–discharge cycling tests of the symmetrical Li/QSSE/Li cells were performed with a Land CT2001A cell test instrument at 25 °C under different current density with 16 min charge and 16 min discharge.

LiFePO₄ electrode was fabricated by spreading the mixture of carbon coated LiFePO₄ (kindly provided by Jiangsu Litian Co., Ltd.;

carbon loading: 1.5%), acetylene black and PVdF (initially dissolved in *N*-methyl-2-pyrrolidone) with a weight ratio of 8:1:1 on an Al current collector (battery use). The CR2016-type coin cells were assembled in the glove box by contacting in sequence a disk of the LiFePO₄ cathode with a thickness of 0.04 mm, the QSSE with a thickness of 0.35 mm and a lithium metal disk anode with a thickness of 1.2 mm. Charge–discharge tests were carried out over a voltage range of 2.5–4.0 V at room temperature (25 °C) with a cell test instrument after the cells were stayed for 12 h. Current rate was determined by using the nominal capacity of 170 mAh g⁻¹ for the Li/LiFePO₄ cell. Electrochemical impedance spectroscopy (EIS) measurements of cells discharged to 2.5 V were performed with a CHI660D electrochemical workstation.

3. Results and discussion

Fig. 1(a) and (b) depict the typical photographs of the as-obtained QSSE powder and pellet, respectively. As expected, the QSSE powder has a white appearance, and the pellet is self-standing. The SEM image (Fig. 1(c)) exhibits that the QSSE has the same morphology as that of SBA-15 [12]. Moreover, the TEM image (Fig. 1(d)) of the QSSE clearly reveals mesoporous channel structure of SBA-15 [16], which is beneficial to the lithium ion transport.

Thermal stability is an important property for evaluating electrolytes. The thermal stability of the QSSE was measured by TGA. It can be found that the as-obtained QSSE shows a one-step thermal decomposition behavior and its decomposition temperature (5% weight loss) is about 370 °C, indicating the favorable thermal stability of the QSSE.

High ionic conductivity is one of the significant characteristics of electrolytes for successful electrochemical applications. The temperature dependence of the ionic conductivities (σ) of the neat IL (PYR_{1,201}TFSI), Li-IL and QSSE is depicted in Fig. 2(a). It is clear that in all cases, the ionic conductivities enhance with the increase of the temperature, which is due to faster migration of the ions at higher temperature [5]. The neat IL and Li-IL show conductivities of 3.77×10^{-3} S cm⁻¹ and 1.17×10^{-3} S cm⁻¹ at 25 °C, respectively. Although the conductivity of the QSSE obtained in this work (2.65×10^{-4} S cm⁻¹ at 25 °C) is lower than that of the neat IL and Li-IL, it is still sufficiently high for application as a promising electrolyte for lithium metal batteries [2]. Fig. 2(b) exhibits the linear sweep voltammogram of the QSSE. It can be found that the cathodic and anodic limiting potentials of the electrolyte are about 0.6 V and 5.1 V versus Li/Li⁺, and the electrochemical window is calculated as about 4.5 V, suggesting good electrochemical stability of the QSSE. These results make the as-prepared QSSE a promising electrolyte candidate for lithium metal batteries.

The charge–discharge cycling tests of lithium symmetrical cells containing the QSSE under different current density (0.05 mA cm⁻² and 0.1 mA cm⁻²) are carried out in order to preliminarily evaluate the influence of the QSSE on the Li electrodeposition, and the voltage–time curves during cycling tests are shown in Fig. 3. As expected, no obvious random fluctuations can be observed, and no sudden voltage drop occurs during the continuous cycles, suggesting that a stable SEI film could form on the lithium metal, and the short circuit does not occur [3]. This result proves that the QSSE is effective in promoting uniform Li electrodeposition and inhibiting the growth of lithium dendrites.

The properties of Li/LiFePO₄ cells containing the QSSE are evaluated at room temperature (25 °C), and the results are shown in Fig. 4. As clearly evidenced in Fig. 4, the Li/LiFePO₄ cells with the QSSE obtained in this work allow successful battery operation at room temperature. Fig. 4(a) shows the charge–discharge curves of the Li/QSSE/LiFePO₄ cells under a current rate of 0.1C at 1st cycle, 25th cycle and 50th cycle, all of which display typical charge/

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