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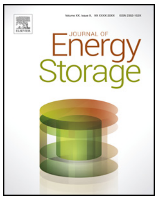

Development of ionic liquid and lithium salt immobilized MCM-41 quasi solid-liquid electrolytes for lithium batteries

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ABSTRACT

Li-ion conducting quasi solid-liquid electrolytes (QS-LEs) containing ionic liquid EMIMTFSI, lithium salt LiTFSI and ordered mesoporous MCM-41 (Mobil Composition of Matter no. 41) have been synthesized and characterized by N_2-sorption, SEM, TEM, DSC, TGA, and complex impedance spectroscopy techniques. The results show that the synthesized QS-LE has good thermal stability (~360 °C; onset temperature) and a wide electrochemical window ~5.23 V. The ionic conductivity is increases with increasing the amount of Li-IL (LIL) solution and attains a value of $\sim 6.37 \times 10^{-4}\,S\,cm^{-1}$ at 30 °C and $1.60 \times 10^{-3}\,S\,cm^{-1}$ at 70 °C for QS-LE containing high amount of LIL solution. The high ionic conductivity is attributed to the enormous adsorption of LIL solution on the external surface and in the ordered mesopores channels of the MCM-41. A high total ionic transference number (~0.99) and cationic transference number ($t_{Li}{}^+ \sim 0.35$) for QS-LE containing high amount of LIL solution have also been obtained. Furthermore, the QS-LE displays outstanding electrochemical properties (specific capacity $\sim 153\,mAh\,g^{-1}$ at C/10 rate; and good high rate capability $\sim 100\,mAh\,g^{-1}$ and $83\,mAh\,g^{-1}$ at 1C and 2C rate respectively) and battery performance with $LiFePO_4$ cathodes.

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1. Introduction

Typical lithium secondary batteries are fabricated using an anode, cathode and an electrolyte. Using liquid electrolyte, the Li metal anode has some issues such as lithium deposition and dendrite formation during repeated charge-discharge cycles, which is responsible for burst risk [1]. In view of battery safety, solid electrolytes are most attractive and have the potential to be a safer alternatives to liquid electrolytes for lithium secondary battery. Solid electrolytes are generally made of polymer and/or inorganic materials [2–8]. To date, very few solid electrolytes have been synthesized which cover the performance of battery as well as their basic requirement of safety.

Ionic liquids (ILs) have been attracted much by their structural diversity and unique profile of physico-chemical properties (like non-flammability, high ionic conductivity, low vapour pressure, high thermal stability, wide electrochemical window, non-toxicity *etc.*). Due to these exotic properties, ILs have been used as potential liquid electrolytes for use in the lithium ion battery (LiB) [7–12]. However, the current use of ILs in battery application as liquid electrolyte adds undue problems associated with their liquidus nature like leakage, lack of processibility etc. From the cost perspective, the need for a physical separator and packaging complications associated with liquid cells impedes development. The incorporation of ILs into host materials (polymer or inorganic porous materials) gives ionogels (IGs) and they are used as solid and/or quasi solid state electrolytes in many electrochemical applications [13–16]. It is well known that the ILs are interacted with host materials. These IGs are stable solid-like electrolytes and found to effectively suppress lithium dendrite growth in LiB [17,18]. However, incorporated IL within polymer host membrane exhibits poor mechanical performance and thermal stability is limited by the nature of the polymer host membrane. Very recently, inorganic solid/quasi solid electrolytes were developed using *in situ* sol-gel route, which consisted of lithium salt, IL and porous inorganic material [2,3,17]. However, it should be noted that *in situ* sol-gel routes had some limitations like rare monolith formation, uncondensed silanol groups may produce water molecules through secondary condensations, long aging time, large shrinkage *etc.* [19–21]. Currently, hybrid electrolytes were also developed by grafting ILs onto nanoparticles for increased containment of electrolytes [22,23]. In these systems, mainly the cations of ILs

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grafted covalently on inorganic nanoparticles and such tethering ILs nanoparticles provides good thermal stability, moderate ionic conductivity and good mechanical properties. However, these systems still suffer from a relatively low Li-transference number (t_{Li+}), narrow electrochemical window and strong polarization.

Recently, ordered mesoporous materials like SBA-15, MCM-41, MCM-48 *etc.* have been used for the immobilization of IL, due to their high thermal stability and attractive textural features (like larger pore diameter and specific surface area) [24–27]. Inspired with the beneficial morphological properties of these ordered mesoporous materials and to overcome the problems associated with liquid electrolytes like leakage, lack of processibility *etc.* and with IGs (like dendrite formation, longer synthesis and aging times, less number of run-through pores, large shrinkage during aging *etc.*), the ordered mesoporous MCM-41 is chosen as an electrolyte host. Since, MCM-41 is standard mesoporous form of silica exhibiting stimulating morphology like high specific surface area (upto 1000 $m^2 g^{-1}$) and ordered cylindrical mesopores with narrow-size regular distribution [28]. The immobilization of liquid electrolyte on ordered mesoporous MCM-41 with high specific surface area is, probably, responsible for the stability of electrolyte at high temperature and at high voltage compared to gel polymer electrolyte without a significant reduction in the liquid like ion mobility.

In the present study, quasi solid-liquid electrolytes (QS-LEs) have been prepared using liquid solution of IL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIMTFSI) and Li-salt, lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) incorporated into ordered mesoporous MCM-41 matrix, where the mesopores of MCM-41 are arranged in a regular form of hexagonal array and the availability of silicon dioxide (SiO_2) on the walls shows an amorphous structure. Earlier, we incorporated the IL [$EMIMBF_4$] in mesoporous MCM-41 using physical imbibition process and found that during incorporation, a fraction of IL got adsorbed on the external surface and the remaining IL entrapped inside the mesopores of MCM-41 [19]. Therefore, after incorporating the liquid solution, the ordered mesopores of MCM-41 and the external surface of MCM-41 particles can provide effective pathway for the transportation of lithium and other ions by their self-assembly. These composite materials come under the novel type of quasi solid-liquid electrolytes because of the high ionic conductivity, enough thermal stability (the inorganic host MCM-41 is very thermally stable and nonflammable), low interface resistance, and good electrochemical stability. The QS-LE is in solid state with liquid electrolyte properties. Such hybrid materials with high amount of ILs possess both advantages of solid and liquid electrolytes. The morphology, thermal stability, ionic conductivity, electrical conductivity and electrochemical stability of prepared QS-LEs have been investigated. The solid state cell was prepared using assembly Li|QS-LE|$LiFePO_4$ and the cell test was also performed at room temperature. The prepared cell shows good discharge capacity, high rate discharge capacity and cycling performance with $LiFePO_4$ cathode and it is founded that they are new potential nominee for new generation of rechargeable LiB.

2. Experimental

2.1. Materials

The IL [EMIMTFSI] (of stated purity > 98.9%), lithium salt [LiTFSI] (>99.95%), and ordered mesoporous MCM-41 were purchased from Sigma-Aldrich. To protect the chemicals from humidity, they were kept in an argon filled glove box (MBraun, O_2 and H_2O content < 0.5 ppm). Solvent, acetone (99.8%, Aldrich) was used as purchased without further drying.

2.2. Synthesis process

The lithium salt-ionic liquid (LIL) solution with the molality of 0.6 mol kg^{-1} was prepared in an argon-filled glove box. The QS-LEs were prepared by vacuum assisted physical imbibition process. Initially, MCM-41 was heated at a temperature 100 °C for 24 h followed by vacuum drying at a pressure of $\sim 10^{-3}$ Torr to remove the air in the pores of MCM-41 particles, so that LIL solution could be entrapped easily within the pores. The binary mixture of LIL solution and PVdF-HFP (0.1 wt.% of the sample; use as a pellet shaping agent) with solvent acetone was prepared at room temperature in a vial (a bottom-flat, two-port glass valve; one port was used as vacuum working port and other was tightly sealed). The required wt.% of MCM-41 powder was placed in a vial and mixed together for several hours and solvent acetone was evaporated by raising the temperature. QS-LEs; LIL@30, LIL@50 and LIL@70 with 30, 50 and 70 wt.% LIL solution loading respectively in MCM-41 were synthesized and its physical appearance was in the powder form.

2.3. Electrode and cell preparation

For the preparation of cathode, a slurry of 80 wt.% $LiFePO_4$, 10 wt.% carbon black and 10 wt.% polyvinylidene fluoride was prepared in solvent *N*-methyl-2-pyrrolidone. The slurry was coated onto aluminum foil and dried at 110 °C in vacuum for 48 h. The areal mass loading of active material in cathode was 1.5–1.7 mg cm^{-2}. Coin cells (CR2032) were assembled using prepared $LiFePO_4$ cathode, pellet of LIL@70 as the electrolyte and lithium metal as the anode in an argon-filled glove box then aged for 24 h before electrochemical testing.

2.4. Characterization

The pore parameters of samples were studied using N_2-sorption (adsorption-desorption) measurement carried out at 77 K using Gemini VII 2390t model of Micromeritics Instrument Corporation. Before the measurement, all the samples were degassed under flow of dry N_2 for 24 h at 60 °C.

The phase transition temperatures of prepared QS-LEs were investigated using Mettler Toledo DSC-1.

Surface morphological investigations of the samples were performed using SEM, ZEISS EVO 18.

Morphological investigation of the powdered samples was examined from TEM (Tecnai G^2F30), operated at 120 kV.

The total conductivity of LIL solution and QS-LEs was measured by complex impedance spectroscopy measurements using Novocontrol (Alpha A) Impedance Analyzer in the frequency range 1 Hz–10 MHz. The sample temperature was controlled using Novotherm temperature control system. The LIL solution was placed in a stainless steel parallel plate capacitor with an electrode separation of 2 mm. The QS-LE was sandwiched in pellet (surface area $\sim 78.5 \, mm^2$ and thickness ~ 0.70 mm) form between two gold-plated electrodes and subjected to the conductivity measurement. Since, the conductivity of QS-LEs is influenced by the moisture, therefore, prior to use, QS-LE's pellet in conductivity measurement, the pellets were dried at 110 °C under vacuum (10^{-3}). The total conductivity (σ_T) of all samples was calculated using the following equation-

$$\sigma_T = \frac{1}{R_b} \frac{l}{A} \tag{1}$$

Where l is the thickness of the sample, A is the cross sectional area of the sample and R_b is the bulk resistance obtained from the complex impedance plots.

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