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A dual membrane composed of composite polymer membrane and glass fiber membrane for rechargeable lithium-oxygen batteries

Hyun-Sik Woo[a], Jae-Hong Kim[a], Yong-Bok Moon[a], Won Keun Kim[b], Kyoung Han Ryu[b], Dong-Won Kim[a,*]

[a] Department of Chemical Engineering, Hanyang University, Seongdong-Gu, Seoul 04763, Republic of Korea
[b] Research and Development Division, Hyundai Motor Group, Uiwang-Si, Gyeonggi-Do 16082, Republic of Korea

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ABSTRACT

Development of the lithium ion-conducting membrane with high ionic conductivity and good interfacial stability is a major challenge for lithium-oxygen batteries with high energy density. Herein, we design the dual membrane composed of Li^+ ion-conducting ceramic-based composite polymer membrane and glass fiber membrane. The optimized membrane exhibited a high ionic conductivity of 8.1×10^{-4} S cm^{-1} at ambient temperature and retained an electrolyte solution well in the membrane. The dual membrane also effectively suppressed the lithium dendrite growth and blocked superoxide anion radical attack toward polymer in the composite polymer membrane. The lithium-oxygen cell employing dual membrane exhibited improved cycle life (> 70 cycles) at a constant current density of 0.1 mA cm^{-2}, which was much better than the cell with either a composite polymer membrane alone or a glass fiber membrane alone.

1. Introduction

The rapid growth of the electric vehicle (EV) market has driven the development of rechargeable batteries with high specific energy and long cycle life. Lithium-ion batteries currently used in EVs have reached practical limits in terms of their energy density. As a promising alternative to lithium-ion batteries, a non-aqueous lithium-oxygen battery gas has received great attention due to its high theoretical energy density [1–12]. However, an implementation of the lithium-oxygen battery faces many challenges, such as the growth of lithium dendrite during charge and discharge cycles, evaporation of liquid electrolyte, and electrolyte decomposition by reactive superoxide anion radicals formed at cathode side. Therefore, the suppression of lithium dendrite growth, electrolyte depletion and electrolyte decomposition during the repeated cycling is very important for improving the cycling stability of lithium-oxygen batteries. Recent studies demonstrated that gel polymer electrolytes composed of liquid electrolyte in a polymer matrix were stable when in contact with lithium metal, and could effectively suppress the lithium dendrite growth and encapsulate a large amount of liquid electrolyte in the polymer matrix without leakage [13–17]. However, the polymer materials in the gel polymer electrolytes are unstable and degraded in the presence of Li_2O_2 produced at the carbon positive electrode during the discharge cycle in the lithium-oxygen cell [18] Additionally, the host polymer material would lose its mechanical strength when plasticized by organic solution. As an electrolyte with enhanced mechanical stability, inorganic electrolytes have been of particular interest due to their high mechanical strength and the absence of problems relating to vaporization of organic solvents [19]. However, high interfacial resistances between inorganic solid electrolyte and electrodes retard their application in lithium-oxygen cells. In addition, a lack of flexibility results in poor interfacial contacts between electrolyte and electrodes in the cell during cycling. Therefore, it is of our interest to develop the fast Li^+ ion-conducting membrane for enhancing the cycling stability of lithium-oxygen cells by suppressing the lithium dendrite growth and encapsulating the liquid electrolyte effectively in the cell, while maintaining both mechanical stability and interfacial contacts with electrodes during cycling.

In order to achieve this goal, we suggest the dual membrane composed of a composite polymer membrane and a glass fiber membrane for use in the lithium-oxygen cell. The composite polymer membrane was prepared with Li^+ ion-conducting lithium aluminum germanium phosphate (LAGP) particle and poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP)) copolymer. It was employed with a glass fiber membrane in the form of a dual membrane to fabricate the lithium-oxygen cell, as schematically illustrated in Fig. 1(a). The results presented herein demonstrate that the composite polymer membrane in the dual membrane can effectively suppress the drying out of liquid electrolyte and growth of lithium dendrite during cycling, while the

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[*] Corresponding author.
E-mail address: dongwonkim@hanyang.ac.kr (D.-W. Kim).

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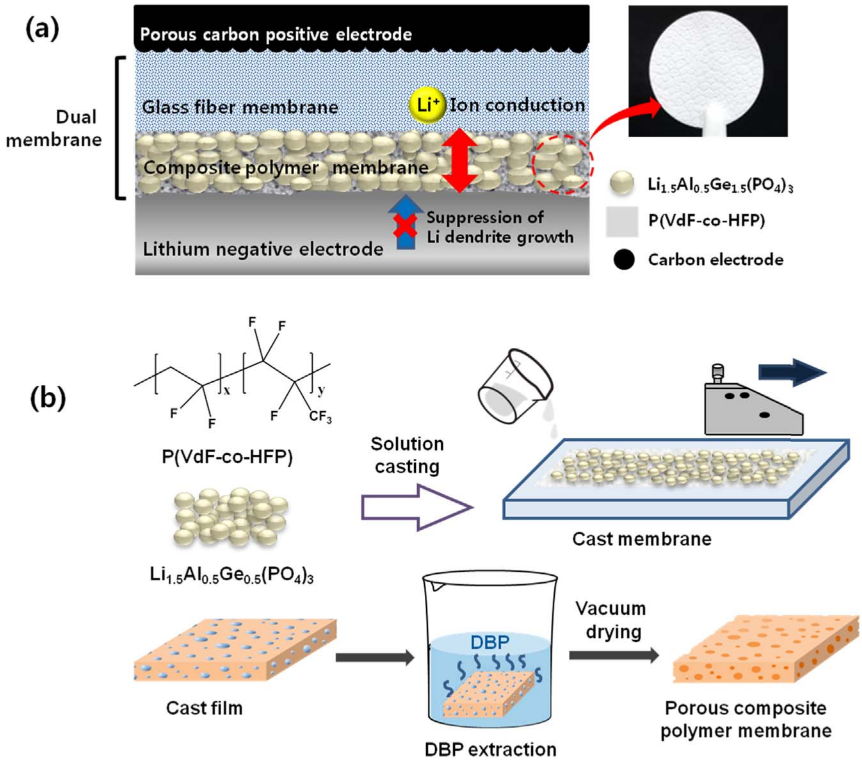

Fig. 1. (a) Schematic illustration of the lithium-oxygen cell consisting of a lithium negative electrode, a dual membrane and a porous carbon positive electrode. (b) Preparation of the porous composite polymer membrane composed of LAGP and P(VdF-co-HFP).

glass fiber membrane in the dual membrane is effective in blocking the superoxide anion radical attack toward polymer and maintaining the mechanical stability of the membrane, resulting in a remarkable improvement in the cycling stability of the lithium-oxygen cell.

2. Experimental

2.1. Preparation of the composite polymer membrane

LAGP ($Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$) powder was synthesized by a conventional solid solution method, as reported earlier [20]. A porous composite polymer membrane was prepared by solution casting and phase inversion method [21], as schematically presented in Fig. 1(b). Appropriate amounts of synthesized LAGP, P(VdF-co-HFP) (Kynar Flex 2801, Arkema) and dibutyl phthalate (DBP, Sigma-Aldrich) were uniformly mixed in acetone solvent using ball milling machine for 12 h. The resulting solution was then cast using a doctor blade on the glass plate. After evaporation of the acetone solvent for 1 h at room temperature, the cast film was immersed in methyl alcohol for DBP extraction and dried in a vacuum oven at 100 °C for 12 h to eliminate residual solvents. After vacuum drying, the obtained composite polymer membrane was approximately 80-µm thick. The contents of the LAGP in the composite polymer membranes were 50, 60, 70 and 80 wt%, and the corresponding composite polymer membranes will be designated as LAGP-50, LAGP-60, LAGP-70 and LAGP-80, respectively. As a control sample, non-conductive Al_2O_3 powder (particle size: ≤ 10 µm, Sigma-Aldrich) instead of LAGP was used in preparing the composite polymer membrane with the same thickness (80 µm).

2.2. Fabrication of lithium-oxygen cell

The positive electrode was prepared by doctor-blade casting of a slurry composed of 90 wt% Ketjen black EC600JD and 10 wt% poly (vinylidene fluoride) (PVDF, Solvay) binder dispersed in N-methyl pyrrolidone (NMP) on a gas diffusion layer (SGL GROUP, 35 BCE, Germany). Disk-shaped electrode having an area of 1.13 cm^2 was punched and vacuum-dried for 12 h at 110 °C. The specific mass of carbon in the positive electrode was approximately 1.0 mg cm^{-2}. The negative electrode was prepared by pressing lithium foil (Honjo Metal Co. Ltd., 200 µm) onto a copper current collector. A Swagelok-type lithium-oxygen cell was fabricated using a lithium negative electrode, a dual membrane (composite polymer membrane and glass fiber membrane) soaked with liquid electrolyte and a carbon positive electrode, as previously reported [22,23]. The liquid electrolyte was prepared by dissolving 1.0 M lithium bis(trifluoromethane) sulfonylimide (LiTFSI) in tetra(ethylene glycol) dimethyl ether (TEGDME). Karl Fisher titration using Mettler-Toledo Coulometer confirmed that the water content in the liquid electrolyte was less than 20 ppm. Cell assembly was carried out in an argon-filled glove box.

2.3. Characterization and measurements

X-ray diffraction (XRD) patterns of LAGP, P(VdF-co-HFP) and composite polymer membrane were obtained using an X-ray diffractometer (Rigaku M2500) with Cu Kα radiation. The morphological characterization of composite polymer membrane was performed by a scanning electron microscope (SEM, JEOL JSM-6300). Energy dispersive X-ray spectroscopy (EDS) was conducted to investigate the elemental distribution on the composite polymer membrane. To measure the ionic conductivity, the membrane soaked with liquid electrolyte was sandwiched between two stainless steel electrodes. The symmetric cell was put into an aluminum plastic pouch and sealed to permit measuring the ionic conductivity outside of a glove box. AC impedance measurements were carried out in the frequency range of 10 Hz to 100 kHz with an amplitude of 10 mV using a Zahner Electrik IM6 impedance analyzer. Raman spectra of the composite polymer membrane were obtained using a Raman spectrometer (NRS-3100) over the wavelength range of 100–2000 cm^{-1} at room temperature. The laser power was set to 2.5 mW and the resolution to 8.5 cm^{-1}. Cycling tests of the lithium-oxygen cells were performed within a limited capacity range of 1000 mAh (g carbon)$^{-1}$ at a constant current rate of 100 mA (g carbon)$^{-1}$ in the voltage range of 2.0–5.0 V under high-purity oxygen atmosphere. The morphologies of lithium electrodes and membranes after cycling were examined using field-emission scanning