



Exchange current density of the hydrogen oxidation reaction on Pt/C in polymer solid base electrolyte



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ABSTRACT

The exchange current density of the hydrogen oxidation reaction (HOR) on platinum supported on carbon (Pt/C) has been widely studied for liquid base electrolyte (LBE), but has yet to be reported for a polymer solid base electrolyte (SBE). The goal of this study is to determine the exchange current density for the HOR on Pt/C in an SBE using a hydrogen pump and to compare it with those in LBE and a polymer solid acid electrolyte (SAE). We find that the HOR activity in the SBE is almost the same as in LBE, and is nearly two orders of magnitude lower than in SAE. The similar HOR activities on Pt/C in SBE and LBE suggest that previously reported exchange current densities measured in LBE accurately reflect Pt/C's activity for the HOR in SBE fuel cells even though the modes of ion conduction in liquid and solid polymer electrolytes are inherently different.

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1. Introduction

Hydrogen fuel cells are a promising alternative power option for transportation because of their high efficiency, quick startup, long range per charge, and carbon-free emissions [1,2]. Fuel cells with a polymer solid acid electrolyte (SAE) provide high power densities but require platinum (Pt) as a catalyst, which costs around \$1300/oz [3]. Substituting SAEs with polymer solid base electrolytes (SBEs) allows for the use of non-precious metal catalysts, which results in more economically feasible fuel cells [4–6].

The two catalytic reactions in hydrogen fuel cells are the oxygen reduction and hydrogen oxidation reactions (ORR and HOR). Although the ORR is the slower of the two reactions, its rate is not significantly different in acid and base electrolytes, and non-precious metal catalysts have already been developed that match Pt's ORR activity in base [7–10]. However, the HOR activity, even on Pt, significantly drops when switching from acid to base systems [11,12]. Therefore, studying pH effect on Pt's HOR activity is high priority in low temperature fuel cell research [10–14].

The HOR's activity is traditionally measured in liquid electrolyte using a rotating disk electrode (RDE) [15]. However, inherent diffusion limitations in an RDE system prevent measuring Pt's extremely high activity in liquid acid electrolyte (LAE) [11]. To remedy this issue, a hydrogen pump [16] is used in which gaseous H₂ is supplied to Pt interfaced with an SAE [16–18]. In contrast, the HOR on Pt in liquid base electrolyte (LBE) is considerably slower than in acid, meaning RDE can be used to

determine its activity [11]. However, to the best of our knowledge, there is no reported HOR activity on Pt in an SBE, and it is uncertain how this activity will compare with its counterparts in LBEs and SAEs. In this study, we use an H₂ pump to measure, for the first time, the HOR activity for Pt supported on carbon (Pt/C) interfaced with an SBE.

2. Methods and materials

2.1. Rotating disk electrode

RDE measurements were performed using a Princeton Applied Research VMP2 potentiostat. The RDE inks were prepared by suspending 13.1 mg of 5 wt.% Pt/C (E-TEK) in a mixture of 3.5 mL deionized water (18.2 MΩ cm) and 1.5 mL isopropyl alcohol (IPA). The ink was vortexed and then sonicated in an ice bath and for 12 h before dispensing a 5.25 μL aliquot onto a glassy carbon electrode (Pine Instruments, 0.196 cm²) to achieve a final loading of 3.5 μg_{Pt}/cm². The electrodes were polished with Buehler 0.05 μm alumina polishing suspension and rinsed thoroughly with DI water before ink application. After the ink air dried for 24 h, the catalyst-loaded working electrode (WE) was submerged in either 0.1 M perchloric acid (HClO₄, diluted from 70% HClO₄, EMD Millipore) or 0.1 M potassium hydroxide (KOH, Sigma-Aldrich 99.99% metal basis, semiconductor grade) in a three-electrode cell. Platinum wire was used as the counter electrode (CE), and a saturated calomel electrode (SCE) was used as the reference electrode (RE). The electrolyte was saturated with argon to record cyclic voltammograms (CVs) for electrochemical surface area (ECSA) calculations. Afterwards, the electrolyte was saturated with H₂ to record polarization curves.

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2.2. Hydrogen pump

Nafion 211 and LIQUion 1100 (5 wt.%) were used as the SAE membrane and ionomer materials, respectively. The Nafion membranes were pre-treated with the following steps: 1) boiled in 3% hydrogen peroxide for 1 h, 2) boiled in DI water for 1 h, 3) boiled in 0.5 M sulfuric acid for 1 h, and 4) rinsed and boiled in DI water for 1 h. The SAE was held taut and dried using compressed air. Tokuyama A201 and AS-4 (5 wt.%) were used as the SBE membrane and ionomer materials, respectively. Dry A201 membranes were used directly without any pre-cleaning treatment.

Pt/C ink was applied onto each side of the Nafion and Tokuyama membranes using an automated spray nozzle system (Sono-Tek Exactacoat Ultrasonic Coating System) so that four duplicate 5 cm² catalyst-coated membrane samples could be fabricated at one time to insure reproducible data. The inks were prepared by suspending 0.3 g Pt/C and 1.5 g ionomer solution in 11 g DI water and 9.575 g IPA. The inks were vortexed and then sonicated in an ice bath for 1 h. One side of each membrane was loaded to 0.4 mg_{Pt}/cm² using 47.2 wt.% Pt/C (TKK, Tanaka) to serve as a combined CE and reference electrode (CE/RE). The opposite side of each membrane was loaded to ~6 μg_{Pt}/cm² using 5 wt.% Pt/C (E-TEK) and was used as the WE. The ultra-low Pt loading on the WE facilitated the kinetics measurements, and the high Pt loading on the CE/RE side insured a reliable reversible hydrogen electrode (RHE). The final ionomer content in the WE and CE/RE was

20 wt.%. After each electrode ink application, the membrane was dried for 1 h using compressed air and then weighed to calculate Pt loading.

The catalyst-coated Nafion membranes were hot pressed at 143 °C between two gas diffusion layers (10 wt.% PTFE Toray TGP-H-060) under 1200 lb_f for 3 min before being placed into an H₂ pump assembly, which consists of two gold-plated current collector plates, two graphite flow channel plates, and two 5 μm thick silicone gaskets. The catalyst-coated A201 membrane was not hot pressed, but simply sandwiched between two gas diffusion layers (0 wt.% PTFE Toray-H-060) during cell assembly [19]. The cell was assembled with 30 in-lbs of torque.

A Scribner 850e fuel cell test station controlled the temperature of the cell and the humidifiers. A Princeton Applied Research VMP2 and a Solartron SI 1287 potentiostat were used for collecting CV and polarization curves, respectively. For collecting the CV curves, humidified argon was supplied to the WE and humidified hydrogen was supplied to the CE/RE while the cell was kept at ambient temperature and pressure. To obtain the polarization curves, humidified hydrogen was supplied to both the WE and CE/RE while the cell was heated to 333 K (60 °C) and pressurized to 200 kPa_g. Each current step was held for 5 min, and the average potential was used.

2.3. Resistances

Polarization curves for both RDE and H₂ pump tests were iR-corrected for ohmic losses using AC impedance spectroscopy. The

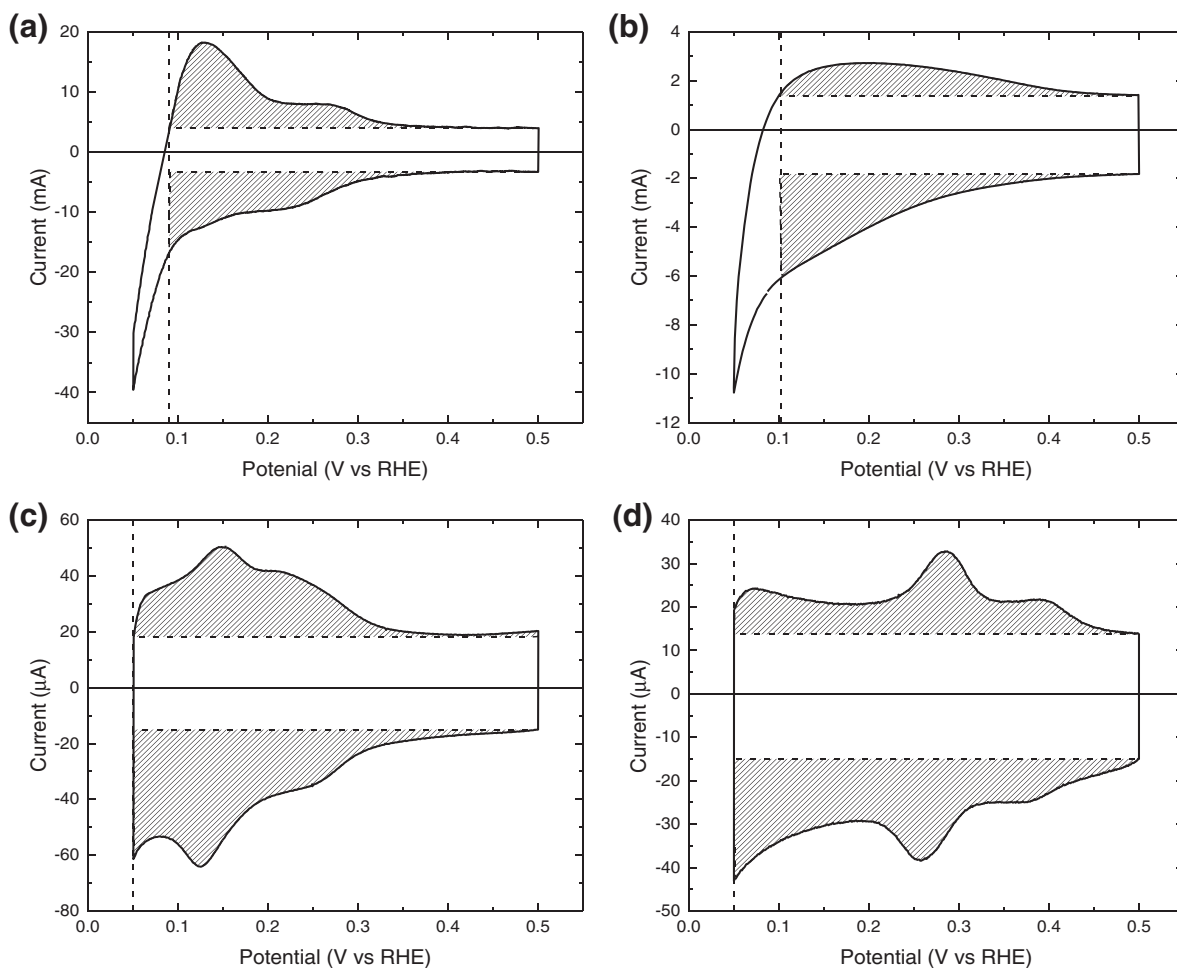


Fig. 1. Cyclic voltammograms for Pt/C at 293 K (20 °C) and ambient pressure in various electrolytes. Shaded regions were integrated and averaged to calculate ECSA. (a) & (b) SAE and SBE, respectively, collected at 300 mV/s (SAE) and 500 mV/s (SBE). WE loaded to 6 μg_{Pt}/cm² with 5 wt.% Pt/C and purged with 0.05 L/min Ar. CE/RE was loaded to 0.4 mg_{Pt}/cm² with 47.2 wt.% Pt/C and purged with 0.2 L/min H₂. (c) & (d) LAE (0.1 M HClO₄) and LBE (0.1 M KOH), respectively, purged with Ar and both collected at 50 mV/s. Glassy carbon WE loaded to 3 μg_{Pt}/cm² with 5 wt.% Pt/C.

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