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Impacts of anion-exchange-membranes with various ionic exchange capacities on the performance of H_2/O_2 fuel cells

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HIGHLIGHTS

- Impacts of varying IECs in AEMs on the performance of H_2/O_2 fuel cells were studied.
- The power density of fuel cells using the AEM (0.90 mmol g^{-1}) reached 285 mW cm^{-2} at 50 °C.
- EIS revealed that the OH^- transport resistance was a key factor limiting AEMFC performance.
- The OH^- transport resistance depended on the nature of the AEM and the cell voltages.

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ABSTRACT

Anion-exchange membranes (AEMs) with varying amounts of quaternary ammonium groups (0.51, 0.70, and 0.90 mmol g^{-1}) grafted onto a styrene–ethylene/butylene–styrene (SEBS) block copolymer were prepared and studied for their impact on the performance of solid electrolyte H_2/O_2 fuel cells. A higher content of quaternary ammonium groups in the membranes resulted in higher ionic conductivity and lower OH^- transport activation energy in the membranes, which in turn resulted in lower cell overpotentials and higher power density in the performance of the AEM fuel cells. By increasing the quaternary ammonium group from 0.51 to 0.90 mmol g^{-1} in the AEMs, the power density of the AEM fuel cells at 50 °C was found to increase from 169 to 285 mW cm^{-2}. For comparison, the performance of AEM fuel cells using a commercial Tokuyamma A901 AEM was also tested. Electrochemical impedance spectra (EIS) recorded during the operation of the AEM fuel cells revealed that the transportation resistance of the OH^- ions from the cathode to the anode through the AEM depended on the nature of the AEM and the cell voltage and is a critical factor to consider for improving the performance of AEM fuel cells.

1. Introduction

Alkaline-based fuel cells as low-cost, high-performance power sources can potentially replace state-of-the-art proton exchange membrane fuel cells (PEMFCs) in many applications [1–10]. Compared with the PEMFCs, the alkaline-based fuel cells have a wider choice of stable and active non-Pt catalysts for oxygen reduction reactions and hydrogen oxidation reactions [11–18]. Using a concentrated alkaline solution, alkaline fuel cells (AFCs) were used as a power source for space shuttle applications, but they continue to face fundamental challenges for applications on the earth because the aqueous KOH electrolyte reacts with the CO_2 from the air to form carbonate species that lower the AFC performance and reduce the lifetime of the cell through the formation of carbonate precipitates on the electrodes [19]. The recently developed alkaline exchange membrane fuel cells (AEMFCs) [20–23] aim to overcome the challenges faced by the AFCs. Since there is no mobile cation in either the AEMs or the electrodes, the formation of carbonate precipitates on the electrodes is no longer a major issue. However, a lack of suitable AEMs and ionomers to meet performance and durability requirements is still one of the major challenges in developing AEMFCs for many applications.

Since 2005, there have been significant efforts to develop AEMs and ionomers by grafting quaternary ammonium groups or quaternary phosphonium groups onto different polymers. The polymers include poly(vinylidene fluoride) (PVDF) [24], poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) [25], poly(ethylene-co-tetrafluoroethylene), poly(ether imide) [26],

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poly(arylene ether sulfone) [27], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [28], poly(phthalazinone ether ketone) (PPEK) [29], etc. In the last few years, the performance of AEMFCs has been improved significantly, e.g. the peak power capacity has been increased from initially a few mW cm^{-2} to currently 500 mW cm^{-2} [30]. In our previous work [31], we demonstrated that styrene–ethylene/butylene–styrene (SEBS)-based ionomers had excellent dimensional stability and superior performance in AEMFCs due to their unique nanostructures. This work aims to study how varying OH^- conductivity affects the performance of AEMFCs. Three anion exchange membranes were prepared by grafting varying numbers of quaternary ammonium groups onto the SEBS block co-polymer. The ion exchange capacity (IEC), water uptake, swelling, ionic conductivity, and thermal stability of the membranes were tested. Both the performance and the electrochemical impedance spectra (EIS) of AEMFCs with the prepared membranes were studied and compared with those obtained in AEMFCs using the commercial Tokuyamma A901 AEM.

2. Experimental

2.1. Membrane synthesis

Kraton G SEBS A1535 H was purified by precipitation from a 5 wt.% chloroform solution to methanol before chloromethylation. Chloromethylation was carried out following a modified procedure disclosed in our previous work [32]. Specifically, for the chloromethylated SEBS (CMSEBS), 2.5 ml of chloromethyl methyl ether was diluted in 10 ml of chloroform followed by the slow addition of 30 μl of $SnCl_4$ in a three-neck flask equipped with a condenser in an oil bath at 65 °C. After mixing for 30 min, a 5 wt.% SEBS (2 g) chloroform solution was added to the above mixture drop-wise. The solution was stirred for 6–48 h at 65 °C. Chloromethyl functionality was controlled by conversion, which was monitored by ^1H NMR and recorded on a 500 MHz NMR (Bruker Avance II 500 MHz) spectrometer in $CDCl_3$, as shown in Fig. 1. The crude CMSEBS was precipitated in a methanol solution and then washed several times with methanol before being vacuum dried overnight at room temperature. Quarternized SEBS (QSEBS) ionomers were derived from the amination of the CMSEBS with trimethylamine. 2 g of CMSEBS was first dissolved in 40 ml of THF. 10 ml of methanol was then added to the solution to ensure no gelation or precipitation occurred during the quaternization reaction. 2 mol folds of trimethylamine, relative to the chloromethyl group, were slowly added to the solution with adequate agitation. The solution was kept at 40 °C for at least 12 h to guarantee a complete conversion. Membranes (~30 μm thickness) were obtained by casting a quaternized ionomer solution on a PTFE substrate and slowly evaporating the solvents. Then the membranes were heated at 110 °C for 3 h.

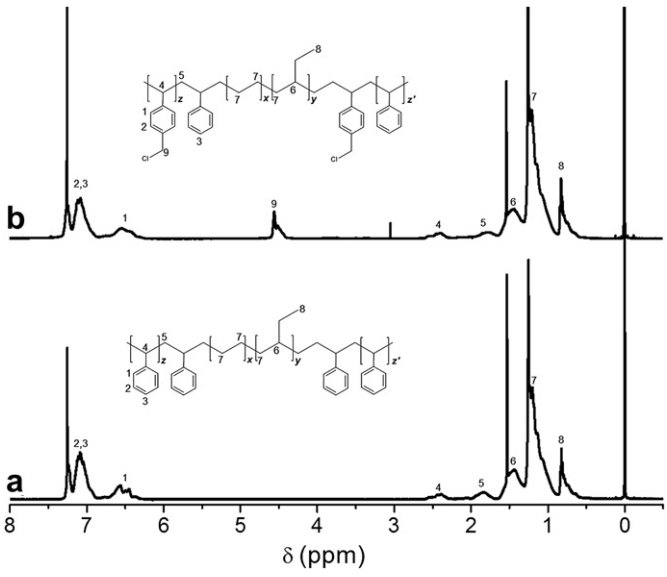

Fig. 1. (a) ^1H NMR spectra of Kraton G SEBS A1535 H and (b) CMSEBS-M in chloroform-*d*.

2.2. NMR characterization

A ^1H NMR (500 MHz) analysis of SEBS for both the starting material and the CMSEBS was performed on a Bruker Avance II 500 MHz instrument using chloroform-*d* as the solvent and tetramethylsilane (TMS) as the internal reference. Since the final ionomers after amination were insoluble in chloroform-*d*, NMR spectra were not acquired.

2.3. Ionic conductivity

Membranes were immersed in 1 M KOH for 48 h to exchange the Cl^- with OH^-. The OH^- ionic conductivity of the membrane was measured using AC impedance spectroscopy with a Solartron 1250 frequency response analyzer interfaced with a Solartron 1287 potentiostat/galvanostat. The measurements were conducted in galvanostatic mode with set frequencies ranging from 0.1 Hz to 60 kHz with the galvanostatically controlled AC current as 5 mA. A standard four-probe conductivity cell (BekkTech LLC, Loveland, CO) was used to assemble the membrane test samples. The tested assembly was completely immersed in de-ionized water pre-equilibrated to the temperature of 30 °C, 40 °C, 50 °C, 60 °C, and 80 °C respectively, and then immediately measured. This was done to eliminate any potential interference caused by reaction of hydroxide ions with dissolved carbon dioxide. Ionic conductivity was calculated as follows:

$$\sigma = \frac{L}{RTW} \tag{1}$$

where L is the length of the membrane between two potential sensing platinum wires in centimeters (cm), R is the membrane resistance in ohms (Ω), T is the thickness of the membrane in cm and W is the width of the membrane in cm.

2.4. Ion-exchange capacity (IEC)

The IEC of the membranes was determined by the back titration method. Approximately 200 mg of membranes (in OH^- form) were immersed in 20 ml of a 0.1 M HCl standard solution for 48 h. The solution was then titrated with a standard solution of potassium hydroxide (0.1 M) to pH 7. After titration, the membrane was soaked in 0.1 M HCl for 48 h then washed and immersed in DI water for 48 h to remove the remaining HCl. It was then vacuum dried at 70 °C for 24 h before being weighed to determine the dry mass (in Cl^- form). The IEC of the membrane was calculated by

$$\mathrm{IEC}\left(\mathrm{mequiv\ g^{-1}}\right) = \frac{M_i - M_f}{m_d} \tag{2}$$

where M_i is the milliequivalents (mequiv) of HCl before membrane neutralization, M_f is the mequiv of HCl measured after neutralization, and m_d is the mass of the dried membrane in grams with Cl^- form.