

Fabricating and Measuring Low-Platinum Content HOR/HER Gas Diffusion Electrodes

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For the facile hydrogen oxidation and evolution reactions (HOR and HER) on Pt in acidic electrolytes, it is difficult to determine the kinetic currents using the conventional rotating disk electrode (RDE) method because of insufficient mass transport rates. The HOR polarization curves on ultra small microelectrodes, with the mass-transport limiting currents about two order-of-magnitude higher than those obtained in RDE measurements, featured a plateau after a rapid current rise with increasing overpotentials (1). Kinetic analysis using a dual-pathway kinetic equation found that the Tafel-Volmer pathway dominates at small overpotentials (± 40 mV) with an exchange current of 0.47 A cm^{-2} (2). For the HOR at the anode of PEM fuel cells, a Pt loading of 0.05 mg cm^{-2} was demonstrated to be sufficient, supporting the exchange current being $0.4 \pm 0.2 \text{ A cm}^{-2}$ (3). However, the high exchange current has not been directly verified by a simple experimental method that can be employed for testing HOR/HER gas diffusion electrodes (GDEs).

In this study, we first obtained HOR-HER polarization curves on GDE samples in H_2 -saturated 1 M HClO_4 solutions. As shown in Figure 1a, the currents can rise without deviation from the linear behaviors to 100 mA cm^{-2} (red curve), which is more than 20 times higher than the HOR mass transport limiting current on RDE (blue curve, $\sim 4 \text{ mA cm}^{-2}$), demonstrating that metal nanoparticles on GDEs act as an assembly of nanoelectrodes similar to single-particle microelectrodes. Next, we corrected the contact and ionic resistances in the circuits using the high frequency resistance (HFR) determined by electrochemical impedance spectroscopy (EIS).

Figure 1b plots the polarization curves after the iR correction. From the linear fitting of these curves over the ± 1 mV overpotential region, the kinetic resistances (R_k) were obtained as listed in the figure. Apparently, a densely-packed catalyst layer on RDE is at least one order-of-magnitude less active than the GDE samples with comparable Pt loadings. Among the three GDEs, the best one ($0.03 \text{ } \Omega \text{ cm}^2$) is not the one with the highest Pt loading, but with a better microporous layer, illustrating a key role of an effective assembly of nanocatalysts in fabricating high-performance GDEs.

Based on the dual-pathway kinetic equation with a 0.47 A cm^{-2} exchange current, an i/V slope of $0.030 \text{ A cm}^{-2} \text{ mV}^{-1}$ is obtained, and its reciprocal yields $0.033 \text{ } \Omega \text{ cm}^2$ at room temperature (black curve in Figure 1b). While kinetic current increases with the increasing Pt surface area ratio (sar) to the electrode, the kinetic resistance, $R_k = \eta/j_k = 33/sar$, decreases. Figure 2 shows that R_k drops to $1 \text{ m}\Omega \text{ cm}^2$ with a Pt sar of 33 at $23 \text{ }^\circ\text{C}$. Using an apparent activation barrier of 0.2 eV , the curves for the operating temperatures of PEM fuel cells ($80 \text{ }^\circ\text{C}$) and water electrolyzers ($50 \text{ }^\circ\text{C}$) are generated. The results indicate that R_k can be reduced to $1 \text{ m}\Omega \text{ cm}^2$ by having a 10 and 17 Pt sar at 80 and $50 \text{ }^\circ\text{C}$, respectively. Likewise, assuming a fully utilized Pt specific surface area (ssa) of $1 \text{ cm}^2 \mu\text{g}^{-1}$, the 10 and $17 \text{ } \mu\text{g cm}^{-2}$ Pt loading, respectively,

would be adequate to make the kinetic loss on the HOR and HER negligible (1 mV at 1 A cm^{-2}).

While much has been learned in the past ten years on nanoscale in developing metal electrocatalysts, understanding the assembly at a step up in size and complexity becomes substantially important (4). Efforts in this area may enable us to reach the predicted performance in PEM fuel cells and water electrolyzers.

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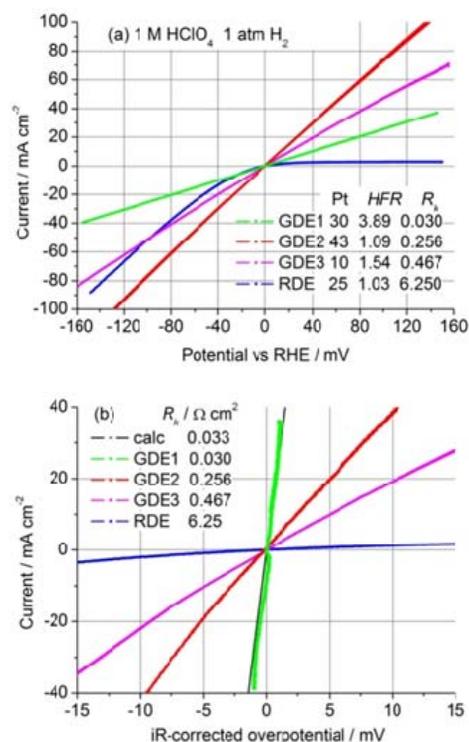


Figure 1. (a) HOR-HER polarization curves measured for three GDE samples with PtRu/C catalysts, in comparison with the one measured on RDE at 2500 rpm. (b) The corresponding i/V curves after the iR correction. The Pt loading is given in $\mu\text{g cm}^{-2}$, HFR and R_k in $\Omega \text{ cm}^2$.

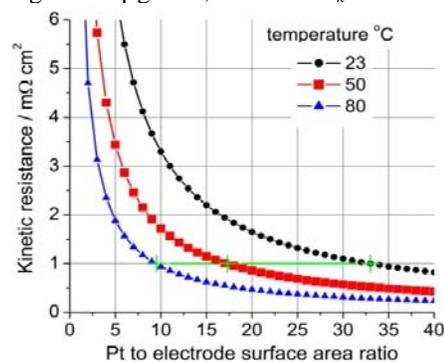


Figure 2. HER-HOR kinetic resistance as a function of the Pt surface area ratio (sar) to the electrode and temperature calculated for fully utilized Pt nanocatalysts.