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Surface-initiated fluoride-scavenging polymeric layer on cathode materials for lithium-ion batteries

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Introduction

ABSTRACT

Spinel-structured lithium manganese oxides (LMOs) suffer from manganese dissolution at elevated temperatures, which leads to severe capacity fading. In this work, a novel strategic approach was developed to alleviate this phenomenon by using poly(dimethylsiloxane) (PDMS) as a simple and scalable electrode additive. LMO electrodes containing finely dispersed PDMS were prepared using a conventional electrode coating process. Electrochemical studies showed that the PDMS-dispersed LMO electrodes had significantly improved cycling retentions. Ex-situ FT-IR and ¹⁹F NMR spectra indicated PDMS chemically scavenged the F⁻ species, which cause manganese dissolution in LMO-based cells. In addition, a plausible mechanism was proposed based on the spectroscopic evidences.

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mance of LIBs constructed using LMO.

effective in preventing the erosion of Mn at the electrode/

electrolyte interfaces. On the other hand, functional electrolyte

additives have also been widely investigated to reduce the Mn

dissolution behavior [29-35]. This approach is based on the

chemical scavenging of nucleophilic F⁻ by additives. Although

these additives are effective, they have several practical limi-

tations. For instance, F⁻-scavenging additives often decrease the

ionic conductivities of the electrolytes, resulting in poor Li⁺

transportation kinetics. In addition, these types of additives are

usually extremely electrophilic and easily decompose on the anode

Lithium-ion batteries (LIBs) entered commercial markets in 1991. Since their introduction, their application has rapidly expanded from small- to large-scale devices, such as smartphones, laptop computers, electric vehicles, and uninterruptible power supplies [1–3]. The properties of LIBs depend primarily on their electrode materials, which determine the electrochemical performance of the cells, including their capacities, operating voltages, and rate capabilities. Therefore, many types of electrode materials have been developed to meet the specific requirements of LIBs used in a variety of applications [4–10].

Recently, the use of spinel-type lithium manganese oxides (LMOs) as a cathode material in LIBs for electric vehicles has gained much interest. LMOs contain three-dimensional diffusion channels, which provide favorable pathways for Li⁺ ion intercalation. Thus, LMOs show significantly improved kinetic behavior compared to that of LiCoO₂, a conventional layered cathode material [11–14]. Therefore, LMO may be a suitable electrode material for use in high-power devices. However, the practical application of LMO is seriously hindered by its chemical instability at elevated temperatures, which leads to poor cycling behavior of the resultant cells [15,16]. An LMO electrode charged to a high potential and an

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via irreversible reduction reactions. Hence, these additives are often incompatible with anode materials.

With these previous approaches in mind, we developed a PDMS-dispersed LMO cathode for the first time and systematically investigated its effectiveness by the combination of experimental and analytical methods. We believe that this methodology can be applied not only to the LMO materials, but also to a variety of advanced cathode materials previously reported, which suffer from similar continuous manganese dissolution.

65 Material and methods

66 Al-doped LMO (LiAl_{0.1}Mn_{1.9}O₄) was synthesized via a solid-state 67 method using Li₂CO₃, Al(OH)₃, and Mn₃O₄. The precursors were 68 ball-milled (300 rpm, 2 h) and subjected to heat-treatment at 69 800 °C for 12 h and at 600 °C for a further 6 h in air. The cathodes 70 were prepared from a homogenous mixture of LMO, poly(vinylene 71 difluoride) (PVdF) binder, and Super P (87:8:5, w/w/w) in N-72 methyl-2-pyrrolidone (NMP). A clear solution of 4wt% poly 73 (dimethylsiloxane)(PDMS)(Aldrich) in tetrahydrofuran was added 74 to the mixture with constant stirring for 1 h. The PDMS to LMO 75 ratio of the resultant slurry was adjusted to 0.02. Thereafter, the 76 slurry was cast onto an aluminum foil, and the electrode was dried 77 in a vacuum oven at 120 °C overnight. The loading densities of the 78 cathodes were around 7.5 mg cm^{-2} . The morphologies of the 79 cathodes were analyzed using a scanning electron microscope (FE-80 SEM, Hitachi, S-4200) equipped with an energy-dispersive X-ray 81 spectroscope (EDS).

To evaluate the electrochemical performance of the cathodes, To evaluate the electrochemical performance of the cathodes, 2032-type coin cells were assembled in a dry room using a commercial electrolyte (1.15 M LiPF₆ in 1:1 (v/v) diethyl carbonate and ethylene carbonate co-solvent; PanaxEtec) and a separator (Celgard 2325). The cells were subject to galvanostatic cycling in the range of 3.0–4.3 V at a rate of C/10 for the first cycle and C/1 for the subsequent cycles (1C = 148 mA h g⁻¹ of LMO) for 100 cycles at 25 and 60 °C. After cycling was complete, each cell was dismantled inside a glove box and the cathodes were recovered. The cathodes were washed with dimethyl carbonate and analyzed by Fourier-transform infrared spectroscopy (FT-IR) to determine the chemical moieties on the surfaces of the cathodes. FT-IR was conducted in an attenuated reflection mode under N₂ atmosphere in a dry room, where the dew point was maintained below -100 °C.

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To determine the F⁻ scavenging mechanism of PDMS, *ex situ* nuclear magnetic resonance spectroscopy (NMR; Bruker Advance 300 MHz spectrometer) was performed. In summary, 5.00 g of PDMS and 10 mL of electrolyte were thoroughly mixed in a plastic bottle. Thereafter, 10,000 ppm of water (H₂O) was added to the PDMS solution to generate hydrogen fluoride (HF) by the reaction of LiPF₆ with H₂O. The mixture was stirred for 3 h, and the supernatant was analyzed by ¹⁹F NMR to determine the changes in the chemical environment of PDMS.

Results and discussion

In this study, we developed a simple and efficient method to improve the electrochemical performance of LMO-based cells at elevated temperatures. The method involved embedding a fluoride-scavenging polymer onto the LMO electrodes, which greatly increased the chemical resistance of LMO against the nucleophilic attack of the F⁻ species (Fig. 1a and b). PDMS, a siloxane-functionalized polymer, was homogenously dispersed onto the LMO electrodes during the electrode coating process. The PDMS laver can scavenge nucleophilic F⁻ because silicon (in the siloxane groups) has a high binding affinity for F^- (Fig. 1c) [36,37]. Therefore, PDMS can effectively prevent the corrosion of LMO cathodes. Furthermore, only a small quantity of PDMS needs to be embedded to achieve this effect because of the large quantity of siloxane functional groups on the polymer backbone. Thus, the kinetic behavior of the cell will not be significantly affected by the presence of PDMS. Moreover, the embedding process is highly



Fig. 1. Schematics representing possible HF attack on the LMO cathode materials (a) without and (b) with the PDMS additive. (c) Proposed fluoride-scavenging mechanism of PDMS.

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