



Effect of alkaline exchange polymerized ionic liquid block copolymer ionomers on the kinetics of fuel cell half reactions



Jacob R. Nykaza^a, Yawei Li^a, Yossef A. Elabd^b, Joshua Snyder^{a,*}

^a Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States

^b Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, United States

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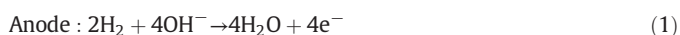
ABSTRACT

Rotating disk electrode (RDE) half-cell experiments were used to determine the impact of a hydroxide-conducting polymerized ionic liquid block copolymer (PILBCP) ionomer on the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) activity of a commercial Pt/C catalyst at three PILBCP loadings (23, 41, and 57 wt.% total solids). Increasing loadings of PILBCP resulted in reduced surface coverage of both the hydrogen (H_{UPD}) and hydroxide/oxide (OH_{ad}/O_{ad}) as evidenced by the cyclic voltammograms due to both a physical blocking of surface catalytic sites and a water/ion diffusional resistance imparted by the presence of the film. With the maximum loading of 57 wt.% PILBCP, a decrease of 88% for the kinetic current density (j_k) and 42% for the diffusion limited current (I_d) in the ORR and a decrease of 29% for the I_d in the HOR compared to bare Pt/C nanoparticles was observed. Similar trends were observed with 60 wt.% Nafion on Pt/C nanoparticles. These results indicate that while substantial, the detrimental effects of PILBCP ionomers on the half-cell reaction kinetics are no worse than those observed with the Nafion ionomer. AEMFC performance optimization for polymers with sufficient hydroxide conductivities should focus on AEM ionomer integration strategies with the goal of optimizing the triple phase boundary and limiting the interfacial resistance between the AEM and the corresponding ionomer in the catalyst layer.

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1. Introduction

The continued development of alkaline exchange membranes (AEMs) with increasing ion conductivities and mechanical/chemical stability has renewed interest in alkaline chemistry-based fuel cell technologies (alkaline exchange membrane fuel cells, AEMFCs) as an alternative to proton exchange membrane fuel cells (PEMFCs). The passivity of non-noble metals at AEMFC operating/electrochemical conditions facilitates the replacement of the Pt-based catalysts required in the acidic conditions of the PEMFC, making AEMFCs a less expensive and potentially more commercially viable alternative [1–3]. Power is generated in AEMFCs, as with other fuel cell configurations, through the hydrogen oxidation reaction (HOR) (reaction 1) at the anode producing electrons and the oxygen reduction reaction (ORR) (reaction 2) at the cathode. Hydroxyl ions produced at the cathode are transported through the AEM to participate in the HOR. The AEMFC half-cell and overall reactions are listed below.



To date, commercial integration of AEMFCs is limited by the moderate hydroxyl ion conductivity and low chemical stability of currently available AEM chemistries [4]. Research and development has focused on material optimization through the use of various cations [5–9] (e.g., ammonium, imidazolium, phosphonium), polymer structures [10–13] (e.g., grafted, random, block), and cation location [14,15] (e.g., alkyl chain length) in order to address these limitations. While *ex situ* conductivity and stability data is readily available for a broad range of AEM chemistries [5,7,16,17], few have been successfully integrated into a full cell AEMFC as there are difficulties in solubilizing the AEM polymer into an ionomer for integration into the catalyst layer [3,18–23]. Inefficiencies associated with the ability to convert the AEM polymer or a polymer of similar chemistry into an ionomer and integrate into a catalyst layer limits ion transport between the catalytic sites at the triple phase boundary and the ion conducting membrane, manifested as an interfacial resistance [24–26]. The slow development of AEM ionomers has also resulted in little understanding of the impact of AEM polymer chemistries on the cathodic ORR and anodic HOR in

* Corresponding author.

E-mail address: jds43@drexel.edu (J. Snyder).

AEMFCs, where both have a major role in defining the peak power density and performance of the fuel cell.

Previous work in our laboratory has focused on improving the ionic conductivity, chemical stability, and mechanical properties of AEMs by exploring polymerized ionic liquid block copolymers (PILBCPs) [14,15,27–30]. PILBCPs are a new class of block copolymer, which combines the benefits of both PILs and block copolymers. PILs possess unique properties, such as high solid-state ionic conductivity, high chemical, electrochemical, and thermal stability, and a widely tunable chemical platform, where significant changes in physical properties have been observed with subtle changes in chemistry [27,31]. Block copolymers are known to self-assemble into well-defined nanostructures with long-range order where both morphology and domain size are tunable [32–35]. When PILs are incorporated into the block copolymer, the resulting PILBCP possesses numerous orthogonal properties in the solid-state, such as excellent mechanical properties from the nonionic polymer and high ion transport from the PIL and block copolymer morphology. We have recently synthesized a PILBCP, poly(MMA-*b*-MUBIm-OH), comprised of a PIL component (MUBIm-OH = 1-[(2-methacryloyloxy)undecyl]-3-butylimidazolium hydroxide) and a non-ionic component (MMA = methyl methacrylate) [30]. The family of polymerized ionic liquid block copolymers containing the PILBCP used here has demonstrated sufficient chemical stability at AEMFC relevant conditions [5,7,36]. Membrane electrode assemblies (MEA) were fabricated and tested in a single-cell stack with this PILBCP as both the solid-state membrane separator and the ionomer in the catalyst layers [30]. A peak power density of approximately 30 mW cm⁻² (60 °C with H₂/O₂ at 25 psig (172 kPa) backpressure) was achieved. The resulting AEMFC performance was considerably lower than expected given the high hydroxide conductivity of approximately 56 mS cm⁻¹ at 60 °C and 95% RH for the PILBCP [30]. There are two likely sources of the observed low AEMFC power density: (1) physical/chemical blocking of catalytic sites by the PILBCP (poor triple phase boundary geometry) adversely affecting the kinetics of the anodic and cathodic reactions through both an inactivation of blocked catalytic sites and an ionic/reactant diffusional resistance imparted by the polymer film and/or (2) interfacial resistance between the ion conducting species in the AEM and ionomer within the catalyst layer as a consequence of sub-optimal ionomer integration, catalyst layer fabrication and MEA assembly.

In this work we attempt to address the first of these limiting factors by using rotating disk electrode (RDE) half-cell experiments to determine the impact of the PILBCP, poly(MMA-*b*-MUBIm-OH), on the ORR and HOR activity of a commercial Pt/C nanoparticle catalyst. The effect of PILBCP on both the ORR and HOR was investigated at three PILBCP loadings within the catalyst layer at 23, 41, and 57 wt.% of total solid. The PILBCP results were then compared to Nafion coated Pt/C nanoparticles to determine if Nafion exerts a similar impact on half-cell reaction kinetics.

2. Experimental

2.1. Materials

Acetonitrile (ACN, anhydrous, 99.8%), 2-propanol (IPA, electronic grade, 99.999%), sulfuric acid (H₂SO₄, ACS reagent, 95–98%), and potassium hydroxide (KOH, semiconductor grade, 99.99%) were used as received from Sigma-Aldrich. Nitric acid (HNO₃, ACS plus, 70%) was used as received from Fisher Scientific. Perchloric acid (HClO₄, omnitrace ultra, 65–71%) was used as received from EMD Millipore. Millipore (Milli-Q Synthesis A10) water with resistivity ≈ 18.2 MΩ cm was used to make all electrolyte solutions. Research grade (99.999%) oxygen (O₂), hydrogen (H₂), and argon (Ar) were used as received from Airgas. Liquion solution LQ-1105 1100 EW (5 wt.% Nafion) was used as received from Ion Power. The PILBCP was prepared according to literature and the synthetic procedure and properties can be found elsewhere [14,30].

2.2. Electrochemical measurements

PILBCP and Nafion coated Pt/C nanoparticle catalysts were electrochemically characterized in a three-electrode cell with a Pt mesh (Alfa Aesar) counter electrode and a Ag/AgCl (BASi) reference electrode. The reference electrode was calibrated against a hydrogen reference and found to have an offset of 0.97 V and 0.27 V at 25 °C for 0.1 M KOH and 0.1 M HClO₄, respectively. All potentials listed are referenced to the reversible hydrogen electrode (RHE). Prior to any electrochemical experiments, all glassware was cleaned by soaking in a solution of concentrated 1:1 H₂SO₄:HNO₃ for at least 8 h followed by rinsing and boiling in Millipore water.

Pt/C thin films on glassy carbon (GC) disks (5 mm diameter, 0.196 cm², HTW GmbH) were synthesized by drop casting from a catalyst ink in which Pt/C (40 wt.% Pt, Fuel Cell Store HiSPEC 4000) was dispersed in H₂O at a concentration of 1 mg_{catalyst} mL⁻¹. Prior to loading with catalyst, the GC disks were polished to a mirror finish using progressively finer diamond paste down to 0.05 μm (Buehler). The GC disks were then sonicated in Millipore water to remove contaminants. The appropriate volume (7.35 μL) of catalyst ink to achieve a loading of 15 μg_{Pt} cm⁻² was pipetted onto the GC disks and dried under a flow of argon to form a uniform layer. Catalyst thin films were approximately 10 μm in thickness with a uniform coating on the disk; any non-uniform films were rejected. Catalytic activity is directly dependent on the quality of the catalyst layer on the disk [38,39]. A similar amount (7.35 μL) of PILBCP solution (0.25, 0.5, and 1.0 wt.% in ACN) or Nafion solution (1.0 wt.% in IPA) was then drop cast onto the catalyst layer and allowed to dry under a flow of argon.

Cyclic voltammetry (CV) was performed in Ar purged electrolyte by cycling between 0.18 and 1.07 V vs. the reversible hydrogen electrode (RHE) (Autolab PG Stat 302N) at 50 mV s⁻¹ for at least 30 cycles or more until the CV curve reached a steady state. All potentials are referenced vs. RHE. The polymer-coated catalysts were then transferred to O₂ saturated electrolyte for ORR activity measurements or H₂ saturated electrolyte for HOR activity measurements. Using a Pine Instruments rotator (AFMSRCE), the GC disk was rotated at 1600 rpm while running linear sweep voltammetry from 0.18 to 1.07 V vs. RHE at 20 mV s⁻¹. Ohmic iR drop was compensated for through the process described in ref. [40].

3. Results and discussion

The chemical structure of the PILBCP, poly(MMA-*b*-MUBIm-OH), used here is shown in Fig. 1. This PILBCP was synthesized through an anion exchange metathesis reaction. The bromide form of the conducting PILBCP as reported in [14], poly(MMA-*b*-MUBIm-Br), was used to coat the Pt/C nanoparticles due to its favorable solubility in organic solvents compared to other hydrophilic ions, such as bicarbonate (*i.e.*, HCO₃⁻) [30]. The uniform solution of poly(MMA-*b*-MUBIm-Br) in acetonitrile resulted in evenly distributed films of the PILBCP on the Pt/C nanoparticles. The PILBCP films were then ion exchanged to the hydroxide form, poly(MMA-*b*-MUBIm-OH), by cycling the potential between 0.18 and 1.07 V vs. RHE in Ar purged 0.1 M KOH electrolyte until the CV reached steady state. The large excess of electrolyte in the electrochemical cell results in sufficient dilution of any bromide ions after complete anion exchange, ensuring that bromide ions do not interfere with electrochemical experiments. However, as a precaution, the electrolyte was replaced with fresh 0.1 M KOH for the kinetic measurements after completion of the anion exchange.

Fig. 2 contains the CVs for commercial 40 wt.% Pt/C as a function of PILBCP content. With the addition of the PILBCP to the Pt/C film, adsorption features associated with hydrogen (between 0.5 and 0.1 V vs. RHE) and hydroxide/oxide (between 0.7 and 1.0 V vs. RHE) are significantly suppressed. This depression in current is a consequence of both the physical blocking of the platinum sites by the PILBCP, lowering the number of electrochemically active sites

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