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Effect of co-doping nano-silica filler and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide into polymer electrolyte on Li dendrite formation in Li/poly(ethylene oxide)-Li(CF_3SO_2)$_2$N/Li

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ABSTRACT

Lithium metal dendrite growth in Li/poly (ethylene oxide)-lithium bis (trifluoromethanesulfonyl) imide (PEO$_{18}$LiTFSI), nano-silica, and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI) composite solid polymer electrolyte/Li was investigated by direct *in situ* observation. The dendrite onset time decreased with increasing current density and deviated from Sand's law in the current density range of 0.1–0.5 mA cm^{-2} at 60 °C. Lithium dendrite formation was not observed until 46 h of polarization at 0.5 mA cm^{-2} and 60 °C, which is a significant improvement compared to that observed in Li/(PEO$_{18}$LiTFSI)/Li, where the dendrite formation was observed after 15 h polarization at 0.5 mA cm^{-2} and 60 °C. The suppression of dendrite formation could be explained by the electrical conductivity enhancement and decrease of the interface resistance between Li and the polymer electrolyte by the introduction of both nano-SiO$_2$ and PP13TFSI into PEO$_{18}$LiTFSI. The electrical conductivity of 4.96×10^{-4} S cm^{-1} at 60 °C was enhanced to 7.6×10^{-4} S cm^{-1}, and the interface resistance of Li/PEO$_{18}$LiTFSI/Li of 248 Ω cm^2 was decreased to 74 Ω cm^2 by the addition of both nano-SiO$_2$ and PP13TFSI into PEO$_{18}$LiTFSI.

1. Introduction

The motivation for using lithium metal as an anode for high energy density batteries lies in its high theoretical specific capacity of 3861 mAh g^{-1} and high negative potential of −3.05 V vs. NHE. However, lithium metal electrodes in contact with liquid electrolytes cause various problems, and the occurrence of dendrites formation during lithium deposition is particularly adverse, which leads to explosion hazards [1]. This phenomenon exists even with polymer electrolytes, although to a lesser extent than that with liquid electrolytes [2,3].

Lithium-air rechargeable batteries are an attractive energy storage system for electric vehicles (EV), because of their potential to provide acceptably high energy densities for EV applications [4]. They can yield a specific theoretical energy density as high as 11,140 Wh kg^{-1} (excluding oxygen), which is comparable to that calculated for gasoline. The typical lithium-air system consists of a lithium metal anode, a carbon electrode with a catalyst, and a non-aqueous electrolyte [5]. Nevertheless, it is difficult to exclude water from air in the air electrode using a conventional membrane filter, so that the lithium metal electrode may react with the water from the air. A water stable lithium electrode proposed by the current authors [6] has exhibited potential to prevent the reaction between water and lithium metal. The water stable lithium electrode consists of a lithium metal sheet as the active material, a polymer electrolyte buffer layer of poly(ethylene oxide) (PEO) with Li(CF_3SO_2)$_2$N (LiTFSI), and a water stable NASICON-type lithium conducting solid electrolyte ($Li_{1+x+y}Ti_{2-x}Al_xP_{3-y}S_yO_{12}$). The polymer electrolyte hinders the direct contact of lithium metal and the solid electrolyte, because the solid electrolyte is unstable in contact with lithium. This three layer lithium electrode has been confirmed to have stability in water and exhibit reversible lithium dissolution and deposition with low polarization [7]. However, dendrite formation on the lithium electrode remains a problem when charging the cell.

Research addressing the mechanism of dendrite growth in Li/polymer electrolyte/Li has been extensively studied by Brissot et al. and Rosso et al. [2,3,8,9] by means of direct *in situ* observation and simultaneous evaluation of cell potential. They have reported that dendrite formation begins at a time t_0 and follows a power law as a function of the current density that is very close to Sand's law [10,11]. The relationship between the ionic concentration and the onset of dendritic growth was investigated by *in situ* and *ex situ* ionic concentration measurements in Li/polymer electrolyte/Li cells during cycling [12]. Brissot et al. [2] reported that dendrites are generated when the ionic concentration drops to zero at the

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negative electrode, and they also come to the conclusion that the apparent variation of the interface resistance was larger than that of the bulk resistance during polarization [9]. It is well known that a solid electrolyte interface (SEI) is created between lithium metal and a polymer electrolyte. The kinetics of dendrite formation is dependent on the properties of the SEI. Dendrite formation may be suppressed by using a polymer electrolyte that exhibits a low interface resistance with lithium metal. We have previously reported that the addition of nano-SiO$_2$ into PEO$_{18}$LiTFSI reduced the interface resistance of Li/polymer electrolyte/Li from 248 to 97.5 Ω cm^2 at 60 °C and the short circuit time of 20 h at 0.5 mA cm^{-2} was prolonged to 42 h [13]. Furthermore, the short circuit time of a composite polymer electrolyte of PEO$_{18}$LiTFSI and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI) [14] in Li/PEO$_{18}$LiTFSI-1.44PP13TFSI/Li cell was increased to 75 h at 0.5 mA cm^{-2}.

As a continuation of our previous research, a composite polymer electrolyte of PEO$_{18}$LiTFSI with a mixture of PP13TFSI and nano-SiO$_2$ was prepared and dendrite formation in the Li/PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI/Li cell was examined using direct *in situ* observation in the current density range from 0.1 to 1.0 mA cm^{-2}. We have observed that the dendrite formation in the Li/PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI/Li cell was improved further by the addition of nano-SiO$_2$ into PEO$_{18}$LiTFSI-PP13TFSI. In this study, the electrical conductivity of PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI and the interfacial resistance of Li/PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI/Li were examined and the relationship between lithium dendrite formation and the interfacial performance is discussed.

2. Experimental

PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI composite polymer electrolytes were prepared using a previously reported casting method [15]. LiTFSI (Fluka, USA) was completely dissolved in anhydrous acetonitrile (AN). SiO$_2$ (Kanto Chemicals, Japan, average particle size 50 nm) and PP13TFSI (Kanto Chemicals, Japan) were added into the solution and then PEO powder (Aldrich, USA, Mw = 6 × 10^5, Li/O = 1/18) was dissolved. The SiO$_2$ nano-powder was dried at 200 °C for 24 h under vacuum. The mole ratio of Li$^+$/PP13$^+$ was 1/1.44, which showed the best performance for suppression of the dendrite formation [14]. The content of nano-SiO$_2$ was 10 weight % (wt%) to PEO$_{18}$LiTFSI-1.44PP13TFSI. The mixture was stirred at room temperature for 24 h and the obtained homogeneous solution was then cast into a clean Teflon dish. The AN solvent was evaporated slowly at 40 °C in an Ar-filled glove box for 24 h and then dried at 100 °C for 24 h under vacuum. The obtained composite polymer electrolyte was a homogeneous film with an average thickness of 230 μm.

Sandwich cells of Au/PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI/Au with blocking electrodes were used for electrical conductivity measurements, and sandwich cells of Li/PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI/Li with non-blocking electrodes were used for measurement of the interface resistance and electrochemical properties. All cells were sealed in an Ar-filled dry glove box. The cell was sandwiched between two pieces of a plastic film with low water and gas permeability. The plastic film envelope was then evacuated and heat-sealed. Electrochemical impedance spectroscopy (EIS) measurements were conducted using a frequency response analyzer (Solartron 1260) with an electrochemical interface (Solartron 1287) in the frequency range from 1 MHz to 0.01 Hz. A nonlinear complex least squares fitting routine was used for data analysis.

An optical visualization cell was used for *in situ* examination of the formation and growth of lithium dendrites on the lithium/composite polymer electrolyte interface [13]. Two narrow lithium metal strips (0.4 mm wide and 0.02 mm thick) with copper film leads were placed end to end on the composite polymer electrolyte with a distance of ca. 1 mm between the two electrodes. The cells were sealed in the same manner as that for the sandwich cells. Dendrite growth was observed using a digital microscope (Keyence VHX-100).

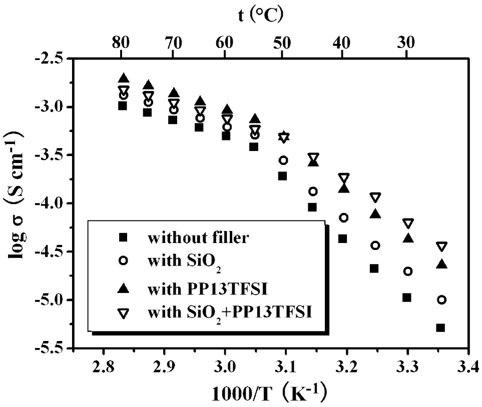

Fig. 1. Temperature dependence of the electrical conductivity for PEO$_{18}$LiTFSI, PEO$_{18}$LiTFSI-SiO$_2$, PEO$_{18}$LiTFSI-PP13TFSI and PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI.

3. Results and discussion

The electrochemical performance of lithium batteries with a metallic lithium anode depends on the properties of the solid electrolyte interface (SEI), and in particular, the composition and morphology of the SEI formed at the lithium surface. The SEI has a significant effect on lithium dendrite formation [16]. The SEI should protect further reaction of lithium metal and the electrolyte, and should have a high ionic conductivity at the operation temperature. The PEO based polymer electrolyte is stable with lithium metal, however, the interfacial resistance should be significantly reduced to obtain lower cell resistance [7]. The interfacial resistance of a typical polymer electrolyte of Li/PEO$_{18}$LiTFSI/Li is as high as 200 Ω cm^2 at 60 °C and increases with the storage time. Moreover, dendrite formation during lithium deposition should be suppressed. In this study we have examined the effect of co-doping nano-SiO$_2$ and PP13TFSI into PEO$_{18}$LiTFSI on the interface resistance between lithium metal and the composite polymer electrolyte, and also on lithium dendrite formation.

Fig. 1 shows Arrhenius plots of the electrical conductivity for PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI, in addition to that for PEO$_{18}$LiTFSI, PEO$_{18}$LiTFSI-10 wt%-nano-SiO$_2$ and PEO$_{18}$LiTFSI-1.44PP13TFSI reported previously [14,15]. Conductivity enhancement at higher temperature by co-doping is not obvious, where the PEO melts, but at low temperature the enhancement by addition of both nano-SiO$_2$ and PP13TFSI is significant. The conductivity of PEO$_{18}$LiTFSI-SiO$_2$-PP13TFSI at 25 °C is 3.68 × 10^{-5} S cm^{-1}, which is higher than those for PEO$_{18}$LiTFSI-PP13TFSI (2.34 × 10^{-5} S cm^{-1}), PEO$_{18}$LiTFSI-SiO$_2$ (1.00 × 10^{-5} S cm^{-1}), and PEO$_{18}$LiTFSI (5.13 × 10^{-6} S cm^{-1}). The Arrhenius plots of all the electrolytes have a conductivity knee at 55 °C, which reflects the crystalline to liquid phase transition [17]. The activation energies for electrical conduction obtained from the Arrhenius plots are listed in Table 1. Addition of nano-SiO$_2$ and PP13TFSI to PEO$_{18}$LiTFSI results in a slight decrease of the activation energy in the low temperature region, while that in the high temperature region is almost constant. PEO$_{18}$LiTFSI with both nano-SiO$_2$ and PP13TFSI has the lowest activation energy, which suggests that the lithium cations are more mobile in the PEO chains [18].

The interface resistance dominates the cell resistance of the Li/PEO$_{18}$LiTFSI/Li cell. Previous studies [13,14] have shown that