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Effect of nano-silica filler in polymer electrolyte on Li dendrite formation in Li/poly(ethylene oxide)–$Li(CF_3SO_2)_2N$/Li

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ABSTRACT

Lithium dendrite growth in Li/poly(ethylene oxide) (PEO)–$Li(CF_3SO_2)_2N$ (LiTFSI)–nano-SiO_2/Li was examined using direct *in situ* observation under galvanostatic conditions at 60 °C. Both the onset time of dendrite formation and the short-circuit time of the cells were extended by the addition of nano-SiO_2 filler into the polymer electrolyte, of which an acid-modified nano-SiO_2 filler was the most effective. The onset time was dependent on the current density in the range from 0.1 to 1.0 mA cm^{-2}. Li dendrite growth in Li/PEO_{18}LiTFSI/Li at 60 °C for current densities of 0.1 and 0.5 mA cm^{-2} started at 125 and 15 h, respectively. PEO_{18} LiTFSI with addition of 10 wt% acid-modified 50 nm SiO_2 showed extended dendrite formation onset times of 250 h at 0.1 mA cm^{-2} and 32 h at 0.5 mA cm^{-2}. The suppression of dendrite formation at the Li/PEO_{18} LiTFSI interface could be explained by enhancement of the conductivity and suppression of the interface resistance between lithium and the polymer electrolyte by addition of the nano-SiO_2 filler. The electrical conductivity of 4.1×10^{-4} S cm^{-1} and interface resistance of 405 Ω cm^2 for PEO_{18} LiTFSI at 60 °C were respectively increased to 7.2×10^{-4} S cm^{-1} and decreased to 77 Ω cm^2 by the addition of 10 wt% acid-modified nano-SiO_2.

1. Introduction

Increasing efforts have been devoted to the improvement of battery performance in order to develop high energy density batteries. Metallic lithium is a particularly good anode candidate for high energy density batteries, because it has a high theoretical specific capacity (3860 mAh g^{-1}) and high negative potential (−3.05 V vs. NHE). Nevertheless, the use of a metallic lithium anode is limited, due to the occurrence of dendrite growth during charging of the battery [1]. This phenomenon occurs even in polymer electrolytes, although to a lesser extent than in liquid electrolytes [2,3]. Dendrite formation is very detrimental to the operation of lithium batteries with respect to safety and battery life time [4].

Recently, lithium–air secondary batteries have been considered as the most attractive high specific energy battery for electric vehicles [5]. Their calculated energy density is as high as 11,140 Wh kg^{-1}, which is comparable to that of gasoline. The typical lithium–air battery consists of a lithium metal anode, a carbon air electrode, and a non-aqueous electrolyte. The lithium metal electrode is sensitive to water; therefore, protection of the lithium anode to corrosion by water from the air is a critical point for the application of lithium–air batteries. Water stable lithium metal electrodes have been proposed by Visco et al. [6] and by the current authors [7,8] that show prospective promise to solving the water corrosion problem of lithium metal. Our proposed water stable lithium electrode consists of lithium metal, a polymer electrolyte buffer layer of (poly(ethylene oxide) (PEO) with $Li(CF_3SO_2)_2N$ (LiTFSI)), and a water stable high lithium conducting glass ceramic layer of $Li_{1.35}Ti_{0.175}Al_{0.25}P_{2.7}Si_{0.3}O_{12}$. The polymer electrolyte interlayer serves to protect from the direct reaction of lithium metal and the solid electrolyte. The interface resistance of the three-layer lithium electrode is predominantly between the lithium metal and polymer electrolyte. However, for the application such lithium electrodes in high specific energy density lithium air batteries reduction of the Li/polymer electrolyte interface resistance as well as suppression of the lithium dendrite growth in the interface is required to obtain high power and energy density and a long cycle life. Short circuiting by dendrite formation in the Li/ethylene carbonate–ethyl methyl carbonate–dimethyl carbonate (1:1:1)–$LiPF_6$/Li cell was observed at 0.2 h during polarization under 1.0 mA cm^{-2} at 15 °C with a 1.0 mm thick separator [9]; the period until short circuit is too short. A gel-type polymer electrolyte comprised of 30 wt% PEO and poly(propylene oxide) (PPO) (5:1, w/w) copolymer and 70 wt% ethylene carbonate–propylene carbonate (1:1, w/w) showed improved suppression of dendrite formation, with dendrites appearing at 1 h under polarization at 0.8 mA cm^{-2} with a 1.0 mm thick separator [10]. In the case of a dry polymer electrolyte, a similar result with the gel-type polymer

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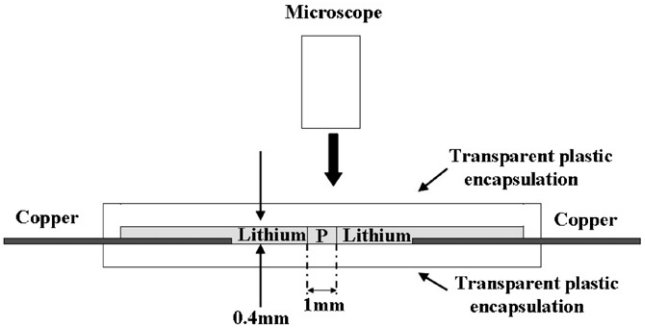

Fig. 1. Schematic presentation of assembly of the optically visible test cell.

electrolyte was reported. The Li/PEO–LiTFSI/Li cell showed dendrite growth at 0.6 h with a polarization of 0.7 mA cm^{-2}, where the separator was approximately 1 mm thick [11]. The lithium dendrite growth is dependent on the current density. Dendrite formation of the same cell configuration started at 42 h for a polarization of 0.05 mA cm^{-2} [12]. For practical applications, the dendrite formation onset time should be more prolonged at higher current density.

In this study, the dendrite formation in Li/PEO–LiTFSI/Li has been examined by direct *in situ* observation, and the effect of the addition of nano-SiO_2 and acid-modified nano-SiO_2 into PEO–LiTFSI on the lithium dendrite growth is described as a function of the current density. The relationship between lithium dendrite formation and the Li/polymer electrolyte interfacial resistance is also discussed.

2. Experimental

The PEO–LiTFSI–SiO_2 composite polymer electrolyte was prepared using a previously reported casting technique [13]. PEO powder (Aldrich, average molecular weight of 6×10^5) and LiTFSI (Fluka, Li/O = 1/18) were completely dissolved in anhydrous acetonitrile (AN). SiO_2 (Kanto Chemicals, 50 nm average particle size) was dried at 200 °C for 24 h under vacuum. The acid-modified nano-SiO_2 was obtained by impregnating the SiO_2 particles with 0.1 M H_2SO_4 solution for 10 h at room temperature, drying at 100 °C in air and then at 200 °C under vacuum for 24 h, followed by milling of the SiO_2 particles for 2 h using a high speed planetary ball mill. The nano-SiO_2 or the acid-modified nano-SiO_2 was homogeneously dispersed in the PEO-LiTFSI solution as a filler (10 wt%) by stirring

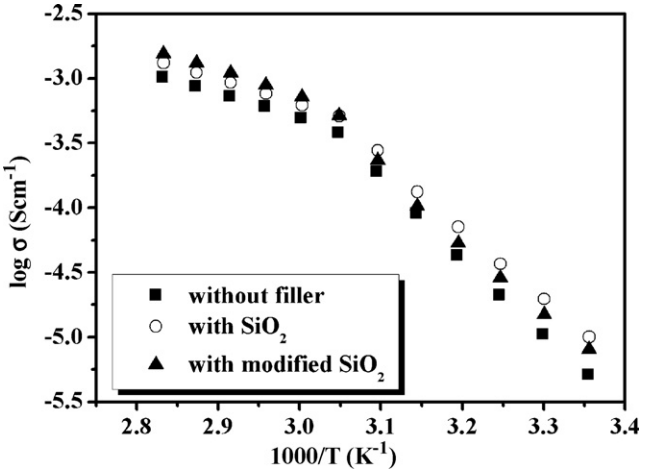

Fig. 2. Temperature dependence of the electrical conductivity of PEO_{18}LiTFSI, PEO_{18}LiTFSI–10 wt% nano-SiO_2, and PEO_{18}LiTFSI–10 wt% acid-modified nano-SiO_2.

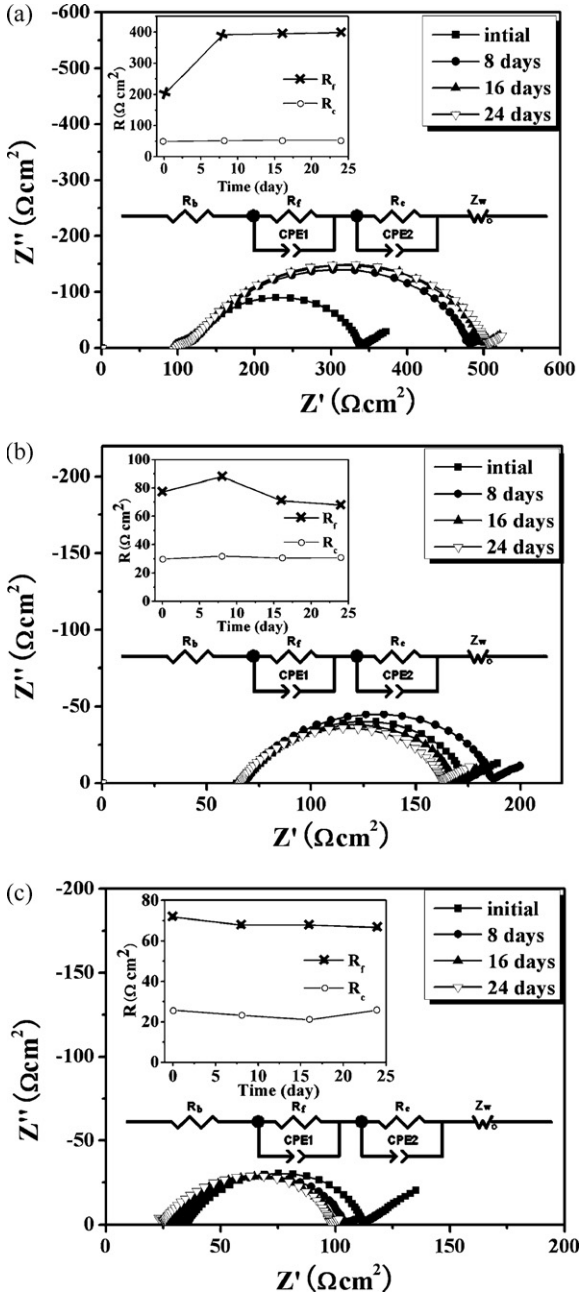

Fig. 3. Impedance spectra of Li/PEO_{18}LiTFSI/Li (a), Li/PEO_{18}LiTFSI–10 wt% nano-SiO_2/Li (b), and Li/PEO_{18}LiTFSI–10 wt% acid-modified nano-SiO_2 (c) at 60 °C as a function of the storage time. The inset figures show changes of R_f and R_c values with storage time.

at room temperature for 24 h in an Ar-filled dry glove box and the mixture was then cast into a clean Teflon dish. The AN solvent was evaporated slowly at 40 °C in a dry Ar atmosphere for 12 h and then dried at 110 °C for 12 h under vacuum. The polymer electrolyte was obtained as homogeneous films with an average thickness of 230 μm.

Two types of cells, a sandwich cell and a visualization cell, were used. A sandwich cell of Au/PEO_{18}LiTFSI–SiO_2/Au was used for electrical conductivity measurements and a Li/PEO_{18}LiTFSI–SiO_2/Li cell was used for interface resistance and electrochemical experiments. The visualization cell was used for the *in situ* examination of the formation and evolution of dendrites. Two narrow lithium metal strips (0.4 mm wide) with copper film leads were placed end to end on the polymer electrolyte with a distance of ca. 1 mm between the two