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Ionomers

A Soluble and Highly Conductive Ionomer for High-Performance Hydroxide Exchange Membrane Fuel Cells

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Hydrogen proton exchange membrane fuel cells (PEMFCs) have been demonstrated to have high power density and reasonable energy density.[1] Their commercialization, however, has been hampered by the high cost and low durability of their electrocatalysts.[2] By switching from an acidic medium to a basic one, hydroxide (OH^-) exchange membrane fuel cells (HEMFCs) have the potential to solve the problems of catalyst cost and durability while achieving high power and energy density. In a basic environment, the cathode oxygen reduction over-potential can be significantly reduced, leading to high fuel cell efficiency, and catalysts in basic medium are also more durable.[3] In addition, the facile cathode kinetics allows nonprecious metals to be used as catalysts, thus drastically reducing the cost of the fuel cell. Further, HEMFCs can offer fuel flexibility (e.g., methanol, ethanol, ethylene glycol, etc.) because of their low over-potential for hydrocarbon fuel oxidation and reduced fuel crossover.[4] One of the most significant problems for HEMFCs is the lack of a soluble ionomer that can be used in the catalyst layer to build an efficient three-phase boundary and thus drastically improve the utilization of the catalyst particles and reduce the internal resistance.

One of the most desirable properties of an ionomer for use in the catalyst layer is high solubility in low-boiling-point water-soluble solvents such as ethanol and (*n*- or 2-)propanol, because these solvents are easy and safe to handle and remove during the electrode preparation. The ionomer should also have high hydroxide conductivity and alkaline stability. For PEMFCs, Nafion has been the ionomer of choice because it meets these requirements. But for HEMFCs, the most commonly used material for the hydroxide exchange membrane (HEM) is a quaternary ammonium hydroxide containing polymer that has poor solubility in the aforementioned simple solvents, low hydroxide conductivity, and poor alkaline stability. For example, Tokuyama Co. very recently reported two types of soluble quaternary ammonium hydroxide containing polymers (product code: A3Ver2, soluble in tetrahydrofuran or *n*-propanol, and AS-4, soluble in *n*-propanol);[5] however, as a result of their low hydroxide conductivity, their incorporation into the catalyst layers of HEMFCs only led to a moderate improvement in performance. In another case, Park et al. prepared an ionomer solution of the trimethylamine (TMA) and *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine (TMHDA) based polysulfone–methylene quaternary ammonium hydroxide (T/TPQAOH) in dimethylacetamide (DMAc, b.p. 166 °C).[6] Similar to the Tokuyama results, the low hydroxide conductivity of the ionomer significantly limited the improvement in fuel cell performance, and in addition, removal of the high-boiling-point solvent is considered difficult and unsafe in the presence of finely dispersed catalysts.[4] Owing to the lack of a soluble highly conductive solid ionomer, aqueous solutions of KOH[7] or NaOH[8] have been previously used in the electrodes, where the introduction of metal cations (M^{n+}) offsets the key advantages of a HEMFC over traditional liquid-electrolyte-based alkaline fuel cells (AFCs). Furthermore, owing to the lack of a good ionomer as the binder, non-ionic conductive PTFE[9] and proton-conductive Nafion ionomers[10] were used as substitutes in the electrodes, even though these materials were known to have no hydroxide conductivity. Recently, Varcoe et al. reported a TMHDA-based polyvinylbenzyl-crosslinked quaternary ammonium hydroxide (TPCQAOH) electrochemical interface to enhance HEMFC performance.[11,12] Because the polymer used was not soluble in ionomer form, one could question its ability to form an efficient three-phase-boundary structure in the catalyst layer, thereby limiting performance. Moreover, the hydroxide conductivity and stability of the electrochemical interface are still of concern because it is based on quaternary ammonium hydroxide groups.

Quaternary phosphonium containing polymers showed excellent solubility in methanol.[13] The strong basicity of the tertiary phosphine[14] suggests that quaternary phosphonium hydroxides are very strong bases. Therefore in this work, we synthesized a new quaternary phosphonium based ionomer that is soluble in low-boiling-point water-soluble solvents and is highly hydroxide conductive: tris(2,4,6-trimethoxyphenyl) polysulfone-methylene quaternary phosphonium hydroxide (TPQPOH; Scheme 1).

The TPQPOH ionomer exhibits excellent solubility in pure methanol, ethanol, and *n*-propanol and in their aqueous solutions (50 wt % in water, see Table S1 in the Supporting Information). On the other hand, the TPQPOH is insoluble in pure water, even at 80 °C, suggesting that it can be used in the

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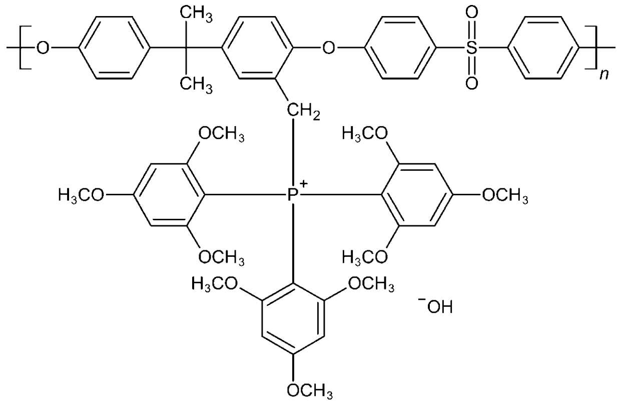

Scheme 1. Chemical structure of the ionomer TPQPOH.

catalyst layer without loss arising from solubility. Further TPQPOH exhibits remarkable hydroxide conductivity (27 mS cm^{-1}, see Table S2 in the Supporting Information) that is 1.6 times that of the commercial FAA HEM (17 mS cm^{-1}), 10.4 times that of A3 Ver2 (2.6 mS cm^{-1}[5]), 2.1 times that of AS-4 (13 mS cm^{-1}[5]), and 2.5 times that of T/TPQAOH ($\approx$11 mS cm^{-1}[6]). At the same time, the ion exchange capacity (IEC) of TPQPOH is 1.09 mmol g^{-1}, apparently lower than that of FAA (1.6 mmol g^{-1}) and that of AS-4 (1.3 mmol g^{-1}). This implies that the basicity of the quaternary phosphonium hydroxide in TPQPOH is much higher than that of the quaternary ammonium hydroxide in FAA and AS-4.

Besides the excellent solubility and high ionic conductivity, TPQPOH also has outstanding stability. TPQPOH membranes maintain their ionic conductivity and flexibility even after immersion in 10 M KOH solution (more than 50 % saturated) at room temperature for 48 h (see Table S3 in the Supporting Information). By contrast, FAA membranes become very brittle, implying severe degradation. In addition, the TPQPOH membranes maintain their ionic conductivity after immersion in either deionized (DI) water or 1 M KOH at 60 °C for 48 h (see Table S4 in the Supporting Information). The thermal stability of TPQPOH is high enough for use in HEMFCs, since the operating temperature of current HEMs has typically been limited to 50 or 60 °C.[4,15] No decrease of ionic conductivity was observed for TPQPOH after immersion in either DI water or 1 M KOH for 30 days (see Table S5 in the Supporting Information), indicating good long-term stability.

Unlike the ordinary aliphatic alkyl or phenyl based quaternary phosphonium hydroxides, which have serious instability problems,[16] TPQPOH has outstanding stability because the 2,4,6-trimethoxyphenyl groups take part in conjugation, and they are also strong electron donors, both of which enhance the stability of the quaternary phosphonium group. Besides, the high steric bulk of tris(2,4,6-trimethoxyphenyl)phosphine also protects the core phosphorus atom and the α-carbon atom against hydroxide attack.

Although the TPQPOH ionomer has been shown to be soluble, conductive, and stable, the most practical evaluation of it is the performance of a HEMFC single cell. Figure 1 shows the polarization curves of H_2/O_2 HEMFC with and without TPQPOH as the ionomer in the catalyst layer. The open circuit voltages (OCVs) are close ($\approx$1.1 V), indicating that the TPQPOH ionomer does not affect the catalyst function of Pt significantly. The peak power density was substantially higher (ca. 3.5 times) for HEMFC with the TPQPOH ionomer than without (138 vs. 40 mW cm^{-2}). The data suggest that with its excellent solubility and high ionic conductivity, TPQPOH may have helped to build a more efficient three-phase boundary in the catalyst layer. Even with a much lower catalyst loading (0.2 vs. 0.5 mg Pt cm^{-2}), a lower IEC (1.6 vs. 1.7 mmol g^{-1}), and much thicker (70 vs. 17 μm) membrane, the peak power density of 138 mW cm^{-2} obtained for the HEMFC with the TPQPOH ionomer is much higher than the 22 and 95 mW cm^{-2} (air as oxidant) obtained for HEMFCs containing A3 Ver2 and AS-4 ionomers.[5] The peak power density is also much higher than that of the HEMFC containing an insoluble electrochemical interface and having higher catalyst loading and a thinner membrane (90 mW cm^{-2} for a catalyst loading of 0.5 mg Pt cm^{-2} and 130 mW cm^{-2} for a catalyst loading of 4.0 mg PtRu/Pt cm^{-2}, no back pressure, IEC of 1.42 mmol g^{-1}, and membrane thickness of 51 μm[11]).

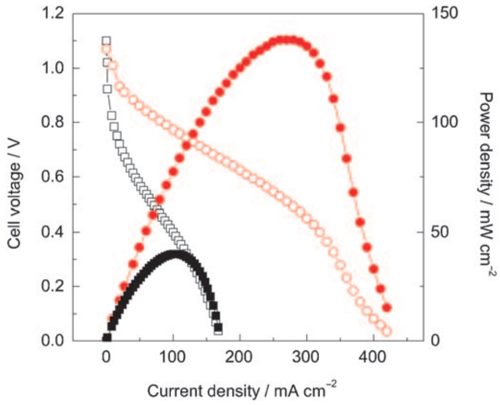

Figure 1. Polarization curves (empty symbols) and power density curves (filled symbols) of an HEMFC with (red circles) and without (black squares) the TPQPOH ionomer. Test conditions: loadings of 0.2 mg Pt cm^{-2} and 0.05 mg TPQPOH cm^{-2} for both anode and cathode, 70 μm thick FAA commercial membrane as the HEM (Fuma-Tech GmbH), cell temperature of 50 °C, humidifier temperatures of 70 °C and 80 °C for H_2 and O_2, respectively, flow rate of 0.2 L min^{-1} and back pressure of 250 kPa for both H_2 and O_2.

In addition, the measured internal resistance was much smaller (0.50 vs. 1.05 Ω cm^2 or a 50 % reduction) for a HEMFC with the TPQPOH ionomer than without. The internal resistance value of 0.50 Ω cm^2 is much smaller than the values of 1.0 and 0.79 Ω cm^2 observed for the HEMFCs with a TPCQAOH electrochemical interface, in spite of their higher catalyst loading of 0.5 mg Pt cm^{-2} and 4.0 mg PtRu/Pt cm^{-2}, respectively, and the thinner HEM as mentioned above.[11] The significantly higher power density and smaller internal resistance indicate that the TPQPOH ionomer is superior to both the above-mentioned quaternary ammonium hydroxide ionomer soluble in low-boiling-point solvents[5] and the insoluble electrochemical interface.[11]

Figure 2 shows the polarization curves of the TPQPOH-containing HEMFC at elevated cell temperatures. The peak power density increases with temperature (141, 157, 178, and

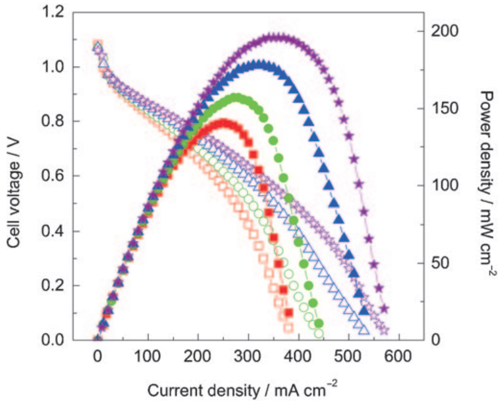

Figure 2. Polarization curves (empty symbols) and power density curves (filled symbols) of an HEMFC with the TPQPOH ionomer at 50 °C (red squares), 60 °C (green circles), 70 °C (blue triangles), and 80 °C (purple stars). Test conditions: loadings of 0.5 mg Pt cm^{-2} and 0.125 mg TPQPOH cm^{-2} for both anode and cathode, 70 μm thick FAA commercial membrane as the HEM (Fuma-Tech GmbH), humidifier temperatures of 70 °C and 80 °C for H_2 and O_2, respectively, flow rate of 0.2 L min^{-1} and back pressure of 250 kPa for both H_2 and O_2.

196 mW cm^{-2} at 50, 60, 70, and 80 °C, respectively), while the opposite is observed for the internal resistances (0.48, 0.46, 0.42, and 0.38 Ω cm^2 at 50, 60, 70, and 80 °C, respectively). With the same catalyst loading of 0.5 mg Pt cm^{-2} and cell temperature of 60 °C, the peak power density of 157 mW cm^{-2} is much higher than the value of 28.2 mW cm^{-2} (no back pressure and air as oxidant) with T/TPQAOH (DMAc solution),[6] and again higher than the value of 110 mW cm^{-2} obtained with the insoluble electrochemical interface.[11] At the same time, the internal resistance of 0.46 Ω cm^2 is also much smaller than the value of 2.3 Ω cm^2 obtained with a HEMFC using T/TPQAOH (DMAc solution),[6] and again smaller than the value of 1.1 Ω cm^2 for the HEMFC with the insoluble electrochemical interface.[11] The results demonstrate that TPQPOH is superior to the quaternary ammonium hydroxide ionomer soluble in high-boiling-point solvents.[6] The TPQPOH-containing HEMFC exhibited improved peak power density up to ca. 200 mW cm^{-2} at elevated temperatures, that is, at 80 °C, confirming the good stability of TPQPOH and its good prospects for use in HEMFCs.

In summary, a novel hydroxide-conductive ionomer, TPQPOH, has been synthesized. TPQPOH has excellent solubility in some low-boiling-point water-soluble solvents, high hydroxide conductivity, and outstanding alkaline stability. The H_2/O_2 HEMFC containing the TPQPOH ionomer exhibits a substantial increase of peak power density and significant reduction of internal resistance.

Experimental Section

Polysulfone (PSf) (Udel P-3500, Amoco) was chloromethylated with paraformaldehyde and trimethylchlorosilane as the chloromethylating agent and stannic chloride as the catalyst, according to the procedure described by Avram and co-workers.[17] Specifically, paraformaldehyde (3.39 g, 11.3 mmol) and trimethylchlorosilane (12.3 g, 11.3 mmol) were added to a solution of PSf (5 g or 1.13 mmol PSf in 250 mL chloroform) in a flask equipped with a reflux condenser and a magnetic stirrer, and then stannic chloride (0.589 g, 0.226 mmol) was added dropwise. The reaction mixture was stirred at 50 °C for 48 h. Subsequently the reaction mixture was poured into ethanol (95 %), and white chloromethylated polysulfone (CMPSf) precipitated immediately. The precipitate was filtrated, washed thoroughly with ethanol, and dried in vacuum at room temperature for 12 h. The degree of chloromethylation (DC) of the CMPSf obtained was 124 % (determined from the ^{1}H NMR spectrum). The chemical structure and the synthesis of CMPSf is given in Figure S1 in the Supporting Information.

TPQPCl was synthesized by quaternary phosphorization of CMPSf with tris(2,4,6-trimethoxyphenyl)phosphine. Specifically, CMPSf (0.503 g, 1.24 mmol -CH_2Cl) was dissolved in 5 mL of dimethylformamide (DMF), and then tris(2,4,6-trimethoxyphenyl)phosphine (0.693 g, 1.24 mmol) was added. The reaction mixture was stirred at 80 °C for 12 h, and then poured into a Petri dish; the DMF was removed by evaporation at 40 °C over 2 days to obtain TPQPCl. TPQPOH was obtained by treating TPQPCl in 1M KOH at room temperature for 48 h; it was washed thoroughly and immersed in DI water for 48 h to remove residual KOH. ^{31}P NMR spectroscopy was used to confirm the synthesis of TPQPOH, and the degree of conversion of the chloromethylated group was close to 100 %.

The catalyst ink was prepared by mixing platinum black (E-TEK, 100 mg), TPQPOH (25 mg, 0.5 g of 5 wt % TPQPOH solution in ethanol/water (50 wt %/50 wt %), additional DI water (1.5 g), and additional ethanol (1.5 g). The catalyst ink was sonicated at 0 °C for 1 h before use. The electrodes (both anode and cathode) were prepared by spraying the catalyst ink onto carbon paper (25CC, SGL) to the desired Pt loading, typically 0.2 and 0.5 mg Pt cm^{-2}.

The membranes electrode assembly (MEA) with an active area of 5 cm^2 was prepared by pressing the anode, FAA commercial HEM, and the cathode at 60 °C under 120 kgf cm^{-2} for 5 min. The FAA commercial HEM (Fuma-Tech GmbH) has an ion exchange capacity of 1.6 mmol g^{-1}, a thickness of 70 μm, and an ionic conductivity of 17 mS cm^{-1} in DI water at 20 °C. The MEA was assembled in a single cell fixture for the HEMFC test. The fuel cell was activated by discharging at constant current density from zero to maximum current density with an increment step of 20 mA cm^{-2} every 5 min. The *I–V* polarization curves were obtained under the following operation conditions: pure H_2 and O_2 as fuel and oxidant with a flow rate of 0.2 L min^{-1} and back pressure of 250 kPa, temperatures of 70 °C and 80 °C at anode and cathode humidifiers, respectively, and a cell temperature of 50–80 °C.

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