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Metallic glass separators for fuel cells at intermediate temperatures

Masaya Takemoto [a], Masatomo Hattori [a], Koichiro Hayashi [a], Shin-ichi Yamaura [b], Wei Zhang [c], Wataru Sakamoto [a], Toshinobu Yogo [a,*]

[a] Division of Materials Research, Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan
[b] Institute of Materials Research, Tohoku University, Sendai 980-8577, Japan
[c] School of Materials Sci. Eng., Dalian University of Technology, Dalian 116024, China

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ABSTRACT

Inorganic-organic hybrid membranes comprising an aliphatic backbone polymer and a trisiloxane bond were synthesized from a trisiloxane derivative, phosphonic acid acrylate, and vinylbenzotriazole, and used to prepare membrane electrode assembly (MEA) sandwiched between metallic glass separators (MGSs). The prepared MEA exhibited a higher cell voltage than that comprising carbon separators at 140 °C and 30% relative humidity for 50 h.

1. Introduction

Perfluorosulfonic polymer membranes show the optimum performance at 100% relative humidity (RH) at around 80 °C when the CO concentration in the H_2 gas is maintained below 20 ppm to prevent CO poisoning on the Pt catalyst [1–3]. If the operating temperature increases to the intermediate temperature values between 100 and 150 °C, CO poisoning decreases and the cell efficiency increases with the simplified system [4]. Therefore, membrane electrolytes exhibiting high proton conductivities ranging from 100 to 150 °C are required. As inorganic-organic hybrids have both the flexibility of an organic material and the chemical, thermal, and mechanical stabilities of an inorganic material, the hybrid membranes are among the best candidates for preparing membrane electrolytes at the intermediate temperatures [5].

A MEA comprises an electrolyte membrane with catalyst layers on both sides, sandwiched with a pair of separators. Separators such as metal and carbon with paths for fuel and oxygen gases should have high electron and heat conductivities [6]. MGSs of Ni-Cr-P-B are characterized by their high corrosion resistance, which improves the demerit of MS [7]. The effect of the surface roughness of separators on the cell properties has not been reported yet, particularly at intermediate temperatures and low humidities: however, the properties of MGSs at 80 °C and 100% RH have been reported [7].

This research describes the cell performance of MEA using MGSs and carbon separators (CSc) at intermediate temperatures and low humidities. The inorganic-organic hybrid membranes were synthesized from 1,5-divinyl-3-phenylpentamethyltrisiloxane (DPPMTS), 2-hydroxyethyl methacrylate acid phosphate (HEMAP), and *N*-vinylbenzotriazole (VBT) via copolymerization.

2. Experimental procedures

2.1. Materials

The molecular structures of DPPMTS (Gelest Inc.), VBT, and HEMAP (2-hydroxyethyl methacrylate acid phosphate ($[CH_2{=}C(CH_3)CO(O)(CH_2)_2O]_nP(O)(OH)_{3-n}$, HEMAP, Johoku Chemical: monoester (n = 1) to diester (n = 2) ratio = 1.35:1.0) are shown in Fig. S1.

2.2. Preparation of membranes

VBT/HEMAP/DPPMTS copolymer was prepared at a molar ratios of VBT/HEMAP/DPPMTS = 1:9:5. VBT (58.1 mg, 0.4 mmol), HEMAP (927.2 mg, 3.6 mmol), and DPPMTS (645.2 mg, 2.0 mmol) were dissolved in 20 ml of DMF with azobis(isobutyronitrile) (7.9 mg, 0.8 mol%). After polymerization in a sealed vessel at 90 °C for 10 h, solid precipitates were obtained upon addition of diethyl ether. The precipitates were redissolved in DMF and were casted onto a polyethylene diphthalate film, which was dried at room temperature for 24 h and then heated from 60 °C to 140 °C, affording hybrid membranes.

* Corresponding author.
E-mail address: yogo@imass.nagoya-u.ac.jp (T. Yogo).

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2.3. Fabrication of metallic glass separators

$Ni_{65}Cr_{15}P_{16}B_4$ metallic glassy powder used as a feedstock of high velocity oxy-fuel (HVOF) spray-coating was prepared by a high-pressure argon gas-atomization process [7]. The HVOF thermal spray system (Praxair/TAFA, JP-5000) was used to produce $Ni_{65}Cr_{15}P_{16}B_4$ thick film on SUS316 plates having a flow channel of separators. The film thickness was about 200 μm.

2.4. Proton conductivity and current-voltage property measurement

The proton conductivity of hybrid membranes was measured by AC impedance [8]. The catalyst ink and membrane-electrode composite were prepared based on our previous study [8]. MEA was constructed from the membrane-catalyst composite and CSs or MGSs. The operated MEA was incorporated into a single-cell test fixture. The current (I)-voltage (V) curves were measured [8]. The impedance spectra were analyzed using the Z-View software.

3. Results and discussion

3.1. Synthesis and properties of trisiloxane-based hybrid membranes

Hybrid membranes with various monomer ratios of VBT, HEMAP, and DPPMTS were prepared. Among them, self-standing and transparent hybrid membranes with uniform thickness below 100 μm were synthesized using VBT, HEMAP, and DPPMTS at a ratio of 1:9:5 (Fig. S2). The ratio was selected for the fuel cell test, as the 1:9:5 membrane possessed the highest strength with a high conductivity.

The FT-IR spectrum showed that the C=C absorption bands around 1640 cm^{-1} for VBT, HEMAP and DPPMTS disappeared after copolymerization (Fig. S3). The hybrid membrane gave rise to broad P-OH absorptions from 2000 to 3500 cm^{-1}, strong absorptions at 1725 and 1195 cm^{-1} derived from the C=O and C(=O)O bonds, and an absorption band at 1000 cm^{-1} derived from the $(Si—O)_3$ backbone. These results indicate that the copolymerization of the starting monomers afforded the hybrid membranes.

The TG curve of the 1:9:5 hybrid membrane was measured under O_2 flow from room temperature to 800 °C. Up to 200 °C, a gradual weight loss of approximately 4 wt% was observed for the membrane, indicating that the hybrid membrane was thermally stable up to 200 °C in oxygen.

The fracture strength obtained from the stress-strain curve (Fig. S4) was 18.6 MPa for the hybrid membrane at 3.3% strain. The tensile modulus E calculated from a tangent for the curve was 980 MPa, which was comparable with those of high-density polyethylene (413–1034 MPa) [9].

3.2. Proton conductivity of the hybrid membranes

The proton conductivity σ for the VBT/HEMAP/DPPMTS membrane with a compositions of 1:9:5 at 19.3–27.0%RH is shown in Fig. S5. The σ value was 4.5×10^{-4} S cm^{-1} at 130 °C and 19.3%

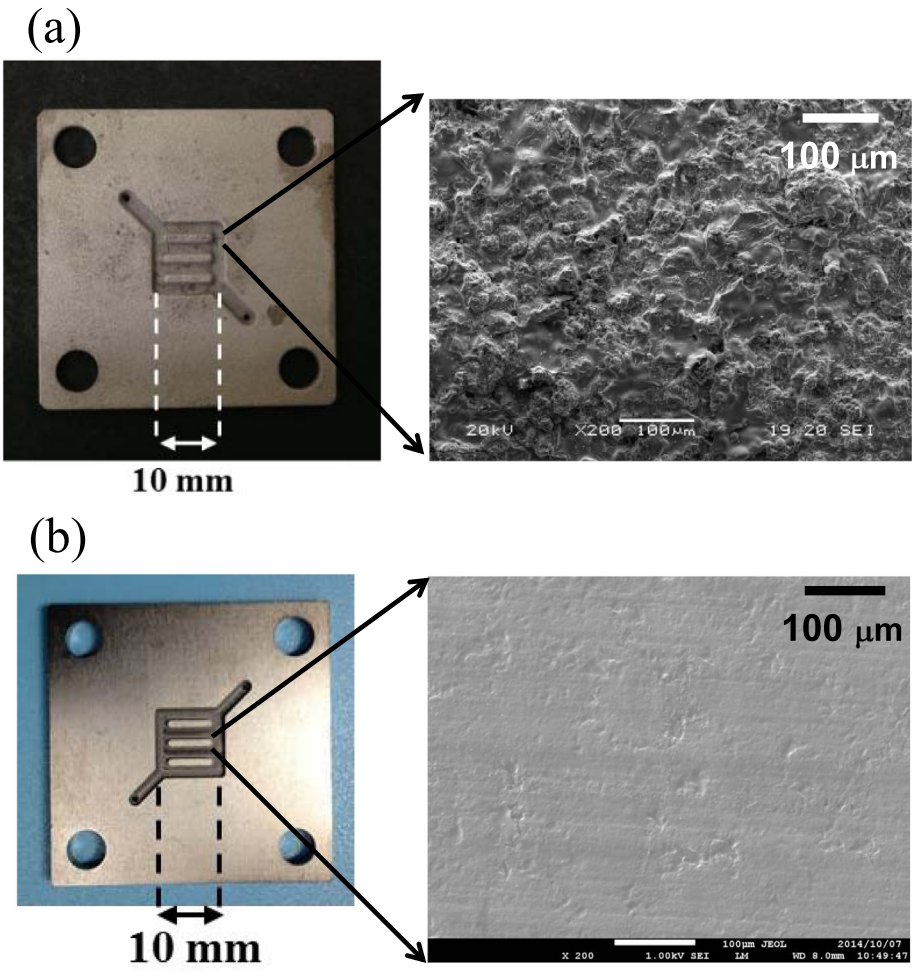

Fig. 1. Photographs of (a) metallic glass separator and (b) carbon separator.