Supporting Information

Pyrochlore zirconium gadolinium oxide nanorod composite membrane for suppressing the formation of free radical in PEM fuel cell operating under dry condition

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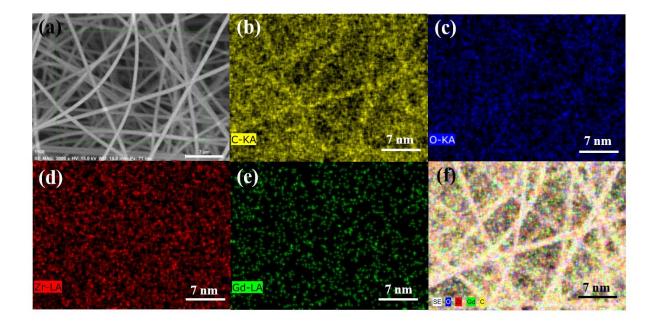


Fig. S1. FE-SEM images of as-spun PAN/Zracac:Gdacac nonwoven fiber; (a) bright field image, (b) C-K edge, (c) O-K edge, (d) Zr-L edge, (e) Gd-L edge and (f) overlay image.

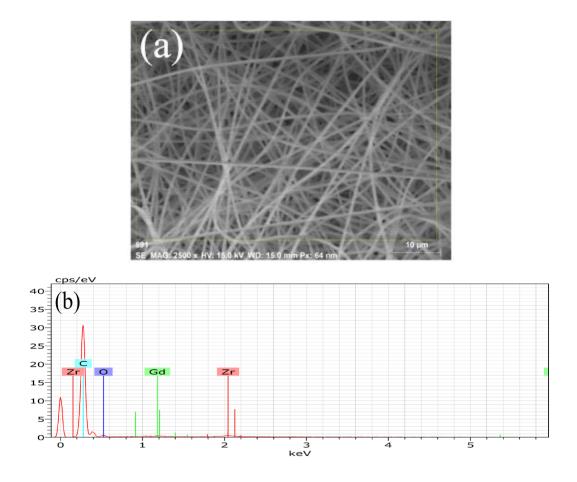


Fig. S2. (a) FE-SEM image of as-spun PAN/Zracac:Gdacac nonwoven fiber mat and (b) Corresponding EDS spectrum.

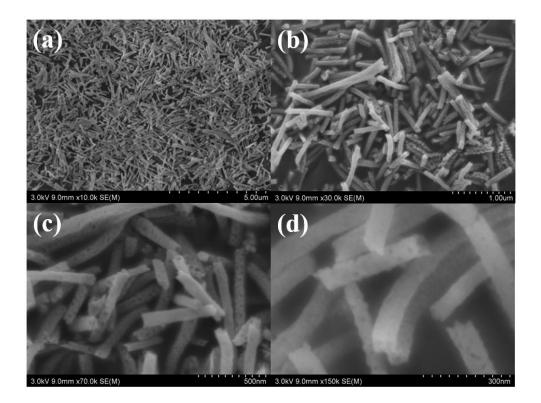


Fig. S3. FE-SEM images of ZrGd oxide nanorods; (a, b) low magnification, (c, d) high magnification images.

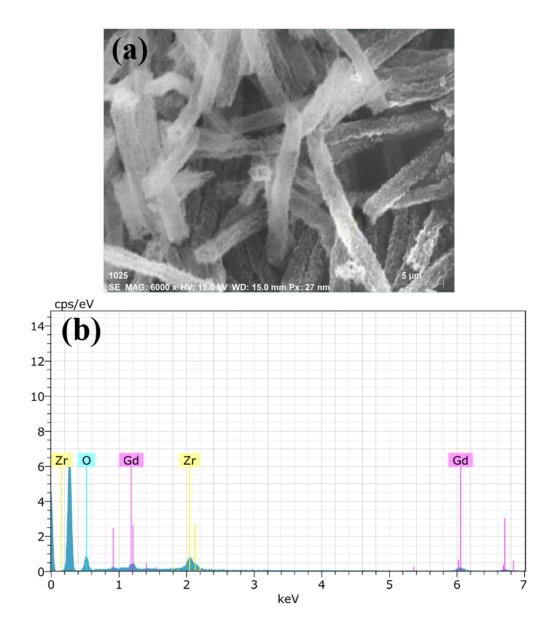


Fig. S4. (a) FE-SEM image of ZrGdNR and (b) Corresponding EDS spectrum.

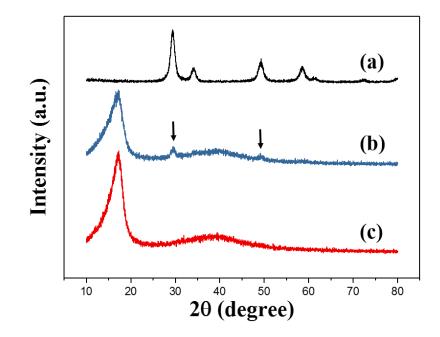


Fig. S5. XRD pattern of (a) ZrGdNR, (b) Nafion-GdZrNR-1.5 composite membrane and (c) Nafion membrane.

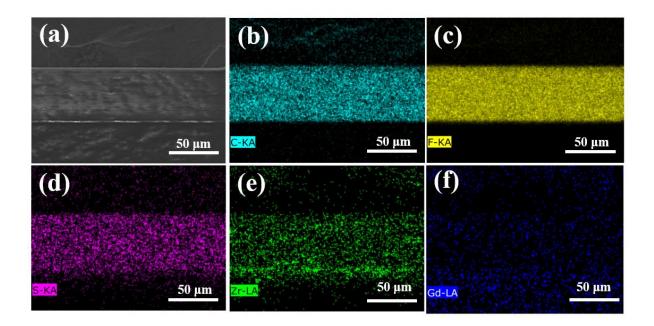


Fig. S6. FE-SEM elemental mapping analysis of Nafion-ZrGdNR-1.5 membrane; (a) bright field image, (b) C-K edge, (c) F-K edge, (d) S-K edge, (e) Zr-L edge, and (f) Gd-L edge.

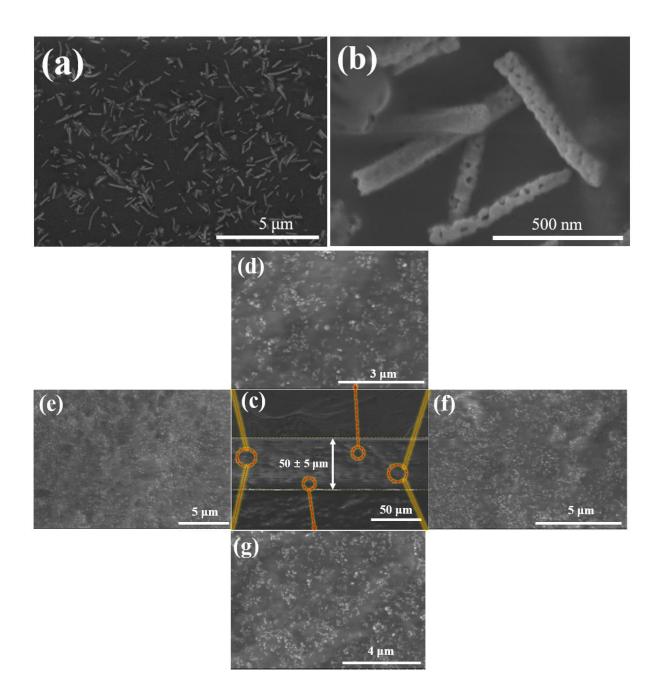


Fig. S7. FE-SEM images of Nafion-ZrGdNR-1.5 composite membrane; (a) low magnification image obtained at surface, (b) high magnification at surface view, (c) low magnification images obtained at different places of the cross-sectioned membrane and (d,e,f and g) high magnification at cross section view. Nanorod appears as particles in the SEM images of cross-sectioned positions. Nanorods are well dispersed within the membrane.

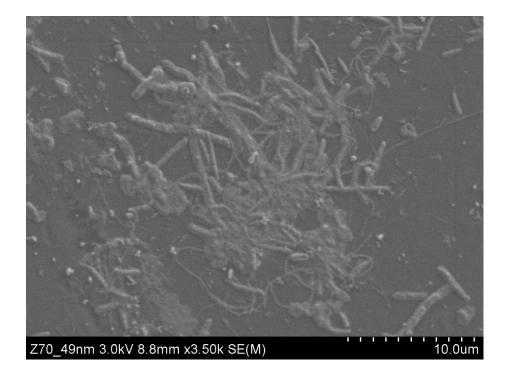


Fig. S8. FE-SEM image; aggregation of Nafion-ZrGdNR-2.0 composite membrane.

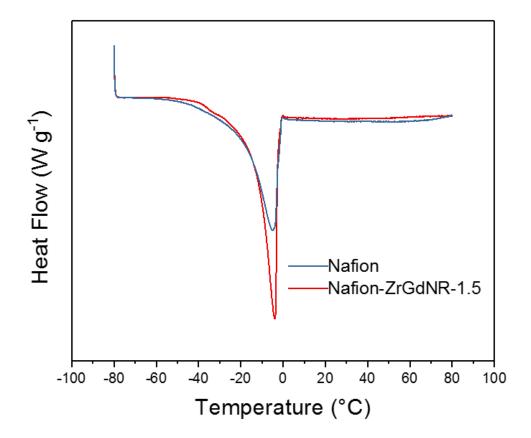


Fig. S9. DSC results of Nafion and Nafion-ZrGdNR-1.5.

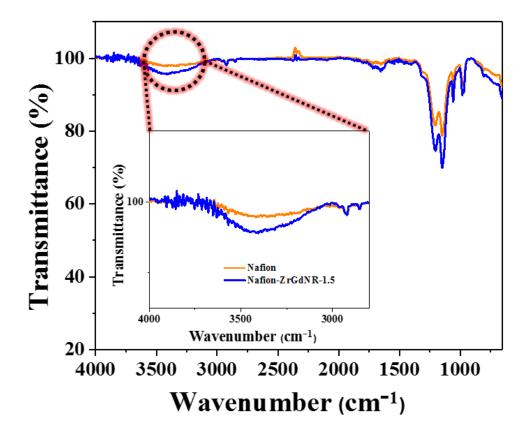


Fig. S10. FT-IR spectra of Nafion membrane and Nafion-ZrGdNR-1.5 composite membrane.

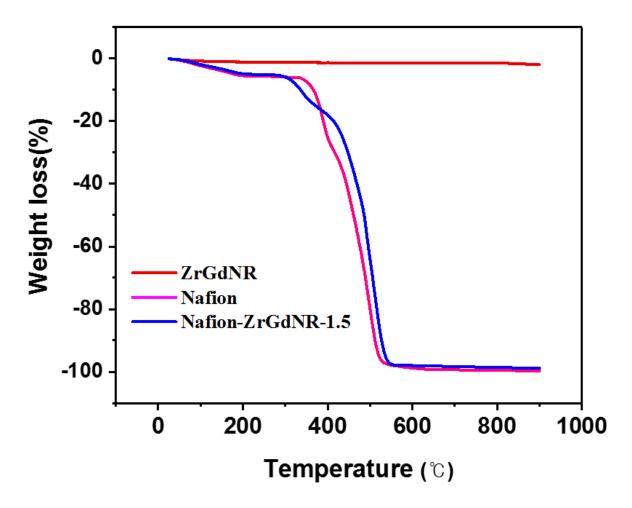


Fig. S11. TGA analysis of GdZrNR, Nafion and Nafion-ZrGdNR-1.5 composite membrane.

Materials and Preparation Methods for Ce₂Zr₂O₇ nanorods

Materials

Polyacrylonitrile (PAN, M_w=150,000 g/mol), Cerium(IV) acetylacetonate (Ceacac), Zirconium(IV) acetylacetonate (Zracac), N,N-dimethylformamide (DMF) and Nafion 212 (NRE-212) membrane were obtained from Aldrich, Korea. Platinum, nominally 40% on carbon black, Hispec – 4000 was used. The gas diffusion layer (35 BC) was obtained from SGL group, Germany. H₂O₂, isopropyl alcohol (IPA), Ethanol, H₂SO₄, were received from Daejung Chemical, Korea. Nafion resin solution (LQ-1115-1100 EW) was procured from Ion Power Inc., USA.

2.2. Preparation of Ce: Zr/PAN electrospun composite mat

Zracac (0.02 g) and Ceacac (0.08 g) salts were entirely dissolved in 3 mL of DMF solvent and continued the stirring for 12 h at 80 °C. Polyacrylonitrile (PAN, 1g) was dissolved in DMF (6 mL) and stirred at 80 °C for 12 h in a separate vial. Then, the metal precursors (1:4) and PAN solutions were stirred continuously at 80 °C until clear and uniformly mixed. After observing evenly mixed the solution, the electrospinning process was carried out. The mixture solution was placed in a plastic syringe (10 mL) and connected a steel needle (21 gauge). The collector of electrospinning machine was covered with aluminum foil, and the solution was electrospun onto the collector under conditions: Traveling distance was 10 cm between the needle and the collector. The voltage power of 14 kV was supplied, and the rotating speed was 300 rpm with the flow rate of 1 mL h⁻¹ under humidity < 45% RH at room temperature.

Preparation of Cerium-Zirconium Oxide Nanorods

The Cerium-Zirconium oxide nanorods (CeZrNR) was obtained from electrospun PAN/Zracac:Gdacac composite nonwoven web by calcination using a tubular furnace (Wisd

Laboratory Instruments) under an air atmosphere. The PAN/Ceacac:Zracac electrospun fibers were heated from room temperature to 250 °C for 1 hour to stabilize the electrospun fiber and temperature was further increased by 5 °C per minute up to 500 °C for the complete decomposition of organic materials. It was heated from 250 °C to 500 °C in 50 min and kept 500 °C for 1 hour.

Preparation of Nafion-CeZrNR composite membrane

The composite membranes were fabricated by incorporating 1.5 weight ratios of CeZrNR into the Nafion ionomer. CeZrNR was dispersed in ethanol as a solvent using ultrasonicator machine for 30 min. Nafion ionomer also was ultra-sonicated with ethanol in a vial for 30 min. Then, CeZrNR solution and Nafion ionomer solution were mixed using ultrasonicator for 30 min. Next, the mixture was stirred for 12 hours. To prepare Nafion-CeZrNR-1.5 composite membrane, the mixture solution was cast on a Petri dish and the solvent was evaporated in a vacuum oven at 50, 60, 70 and 80 °C for 2 h in each case. The composite membrane was separated using water from the Petri dish followed by further drying at 100 °C for 4 hours.

Characterizations for CeZrNR

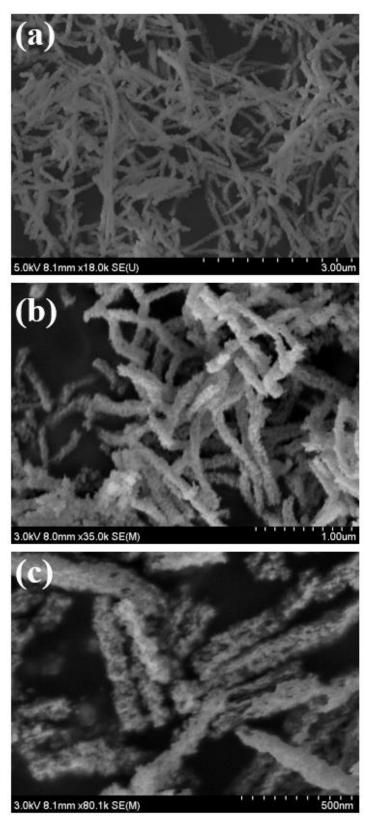


Fig. S12. The FE-SEM images of CeZrNR; (a) low magnification and (b,c) high magnification.

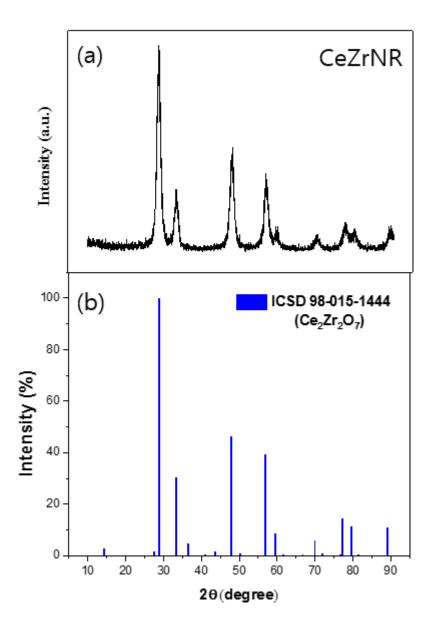


Fig. S13. (a) XRD results of CeZrNR and (b) Reference pattern matched with CeZrNR XRD result.

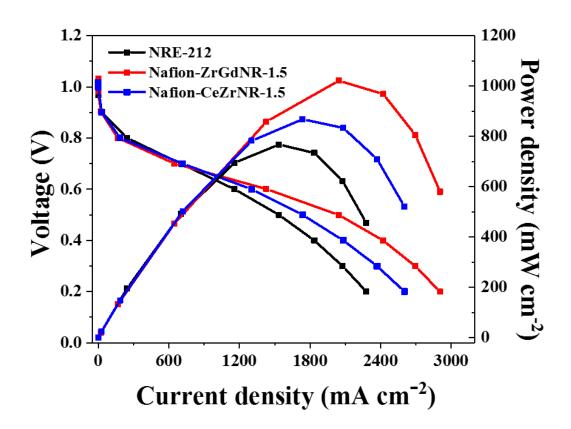


Fig. S14. Polarization plots of NRE-212, Nafion-ZrGdNR-1.5 and Nafion-CeZrNR-1.5 membranes.