Journal of Materials Chemistry A

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Artificially-engineered, bicontinuous anion-conducting/-repelling polymeric phases as a selective ion transport channel for rechargeable zinc-air battery separator membranes

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Abstract

Zinc (Zn)-air batteries have recently garnered a great deal of attention as a promising energy storage system to fulfill our ever-increasing demand for higher energy density power sources. Despite commercial success of primary Zn-air batteries, performances of rechargeable Zn-air batteries are still far below practically satisfactory levels. Among critical challenges facing the electrochemical rechargeability, crossover of zincate $(Zn(OH)_4^{2-})$ ions from Zn anode to air cathode (via separator membranes) has posed a formidable bottleneck. Here, as a facile and scalable polymer architecture strategy to address this ion transport issue, we demonstrate a new class of polymer blend electrolyte membranes with artificially-engineered, bicontinuous anion-conducting/-repelling phases (referred to as "PBE membranes"). As an anion-conducting continuous phase, an electrospun polyvinyl alcohol (PVA)/polyacrylic acid (PAA) nanofiber mat is fabricated. Into the PVA/PAA nanofiber mat, Nafion bearing pendant sulfonate groups is impregnated to form an anion-repelling continuous phase. Such bicontinuous phases-mediated structural uniqueness enables the PBE membrane to act as a selective ion transport channel, i.e., effectively suppresses $Zn(OH)_4^{2-}$ crossover (by continous Nafion phase offering Donnan exclusion effect) with slightly impairing OH⁻ conduction (predominantly through PVA/PAA nanofiber mat), eventually improving the cycling stability (cycle time = over 2500 min for PBE membrane vs. 900 min for a conventional polypropylene separator). The PBE membrane featuring the selective transport of OH⁻ and $Zn(OH)_4^{2-}$ ions is anticipated to pave a new route that leads us closer toward rechargeable Znair batteries.

Keywords: zinc-air batteries; electrochemical rechargeability; separator membranes; bicontinuous phases; selective ion transport

Introduction

Ever-increasing demand for higher energy density power sources has strongly spurred us to search for alternative energy storage systems beyond current state-of-the-art lithium ion batteries that are overwhelmingly widespread as a competent power source for portable electronic devices.¹⁻⁵ Among a vast variety of battery technologies reported to date, zinc (Zn)-air batteries have recently garnered substantial attention owing to their potentially high energy density (theoretically 1084 Wh kg⁻¹), flat working voltage, ecological benefits and low-cost active materials.⁵⁻⁷ Zn-air batteries are generally composed of Zn metal anodes, metal oxide catalyst-incorporated cathodes, potassium hydroxide (KOH)-based alkaline electrolyte solution and separator membranes. Primary Zn-air batteries have already been commercialized for use in medical devices, railway signals, navigation lights and so on.⁷ Despite such a success of the primary Zn-air batteries, development of electrochemically rechargeable Zn-air battery systems is still lagging and far below practically meaningful performance levels. Major challenges facing the rechargeable Zn-air batteries are concerned with electrochemically active materials, including air cathodes, Zn anodes and electrolyte solution.⁵⁻¹⁴

In addition, significant attention should be also paid to suppressing zincate ion $(Zn(OH)_4^{2^-})$ crossover through separator membranes. Upon discharging Zn-air cells, zinc (Zn^{2+}) ions that are oxidized at Zn anode react with hydroxyl (OH⁻) ions and promptly produce $Zn(OH)_4^{2^-}$ ions $(Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2^-})$, eventually converting to zinc oxide (ZnO).¹⁵⁻¹⁷ In order to facilitate reverse reaction $(Zn(OH)_4^{2^-} \rightarrow Zn^{2+} + 4OH^-, Zn^{2+} + 2e^- \rightarrow Zn)$ upon charging, $Zn(OH)_4^{2^-}$ ions should be located preferentially around Zn anode. However, $Zn(OH)_4^{2^-}$ ions, driven by their concentration gradient in Zn-air cells, are forced to migrate from Zn anode to cathode side via separator membranes.^{6,18,19} Meanwhile, conversion of

 $Zn(OH)_4^{2-}$ ions to ZnO is accelerated at the cathode compared to at the anode, because open system-induced asymmetric water evaporation at the cathode gives rise to lowering ZnO solubility in electrolyte solution. The resultant ZnO powders deposited on the air cathode behave as unwanted resistive layers to ion/electron conduction, thereby deteriorating capacity retention during charge/discharge cycling.^{5,6,18} Considering the aforementioned harmful influence of Zn(OH)₄²⁻ crossover and its dependence on separator membranes, development of an advanced separator membrane that can suppress Zn(OH)₄²⁻ crossover without deteriorating OH⁻ conduction is urgently needed, along with ongoing research activities on electrochemically-active battery materials and system design.

Currently, most Zn-air batteries employ microporous polyolefin films as a separator membrane.^{6,7,18,19} The polyolefin separator membranes have many advantageous attributes such as chemical/electrochemical stability and high ionic conductivity, however, their micrometer-sized pores (that are filled with liquid electrolyte) are not appropriate for ensuring selective transport of OH and Zn(OH)₄²⁻ ions. One promising approach to outperform the polyolefin separator membranes is the use of gel-type polymer electrolytes (GPEs) which are generally composed of polymer matrix and alkaline electrolyte solution.²⁰⁻ ²⁴ Representative examples of GPEs include alkaline liquid electrolyte-swollen polyvinyl alcohol (PVA),²¹ polyacrylic acid (PAA),^{22,23} polyvinyl chloride (PVC)²⁴ and their blends/composites.²²⁻²⁴ These previous studies on the GPEs showed some meaningful progresses in membrane structure and properties, however, most of them did not yet deliver compelling results of Zn(OH)₄²⁻ crossover. Moreover, most polymer matrices of the previously-reported GPEs tend to be chemically vulnerable to alkaline electrolyte solution, resulting in unsatisfactory long-term durability during cell operation.

Ion exchange membranes, represented by Nafion (a perfluorinated sulfonic acid

ionomer), are widely used in various application fields such as proton-exchange membrane fuel cells, redox-flow batteries, actuators and water treatments.²⁵⁻²⁷ Besides Nafion, other single ion polymer electrolytes (e.g., containing boronate groups^{28,29}) can be suggested as a potential single cation conductor. A distinctive function of the ion exchange membranes is socalled Donnan exclusion effect, i.e., charge difference-driven selective ion migration through membranes.^{30,31} However, upon their application to Zn-air batteries, the Donnan exclusion effect is not meaningfully realized because OH⁻ and Zn(OH)₄²⁻ ions show the same negative charge. The previous works on cation exchange membranes^{32,33} reported that the Zn(OH)₄²⁻ crossover was prevented, however, the OH⁻ conduction was seriously decreased at the same time. The opposite behavior of ion transport was observed at anion exchange membranes,¹⁹ i.e., good ionic conductivity was achieved, however, Zn(OH)₄²⁻ crossover was hardly suppressed.

Here, as a facile and scalable polymer architecture strategy to address the longstanding issues of ion transport phenomena mentioned above, we demonstrate a new class of polymer blend electrolyte membranes with artificially-engineered, bicontinuous anion-conducting/-repelling phases (referred to as "PBE membranes"). The basic concept of bicontinuous phases has been introduced in a variety of polymer blends and composites³⁴⁻³⁶ as an effective approach to provide synergistic effects of blend (/composite) components. Intrigued by such structural novelty and performance advantages of the "bicontinuous phases" concept, we rationally integrated a three dimensional (3D) interconnected anion-conducting phase with a 3D reticulated anion-repelling phase, in pursuit of building a new selective ion transport channel for OH and $Zn(OH)_4^{2-}$ ions.

As an ion-conducting continuous phase, a PVA/PAA nanofiber mat is fabricated using electrospinning technique. The PVA/PAA nanofiber mat, after being swollen with KOH

electrolyte solution, acts as highly-networked anion-conducting pathways. Into the porous region of the PVA/PAA nanofiber mat, Nafion (containing pendant sulfonate (SO_3^-) groups) is impregnated as an anion-repelling continuous phase. To maximize the Donnan exclusion effect in the PBE membrane while through-thickness directional connectivity of ion-conducting phases is not impaired, it is preferable that the ion-repelling continuous phase (Nafion) occupies relatively larger volume than the ion-conducting continuous phase (PVA/PAA), which thus stimulates us to design the Nafion matrix-impregnated PVA/PAA nanofiber mat architecture. Such structural uniqueness enables unprecedented progress in selective transport of OH⁻ and Zn(OH)₄²⁻ ions, eventually playing a viable role in achieving superior electrochemical rechargeability of Zn-air cells.

Experimental section

Fabrication of PBE membranes via electrospinning/impregnation process

The PVA/PAA nanfiber mat was fabricated using an electrospinning technique. The PVA/PAA solution (concentration = 7.5 wt.%), which was prepared by dissolving PVA (Aldrich, M.W. = 145,000 ~ 189,000 g mol⁻¹) and PAA (Aldrich, M.W. = 89,000 ~ 98,000 g mol⁻¹) in distilled water, was electrospun at 9.5 kV with a feed rate of 8.3 μ L min⁻¹. The electrospun PVA/PAA nanofibers were collected on a stainless steel plate which was placed at a distance of 10 cm from the electrospinning nozzle. To further enhance chemical stability, the PVA/PAA nanofiber mat went through thermal treatment at 150 °C/3 h. The PVA/PAA nanomat was then immersed in 7 wt.% Nafion solution (solvent = DMF) that was prepared by solvent exchange process of Nafion 521 solution (solvent = water/isopropyl alcohol (= 9/1 (w/w))). The Nafion-impregnated PVA/PAA nanomat was annealed at 120 °C for 2 h in argon (Ar) environment, yielding the PBE membrane with a thickness of 29 (± 5 μ m). As a control

6

sample, a commercial microporous polypropylene (PP) membrane (Celgard3501) was chosen. In addition, as other control samples, PVA/PAA film (28 (\pm 5 µm)) and Nafion film (27 (\pm 5 µm)) were respectively prepared with the same polymer solutions used for the PBE membrane.

Structural/physicochemical characterization of PBE membranes

The structural analysis of the PBE membrane was conducted by a field emission scanning electron microscope (FE-SEM, FEI) equipped with an energy-dispersive spectrometer (EDS). The functional groups of the PBE membrane were elucidated using a FT-IR spectrometer (ALPHA-P, Bruker) with a spectral resolution of 4 cm⁻¹. The electrolyte uptake (ΔW (%) = $[(W_{wet} - W_{dry})/W_{dry}] \times 100)$ of the membranes was calculated with weight difference before/after being soaked in the 6M KOH electrolyte solution at room temperature.^{37,38} Additionally, the electrolyte uptake-induced dimensional change of the membranes was also estimated using the equation of ΔV (volume-based, %) = $[(V_{wet} - V_{dry})/V_{dry}] \times 100$.

Analysis of selective ion transport phenomena in PBE membranes

The ion conductivity of the membranes was examined using an AC impedance analysis (VSP classic, Bio-Logic) over a frequency range of 1 - 106 Hz at room temperature.³⁷ The crossover of $Zn(OH)_4^{2-}$ ions through the membranes was investigated using a kind of diffusion cell.^{26-28,30,39} The time-dependent concentration variation of $Zn(OH)_4^{2-}$ ions was quantitatively monitored using inductively coupled plasma atomic emission spectrometry (ICP-OES, Varion). More details on the crossover measurement were described in our previous report.³⁷ In addition, from the experimental data of $Zn(OH)_4^{2-}$ crossover, diffusion coefficients of $Zn(OH)_4^{2-}$ ions across separator membranes were calculated using the

7

following equations^{40, 41}:

$$\ln\left(\frac{C_A}{C_A - C_B}\right) = \frac{DA}{V_B L}t$$
(1)

, where D is the diffusion coefficients of $Zn(OH)_4^{2-}$ ions (m² s⁻¹); A is the effective area of the membrane (m²); L is the thickness of the membrane (m); C_A is the concentration of $Zn(OH)_4^{2-}$ ions in enrichment side (here, left chamber, mol L⁻¹); C_B is the concentration of $Zn(OH)_4^{2-}$ ions in deficiency side (right chamber, mol L⁻¹); and t is the elapsed time (s).

Electrochemical characterization of Zn-air cells assembled with PBE membranes

A Zn-air cell (Supporting Information Figure S1) was elaborately designed to make a relative comparison between different separator membranes, where other cell components such as Zn anode and air cathode were fixed. The major cell components were integrated in the following order: Zn anode electrodeposited on a nickel plate ($2.0 \times 2.0 \text{ (cm x cm)}$), separator membrane ($2.6 \times 2.6 \text{ (cm x cm)}$) and air cathode ($3.0 \times 3.0 \text{ (cm x cm)}$). To make the Zn anode, the nickel plate was electrodeposited in zinc sulfate solution (0.8M in distilled water) at a current density of 50 mA cm⁻² for 1 h.⁴²⁻⁴⁴ As an air cathode, a commercialized one (ADE75 (catalyst = Co_3O_4), MEET) was used. An acryl plate was employed as a top cap to allow passage of air into the cell. The cell performance was examined using a potentiostat/galvanostat (VSP classic, Bio-Logic) at room temperature. The cell was repeatedly discharged and charged at a constant current density of 20 mA cm⁻² with each cycle period being 10 min (5 min discharge followed by 5 min charge) under a voltage range of 0.6 (discharge cut-off) - 2.4 V (charge cut-off).⁴⁵⁻⁴⁷ If the cells may reach the cut-off charge voltage prior to the predetermined time of 5 min due to the unwanted increase of cell polarization, they are programmed to immediately terminate electrochemical reaction.

Fabrication of PBE membranes and their structural/physicochemical characteristics

A salient structural feature of the PBE membrane is the artificially-engineered bicontinuous anion-conducting/-repelling phases. Phase continuity in polymer blends and composites is known to be determined by controlling thermodynamic variables such as composition ratio, temperature, pressure and phase affinity.³⁴⁻³⁶ For this reason, construction of bicontinuous phases often requires complicated experimental procedures and also has difficulty attaining reproducible results. By contrast, the bicontinuous phases of the PBE membrane are artificially engineered without relying on the aforementioned thermodynamic variables and thus their embodiment is relatively simple and reliable.

The manufacturing procedure of PBE membranes was schematically illustrated in Scheme 1a. The PVA/PAA nanofiber mat was fabricated using the electrospinning technique and then was subjected to thermal treatment in order to allow intermolecular condensation reaction²²⁻²⁴ between PVA and PAA. Into the PVA/PAA nanomat, Nafion solution was impregnated, leading to the formation of the PBE membrane. It is again underlined that ion transport in the PBE membrane proceeds predominantly through the anion-conducting PVA/PAA nanofiber mat due to the existence of anion-repelling (i.e., Donnan exclusion effect) continuous Nafion phase (Scheme 1b). This unusual morphology of the PBE membranes appears to be a reverse form of previously-reported reinforced composite membranes (e.g., for use in proton exchange membrane fuel cells), which are composed of ion-conducting matrices and electrochemically-inert fiber scaffolds.⁴⁸⁻⁵⁰

The porous structure of the electrospun PVA/PAA nanomat was characterized as a function of PVA/PAA composition ratio (Supporting Information Figure S2). At the lower

PVA content (PVA/PAA = 5/5 (w/w)), the PVA/PAA nanomat lost its dimensional integrity upon being immersed in 6M KOH electrolyte solution due to poor chemical stability of $PAA^{22,23}$ in alkaline electrolyte solution. Meanwhile, at the higher PVA content (PVA/PAA = 9/1 (w/w)), bead-like, irregularly-shaped nanofibers were produced during the electrospinning process. By comparison, large numbers of well-defined nanofibers were compactly piled up at the composition ratio of PVA/PAA = 7/3 (w/w) and the resultant nanofiber mat showed no significant dimensional disruption in the KOH electrolyte solution.

The electrospun PVA/PAA (= 7/3 (w/w)) nanofiber mat was then subjected to the thermal treatment at 150 °C/3 h, in order to further enhance its chemical stability. At this condition, intermolecular condensation reaction between hydroxyl groups of PVA and carboxylic groups of PAA is allowed to occur,²²⁻²⁴ thereby constructing new chemical bonds between PVA and PAA. Here, in order to better understand the intermolecular condensation reaction, a PVA/PAA film (instead of the PVA/PAA nanofiber mat) was prepared as a model system using a typical solution casting method. The intermolecular condensation reaction of the PVA/PAA film was elucidated by analyzing its FT-IR spectra (Figure 1a). The intensity of characteristic peaks assigned to -OH groups ($3000 \sim 3500 \text{ cm}^{-1}$, originating from PVA chains) and -C=O groups (1750 cm⁻¹, corresponding to PAA chains) was weakened after the thermal treatment, demonstrating the formation of intermolecular ester linkages. In addition, the thermally-treated PVA/PAA film did not show any dimensional change after being soaked in 6M KOH electrolyte solution for 24 h at room temperature (Figure 1b). Moreover, the gel content (= insoluble polymer fraction after solvent (water) extraction) of the thermally-treated PVA/PAA film was found to be approximately 99 % (vs. 45 % for the PVA/PAA film before the thermal treatment).

The PVA/PAA nanomat (after the thermal treatment at 150 °C/3 h) was immersed in

Nafion solution, thus yielding the Nafion-impregnated PVA/PAA nanomat. From the weight difference before/after the impregnation of Nafion, the composition ratio of (PVA/PAA nanomat)/Nafion was estimated to be 47/63 (w/w). Meanwhile, in order to improve structural stability^{51,52} of the impregnated Nafion, the PBE membrane was annealed at 120 °C for 2 h in argon atmosphere. In Nafion-containing polymer blends, sulfonate groups of Nafion tend to attack specific chemical bonds⁵³⁻⁵⁵ of adjacent polymers when the blends are exposed to air environment at high temperature. When the Nafion-impregnated PVA/PAA nanomat was annealed at 120 °C in air environment, its color became brownish and the thermal stability (examined from the TGA profiles) was deteriorated (Supporting Information Figure S3), revealing the air-induced chemical degradation. By comparison, in argon environment, the PBE membrane showed no appreciable change in color and also the superior thermal tolerance.

The surface and cross-sectional SEM images (Figure 1c) exhibit that Nafion was successfully impregnated into the PVA/PAA nanomat without detectable levels of pinholes or structural defects. This morphological uniqueness was further verified by analyzing the EDS image (Figure 1d). The F elements originating from Nafion (represented by yellow dots) were uniformly dispersed over wide area of the PBE membrane. The non-porous morphology of the PBE membrane is a distinctive feature as compared to a conventional microporous PP separator membrane (Celgard3501, Supporting Information Figure S4). Figure 1e shows that the PBE membrane was wound along a plastic rod (diameter = 10 mm) and also not physically broken after being folded, demonstrating its good mechanical flexibility. The tensile properties of the composite membrane and Celgard3501 were measured (Supporting Information Figure S5). The tensile strength at break of the PBE membrane was lower than that of Celgard3501, however, the PBE membrane showed the higher tensile modulus than

Celgard3501. Taking into consideration that tensile modulus of a membrane, along with tensile strength, is an important factor to affect continuous (e.g., roll-to-roll) manufacturing processes, this result demonstrates potential applicability of the PBE membrane. Our future works will be devoted to further improving the tensile strength of PBE membranes.

Bicontinuous anion-conducting/-repelling phases-enabled selective ion transport phenomena

The PBE membrane should absorb KOH electrolyte solution in order to be electrochemically active (i.e., to provide ionic conductivity). Table 1 shows that the electrolyte uptake of the PBE membrane was 31.2 %, which was between those of its components (i.e., thermally-treated PVA/PAA film (= 61.1 %) and Nafion film (= 2.6 %)). It is known that electrolyte uptake of GPEs tends to provoke swelling-induced dimensional change.^{38,56} The volume-based dimensional changes (ΔV) of the PBE membrane, PVA/PAA film and Nafion film were observed to be respectively 35.6 %, 70.1 % and 16.0 %, which seem to be consistent with the results of electrolyte uptake.

Based on an understanding of the electrolyte uptake mentioned above, the ionic conductivity of the PBE membrane was estimated and compared with those of control samples. The Nyquist plots for calculating ionic conductivity were shown in Supporting Information Figure S6. In the PBE membrane, transport of OH⁻ ions proceeds predominantly through the electrolyte-swollen, 3D-interconnected PVA/PAA nanofiber mat, because the Nafion phase bearing pendant sulfonate groups strongly repels anions by its Donnan exclusion effect. Notably, in comparison to Nafion film (= 0.8 mS cm⁻¹), the PBE membrane showed the remarkably higher ionic conductivity (= 6.6 mS cm⁻¹), although which was slightly lower than that (= 11.2 mS cm⁻¹) of the PVA/PAA film. In addition, the OH⁻

transference number $(t_{OH^-} = \frac{nF}{lt} (C^f V^f - C^i V^i))$ was investigated using the Hittorf's method⁵⁷⁻⁵⁹ (Supporting Information Figure S7), wherein *n* is the charge of OH⁻ ions, *F* is the Faraday constant, *I* is the constant current, *t* is the elapsed time, $C^i \& C^f$ are the initial & final concentration of OH⁻ ions, and $V^i \& V^f$ are the initial & final volume of electrolyte in the chamber. The Nafion film presented the lowest OH⁻ transference number than other membranes ($t_{OH^-} = 0.14$ for Nafion, 0.77 for PVA/PAA film, 0.52 for PBE membrane), apparently confirming its Donnan exclusion effect. These results underscore that the through-thickness directional interconnectivity of the anion-conducting phase (i.e., PVA/PAA nanofiber mat) was well developed in the PBE membrane, thereby playing a key role in providing the good ionic conductivity.

The $Zn(OH)_4^{2^{-}}$ crossover through separator membranes was investigated in detail using a diffusion cell. To visualize the crossover phenomena, 0.1 wt.% blue dye aqueous solution was placed in the left chamber of the diffusion cell and then color change in the right chamber was traced as a function of elapsed time (Supporting Information Figure S8). The PBE membrane effectively prevents the crossover of blue dye compared to Celgard3501. Moreover, in order to better mimic the real operating condition of Zn-air cells, 0.5M Zn(OH)₂ solution was poured into the left chamber and the concentration difference-driven Zn(OH)₄²⁻ crossover toward the right chamber via the membranes was quantitatively estimated using the ICP-OES analysis.³⁹ Figure 2a shows that, for all the membranes, the Zn(OH)₄²⁻ concentration in the right chamber increases with elapsed time. Consistent with the results of the blue dye (Supporting Information Figure S8), the PBE membrane significantly prevented the Zn(OH)₄²⁻ crossover while Celgard3501 showed a steep increase in the Zn(OH)₄²⁻ concentration with time. Also, the PBE membrane presented the lower crossover concentration of Zn(OH)₄²⁻ ions than the PVA/PAA film. Meanwhile, as expected, the

13

 $Zn(OH)_4^{2^2}$ crossover was most suppressed at the Nafion film. The above-mentioned results demonstrate the important role of the continuous Nafion phase in preventing the $Zn(OH)_4^{2^2}$ crossover through the PBE membrane. As a supplementary experiment to further elucidate the Nafion phase-driven Donnan exclusion effect, zeta potential of the membranes was measured using a streaming potential technique, where HCl (at pH < 7.0) and KOH (at pH > 7.0)-incorporated KCl aqueous solution was employed.³¹ Whereas the zeta potential of Celgard3501 was not changed over a wide range of pH, the PBE membrane showed a decline in the zeta potential with increasing pH values (Figure 2b), verifying the existence of anionic groups (assigned to sulfonate groups of Nafion phase) in the PBE membrane.

These results of ionic conductivity and $Zn(OH)_4^{2-}$ crossover (expressed by diffusion coefficients (D) of $Zn(OH)_4^{2-}$ ions that were determined from the plots of Figure 2a. More details on the calculation procedure were described in the experimental section) were summarized in Figure 2c. Of the separator membranes investigated herein, the PBE membrane showed the well-balanced ion conduction behavior, i.e., effectively suppressed the $Zn(OH)_4^{2-}$ crossover with slightly impairing the OH⁻ conduction. This quantitative comparison of ion transport phenomena underlines the exceptional function of the bicontinuous Nafion and PVA/PAA nanomat phases as a selective ion conduction channel.

Advantageous effects of PBE membranes on electrochemical rechargeability of Zn-air batteries

The electrochemical stability window of the PBE membrane was investigated using cyclic voltammetry (CV) technique. The CV profiles (Supporting Information Figure S9) show that no appreciable decomposition of any components in the PBE membrane takes

Journal of Materials Chemistry A

place within the operating voltage range (vs. Pt/Pt^{2+}), indicating the good electrochemical stability comparable to that of Celgard3501.

The galvanostatic discharge/charge profiles of Zn-air cells were provided as a function of cycle time (Figure 3). More details on the charge/discharge cycling condition were described in the experimental section. All of the cells, except for the cell incorporating Nafion film, showed the stable voltage profiles at the beginning of cycling. The cell with Nafion film (Figure 3a) presented the considerably large discharge/charge polarization due to its extremely low ionic conductivity, resulting in the very poor cycling stability.

As the cycle time increased, the difference in the electrochemical rechargeability between the separator membranes became pronounced. The cell with Celgard3501 (Figure 3b) showed the continuous increase in cell polarization with cycling, eventually reaching the cutoff charge voltage after cycle time of 900 min. Similar behavior in the cycling performance was observed at the cell with the PVA/PAA film (Figure 3c). By comparison, the cell containing the PBE membrane (Figure 3d) showed the remarkable improvement in the cycling stability. Notably, no appreciable deterioration in the discharge/charge performance was observed even after cycle time of 2500 min. This intriguing dependence of electrochemical rechargeability on separator membranes is quite consistent with the previously observed transport phenomena of OH^{-} and $Zn(OH)_{4}^{2-}$ ions (Figure 2c). The PBE membrane showing the well-balanced OH⁻ conduction and $Zn(OH)_4^{2-}$ crossover achieved the best cycling stability (over 2500 min), demonstrating the advantageous effects of its bicontinuous ion-conducting/-repelling phases on the electrochemical rechargeability of Znair cells. To visualize such performance benefits of the PBE membrane over Celgard3501, hypnosis-spiral wheels were connected to the Zn-air cells and their operation was monitored with cycle time. After the cycle time of 900 min, the hypnosis-spiral wheel connected to the

cell incorporating Celgard3501 stopped its rotating motion (Figure 3e, Supporting Information Figure S10a). By contrast, the cell with the PBE membrane still operated the hypnosis-spiral wheels without any difficulties (Figure 3f, Supporting Information Figure S10b).

To further elucidate the PBE membrane-driven improvement in the cycling stability, morphological change of the separator membranes and the air cathodes before/after the cycling test was investigated, with a particular focus on ZnO deposition (converted from Zn(OH)₄²⁻ ions). For Celgard3501, large numbers of flower-shaped ZnO powders were randomly deposited on the separator surface facing the air cathode (Figure 4a). In addition, the air cathode surface was largely covered with ZnO powders (Figure 4b). The white powders (observed in the digital photograph) and also the presence of Zn elements (represented by yellow dots in the EDS image) verify the deposition of ZnO powders on the air cathode. This morphological result demonstrates that Celgard3501, due to its micrometersized pores filled with liquid electrolyte, does not have the capability to selectively prevent $Zn(OH)_4^{2-}$ crossover, which is conceptually illustrated in Figure 4c. At air-exposed cathodes, driven by lower ZnO solubility in alkaline electrolyte solution, conversion of $Zn(OH)_4^{2-1}$ ions (that reach air cathode through separator membranes) to ZnO powders could be accelerated. The ZnO powders deposited on the air cathode are likely to act as unwanted resistive layers that deteriorate electrochemical activity of bifunctional catalysts, thus exerting harmful effect on capacity retention with electrochemical cycling.^{5,6,18} By comparison, the relatively clean surface, indicating the deposition of negligible amount of ZnO powders, was observed on the PBE membrane (Figure 4d) and also the air cathode (Figure 4e) even after the longer cycle time (2500 min). This result confirms that the PBE membrane effectively prevents $Zn(OH)_4^{2-}$ crossover (the conceptual illustration is depicted in Figure 4f), eventually enabling a

Journal of Materials Chemistry A

remarkable improvement in the cycling stability far beyond those achievable with conventional microporous polyolefin separators (e.g., Celgard3501).

To attain better understanding of this beneficial contribution of the PBE membrane, the Zn-air cells (denoted as 1st cells) that underwent the cycling test were disassembled and then the membranes in the cells were collected. Subsequently, the cycled membranes were combined with fresh electrodes and electrolytes, producing new Zn-air cells (herein, denoted as 2nd cells). The 2nd cell incorporating the reused Celgard3501 (that was obtained after the cycle time of 900 min in the 1st cell) did not present normal charge/discharge profiles, thus yielding no appreciable charge/discharge capacities (Supporting Information Figure S11a). This result is a good evidence to prove that the reused Celgard3501 was already contaminated with large numbers of unwanted ZnO powders in the 1st cell and thus failed to offer meaningful ionic conduction pathways in the 2nd cell. This unusual charge/discharge behavior of the 2nd cell was verified by analyzing the cathode surface after the 2nd cycling test. Because the ZnO-contaminated Celgard3501 lost its ion-conducting capability and consequently did not allow normal charge/discharge reaction any longer (i.e., Zn(OH)₄²⁻ ions were not likely to be generated), no detectable amount of ZnO powders were found on the cathode surface (Supporting Information Figure S11b). In comparison to the results of Celgard3501, the 2nd cell incorporating the reused PBE membrane (obtained after the cycle time of 2500 min in the 1st cell) showed the normal charge/discharge profiles with cycling (Supporting Information Figure S11c). Also, the cathode surface was clean and ZnO powders were hardly observed after the 2nd cycling test (Supporting Information Figure S11d). In overall, no significant difference in the cycling performance and the cathode surface was observed between the 1st cell and the 2nd one. This result exhibits that the ion transport capability of the reused PBE membrane was not impaired after the 1st electrochemical

cycling test (operated for 2500 min), demonstrating the long-term electrochemical durability of the PBE membrane.

Although we achieved significant progress in the separator membranes, there is no doubt that other challenging issues mainly associated with electrodes and electrolytes,⁵⁻¹⁴ including insufficient electrochemical function of Zn anode materials and bifunctional (oxygen reduction reaction/oxygen evolution reaction) catalysts, hydrogen gas-induced structural instability of electrodes and formation of unwanted byproducts (e.g., K₂CO₃), still remain unresolved as formidable obstacles to the realization of practically-meaningful Zn-air batteries. We anticipate that combination of the PBE membrane with next-generation electrodes and electrolytes will allow further improvement in electrochemical rechargeability of Zn-air batteries.

Conclusion

In summary, we demonstrated the artificially-engineered, bicontinuous anionconducting (electrospun PVA/PAA nanofiber mat)/-repelling (Nafion with pendant sulfonate groups) polymeric phases as a selective ion transport channel to bring the separator membrane-driven performance benefits for electrochemically rechargeable Zn-air batteries. Benefiting from to the bicontinuous phases-mediated morphological uniqueness, the PBE membrane enabled the remarkable advances in the selective transport of OH⁻ and Zn(OH)₄²⁻ ions, i.e., suppressed the Zn(OH)₄²⁻ crossover (by the continous Nafion phase offering Donnan exclusion effect) with slightly impairing the OH⁻ conduction (predominantly through the KOH electrolyte-swollen, 3D-interconnected PVA/PAA nanofiber mat). Such unusual ion conduction behavior of the PBE membrane played a viable role in improving the cycling stability far beyond that achievable with Celgard3501. Notably, the cell with the PBE membrane showed the electrochemical rechargeability over 2500 min (at 20 mA cm⁻² and 10 min cycle period), compared to the cell with the Celgard3501 (900 min). These advantageous effects of the PBE membrane were further verified by analyzing the structural change of the separator membranes and also cathode surface after the cycling test. Intriguingly, the PBE membrane preserved its ion-conducting capability after the cycling test and thus was able to be reused in the subsequent 2nd cell, demonstrating the excellent long-term electrochemical durability. Numerous technical challenges (particularly related to electrodes and cell design) still remain unresolved, however, we believe that the PBE membrane featuring the bicontinuous phases-enabled selective ion transport opens a new membrane opportunity that can speed up the realization of electrochemically rechargeable Zn-air batteries.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and future Planning (NRF-2012-M1A2A2-029542). This research was also supported by the Korea Research Institute of Chemical Technology (KRICT) as a cooperation project of KRICT own project. This work was also supported by the 2015 Research Fund (1.150034.01) of UNIST (Ulsan National Institute of Science and Technology).

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Scheme 1. (a) Schematic representation depicting overall manufacturing procedure of PBE membrane. (b) Conceptual illustration underlying the unique function of PBE membrane as a selective ion transport channel, wherein anions are allowed to migrate predominantly through ion-conducting PVA/PAA nanofiber mat due to existence of ion-repelling (i.e., Donnan exclusion effect) continuous Nafion phase.

Figure 1. (a),(b) Effect of thermal treatment (conducted at 150 °C/3 h) on physical properties of PVA/PAA film (chosen as a model system for PVA/PAA nanofiber mat): (a) FT-IR spectra verifying intermolecular condensation reaction between hydroxyl groups of PVA and carboxylic groups of PAA; (b) photographs showing chemical stability against 6M KOH electrolyte solution (after being soaked for 24 h at room temperature). (c),(d) Morphological characterization of PBE membrane: (c) SEM image (surface and cross-sectional (inset)); (d) EDS image (yellow dots represent F elements of Nafion). (e) Photographs showing mechanical flexibility of PBE membrane upon winding (rod diameter = 10 mm) and folding.

Figure 2. Quantitative analysis of selective ion transport phenomena: (a) $Zn(OH)_4^{2-}$ crossover through membranes with elapsed time (estimated by measuring $Zn(OH)_4^{2-}$ concentration in the right chamber of diffusion cells shown in Supporting Information Figure S8); (b) variation in zeta potential of PBE membrane and Celgard3501 as a function of pH; (c) comparison in selective ion transport (ionic conductivity vs. $Zn(OH)_4^{2-}$ crossover (expressed by diffusion coefficients (D) of $Zn(OH)_4^{2-}$ ions) between different membranes.

Figure 3. Galvanostatic charge/discharge cycling of Zn-air cells assembled with different membranes as a function of cycle time: (a) Nafion film; (b) Celgard3501; (c) PVA/PAA film; (d) PBE membrane. The cell was repeatedly discharged and charged at a constant current density of 20 mA cm⁻² with each cycle period being 10 min (5 min discharge followed by 5 min charge) under a voltage range of 0.6 (discharge cut-off) - 2.4 V (charge cut-off). If the cells may reach the cut-off charge voltage prior to the predetermined time of 5 min, they are programmed to immediately terminate electrochemical reaction. (e), (f) photographs showing the operation of hypnosis-spiral wheels connected to Zn-air cells after the cycle time of 900 min: (e) Celgard3501; (f) PBE membrane.

Figure 4. Structural change of separator membranes and air cathodes after the cycle time of 900 min, with a particular focus on deposited ZnO powders. (a)-(c) Celgard3501: SEM and EDS images (yellow dots represent Zn elements of ZnO powders) of (a) Celgard3501 surface facing air cathode and (b) air cathode surface (an inset is a digital photograph); (c) conceptual illustration of $Zn(OH)_4^{2-}$ crossover through Celgard3501. (d)-(f) PBE membrane: SEM and EDS images of (d) PBE membrane surface facing air cathode and (e) air cathode surface (an inset is a digital photograph); (f) conceptual illustration of $Zn(OH)_4^{2-}$ crossover through PBE membrane.

Table 1. Basic membrane properties (thickness, electrolyte uptake, electrolyte uptakeinduced volume change, ionic conductivity and diffusion coefficient of $Zn(OH)_4^{2-}$ ions) of Celgard3501, PVA/PAA film, Nafion film and PBE membrane.



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| Samples | Thickness (µm) | КОН | Volume | Ionic | Diffusion Coefficient |
|--------------|-------------------|----------|------------------|----------------|---|
| | | Uptake | Change | Conductivity | $(Zn(OH)_4^{2-})$ |
| | | (Δm) (%) | (ΔV) (%) | $(mS cm^{-1})$ | $(x \ 10^{-7} \mathrm{cm}^2 \mathrm{min}^{-1})$ |
| Celgard3501 | 24 | 80.1 | - | 12.8 | 232.4 |
| PVA/PAA film | 24 | 61.1 | 70.1 | 11.2 | 110.2 |
| Nafion film | 27 | 2.6 | 16.0 | 0.8 | 0.4 |
| PBE membrane | 26 | 31.2 | 35.6 | 6.6 | 4.1 |
| | | | | | |

Table 1. Basic membrane properties (thickness, electrolyte uptake, electrolyte uptake, induced volume change, ionic conductivity and diffusion coefficient of $Zn(OH)_4^{2-}$ ions) of Celgard3501, PVA/PAA film, Nafion film and PBE membrane.

The artificially-engineered, bicontinuous anion-conducting/-repelling polymeric phases were demonstrated as a selective ion transport channel to bring separator membrane-driven performance benefits for rechargeable Zn-air batteries. The new membrane featuring this structural uniqueness effectively suppressed $Zn(OH)_4^{2^-}$ crossover (by continous Nafion phase) with slightly impairing OH⁻ conduction (through PVA/PAA nanofiber mat). Such selective ion transport phenomena played a viable role in improving cycling stability far beyond those achievable with conventional separator membranes.

Keywords: zinc-air batteries; electrochemical rechargeability; separator membranes; bicontinuous phases; selective ion transport

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Artificially-engineered, bicontinuous anion-conducting/-repelling polymeric phases as a selective ion transport channel for rechargeable zinc-air battery separator membranes

