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 of 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.

Keywords

Hydrogen oxidation reaction
Exchange current density
Hydrogen pump
Hydroxide exchange membrane
Platinum catalyst

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 prices 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 rate limiting, its activity does not drastically in higher pH SBEs, and non-precious metals have already been developed [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 Pt is interfaced with an SAE to eliminate diffusion limitations [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 a 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 1-2 hours 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 hours, 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.

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 hour, 2) boiled in DI water for 1 hour, 3) boiled in 0.5 M sulfuric acid for 1 hour, 4) rinsed and boiled in DI water for 1 hour. 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 hour. 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 RHE 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 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 hour using compressed air. Loadings were calculated by weighing the dried membranes before and after ink application.

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 minutes before being placed into a 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) [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 minutes, 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 impedance was measured with a Princeton Applied Research VMP2 potentiostat for RDE and a Solartron SI 1260 Impedance/Gain-Phase Analyzer for the H₂ pump. Measurements were taken between 100 kHz and 0.1 Hz with 10 mA amplitude. The kinetic currents for Pt/C in SAE and SBE were also corrected for effective proton and hydroxide resistances in the electrodes, respectively, which were calculated using a previously reported method [16] and found to be negligible.

3. Results and discussion

Cyclic voltammograms were collected for Pt/C in all electrolytes. The procedure in Ref. [20] was used for collecting CVs in the SAE and SBE. The ECSA for Pt/C was obtained from integrating and averaging the H adsorption and desorption areas, indicated by the shaded regions in Fig. 1. Table 1 summarizes the calculated ECSAs in each electrolyte. Fig. 1b represents a CV curve for Pt/C in an SBE. One noticeable difference between the CV curves for the SBE and SAE is that the area of the top H-desorption region in the SBE CV is about two times less than the area of its bottom H-adsorption area. This discrepancy may be due to different adsorption/desorption mechanisms that occur at the Pt-SBE interface or due to adsorption/desorption interactions between the cationic polymer in the SBE and the Pt surface. However, a more in-depth CV study for SBEs needs to be conducted in order to make a more concrete conclusion on this observation.

Fig. 1. Cyclic voltammograms for Pt/C at 293 K (20 °C) and ambient pressure in Ar purged electrolyte. 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 $6 \mu\text{g}_{\text{Pt}}/\text{cm}^2$ with 5 wt% Pt/C and purged with 0.05 L/min Ar. CE/RE was loaded to $0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2$ with 47.2 wt% Pt/C and purged with 0.2 L/min H_2 . (c) & (d) LAE (0.1M HClO_4) and LBE (0.1M KOH), respectively, purged with Ar and both collected at 50 mV/s. Glassy carbon WE loaded to $3 \mu\text{g}_{\text{Pt}}/\text{cm}^2$ with 5 wt% Pt/C.

Polarization curves were collected in each electrolyte to quantify Pt/C's HOR activity with the exchange current density (i_o), which was calculated using the Butler-Volmer equation:

$$i_k = i_o \left[e^{(\alpha F/RT)\eta} - e^{(-(1-\alpha)F/RT)\eta} \right] \quad (1)$$

where, i_k is kinetic current density ($\text{mA}/\text{cm}_{\text{Pt}}^2$), i_o ($\text{mA}/\text{cm}_{\text{Pt}}^2$) is the exchange current density, α is a dimensionless transfer coefficient, F is Faraday's constant (96,485 C/mol), R is the universal gas constant (8.314 J/(mol K)), and T (K) is the cell temperature. The kinetic currents, i_k , were extracted from the polarization curve using the Koutecky-Levich equation[11]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (2)$$

where i_d (mA/cm_{Pt}²) represents the hydrogen diffusion limited current. The i_k values were normalized with the roughness factor ($\psi = 2.03$) to insure an accurate interpretation of i_o [21].

In LBE, i_o for Pt/C was determined to be 0.5 ± 0.02 mA/cm_{Pt}² with $\alpha = 0.47$. However, i_k could not be determined in LAEs since the HOR activity on Pt/C is so fast that the iR-free current density overlaps with the Nernstian diffusion overpotential [11, 22]. Although i_o in LAE has been reported previously in various publications [23–26], the range of reported values is too large to make a reliable conclusion.

Conversely, hydrogen diffusion limitations are negligible in a H₂ pump at the low overpotentials used in RDE, allowing for the calculation of i_o for Pt/C in a SAE [16]. Therefore, Eq. 2 simplifies to $i = i_k$, and the Butler-Volmer equation can be fit directly to the iR-corrected polarization curves recorded in SAE and SBE using $\alpha = 0.5$ [27], as shown in Fig. 2a. The i_o values found for the best fits were 171 ± 21 mA/cm_{Pt}² and 2.60 ± 0.03 mA/cm_{Pt}² for the SAE and SBE, respectively. Our results reveal for the first time i_o for Pt/C in an SBE, therefore allowing for the comparison of the of HOR activity in SBE with SAE and LBE. As seen in Table 1 and Fig. 2b, i_o is roughly 100 times larger in SAE than in SBE, consistent with the observations that the HOR kinetics on Pt/C are much faster at a lower pH.

Fig. 2. (a) Butler-Volmer fit to iR-corrected polarization curves for Pt/C in an SAE and SBE at 333 K (60 °C) and 200 kPa_g back pressure. Curves were collected in H₂ pump with 100% humidified H₂ flowing at 0.2 L/min to the WE and CE/RE compartments. The WE was loaded to $\sim 6 \mu\text{g}_{\text{Pt}}/\text{cm}^2$ with 5 wt% Pt/C, and the CE/RE was loaded to $\sim 0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2$ with 47.2 wt% Pt/C. (b) Comparison of i_o for Pt in solid and liquid electrolytes between this work (denoted by **) and literature (denoted by reference number), all at approximately 333K (60 °C). Literature i_o values were extrapolated to 333 K (60 °C) using $E_a = 16$ kJ/mol and $E_a = 29.5$ kJ/mol in SAE and LBE, respectively [11, 18]. The LAE is blank since a reliable i_o cannot be obtained. Inset in (b) shows a linear scaled vertical axis for i_o in SBE and LBE. Error bars were generated using standard error of i_o calculated for two samples in each type of electrolyte.

Table 1. Summary of ECSAs (293 K) and i_o values (333 K) calculated for each electrolyte.

Electrolyte	ECSA ($\text{m}_{\text{Pt}}^2/\text{g}_{\text{Pt}}^2$)	i_o ($\text{mA}/\text{cm}_{\text{Pt}}^2$)
LAE	96	-- ^a
LBE	58	2.15 ± 0.09
SAE	97	171 ± 21
SBE	23	2.60 ± 0.03

^a i_o for LAE cannot be calculated, discussed previously.

However, the most crucial comparison for the Pt/C HOR activities is between the SBE and LBE since the electrolyte-catalyst interfaces are inherently different in each electrolyte. The HOR in an SBE is limited to triple phase boundary regions where the H_2 , active Pt surfaces, and the OH^- conductive cations in the SBE all come together. In an LBE, the aqueous electrolyte covers the entire catalyst surface, allowing H_2 and hydroxide ions to access any available active Pt site on the working electrode. Despite these differences, the HOR i_o in an SBE is similar to that in a LBE obtained by us and others (Fig. 2b). This suggests that the HOR activity is not hindered nor accelerated when the mode of ion-conduction through the electrolyte to the catalyst surface is changed from alkaline liquid solutions to hydroxide-exchange polymers. Note that the pressure in the hydrogen pump is different from that of the RDE, but a simple estimation shows this is unlikely to alter the conclusion.

4. Conclusions

Using a H_2 pump, we obtained, for the first time, the HOR i_o of Pt/C in SBE. We found that the HOR i_o in an SBE is close to that in an LBE, and it is about two orders of magnitude lower than in an SAE. These findings answer an important question regarding how the HOR activity on Pt compares between in SBE and in LBE. The similar HOR activities on Pt/C in SBE and LBE suggests that Pt activities measured with RDE do in fact reflect the HOR activity on Pt/C when interfaced with an SBE in a hydrogen fuel cell. Overall, utilizing a H_2 pump in comparison with RDE measurements provides a more thorough analysis of a catalyst's HOR activity, and these results on Pt/C provide a useful baseline for further studying HOR kinetics in an SBE. Finally, although this study is focused on the HOR, these results are also applicable to electrolyser and solar hydrogen research initiatives that utilize HOR's reverse reaction, hydrogen evolution.

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