Catalyst evaluation for oxygen reduction reaction in concentrated phosphoric acid at elevated temperatures

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Abstract: Phosphoric acid is the common electrolyte for high-temperature polymer electrolyte fuel cells (HT-PEMFCs) that has the advantages such as enhanced CO tolerance and simplified heat and water management. The currently used rotating disk electrode technique is limited to tests in dilute solutions at low temperatures and hence is not suitable for catalyst evaluation for HT-PEMFCs. In this study, we have designed and constructed a half-cell setup for ORR catalyst evaluation. By optimization of the hydrophobic characteristics of electrodes and the catalyst layer thickness, ORR activities of typical Pt/C catalysts are successfully measured in concentrated phosphoric acid at temperatures above 100°C. In terms of mass-specific activities, the catalyst exhibits about two times higher activity in the half-cell electrode than that observed in fuel cells, indicating the feasibility of the technique as well as the potential for further improvement of fuel cell electrode performance.

Catalyst evaluation for oxygen reduction reaction in concentrated phosphoric acid at elevated temperatures

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Phosphoric acid is the common electrolyte for high-temperature polymer electrolyte fuel cells (HT-PEMFCs) that has the advantages such as enhanced CO tolerance and simplified heat and water management. The currently used rotating disk electrode technique is limited to tests in dilute solutions at low temperatures and hence is not suitable for catalyst evaluation for HT-PEMFCs. In this study, we have designed and constructed a half-cell setup for ORR catalyst evaluation. By optimization of the hydrophobic characteristics of electrodes and the catalyst layer thickness, ORR activities of typical Pt/C catalysts are successfully measured in concentrated phosphoric acid at temperatures above 100°C. In terms of mass-specific activities, the catalyst exhibits about two times higher activity in the half-cell electrode than that observed in fuel cells, indicating the feasibility of the technique as well as the potential for further improvement of fuel cell electrode performance.

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1. Introduction

Thanks to the high energy conversion efficiency and environmentally benign operation, polymer electrolyte membrane fuel cells (PEMFCs) are among the most promising candidates of clean energy conversion technologies.[1-3] Compared to conventional fuel cells based on Nafion membrane with the operation temperature below 100 °C, high temperature (HT) PEMFCs that are operated at 120 - 200 °C has several advantages including much enhanced CO tolerance, simplified heat and water management, and the capability to integrate with fuel processors. [4-10] Phosphoric acid-doped polybenzimidazole (PBI) membranes are the most commonly used material in HT-PEMFCs.[8, 11] Accordingly, the environment in HT-PEMFC electrodes is significantly different from that in conventional PEMFCs. The widely used rotating disk electrode (RDE) testing is developed for catalyst evaluation in dilute acid solutions (*e.g.* 0.1 M HClO₄ or 0.5 M H₂SO₄) at room temperature. Such results can hardly give a good indication of the catalyst performance in HT-PEMFCs. Therefore, it is of great importance to develop a fast and efficient approach for catalyst evaluation under conditions more relevant to HT-PEMFC, *i.e.* in concentrated phosphoric acid at typical temperatures of 130 -170 °C.

Theoretically, to measure the activity of an electrocatalyst is simple. A current response at a specific potential needs to be recorded. In practice, however, many factors can affect this process. [12-15] In order to determine the intrinsic activity of a catalyst, the mass transport of relevant species needs to be fast enough, at least at low overpotentials, and the amount of the catalyst involved in the reaction is to be accurately measured. [16] Regarding ORR tests using the RDE technique, the catalyst is first dispersed in a solvent and the mass applied is determined by the volume of the ink. The electrochemical active surface area (ECSA) of Pt/C catalysts can be estimated by conducting hydrogen underpotential deposition or CO adsorption/oxidation tests. By immersing the catalyst layer in an O₂ saturated acidic solution, almost all catalyst particles have good access to the reactants, *i.e.* oxygen, protons, and electrons.[17] The challenge is the big mass transport resistance from the low solubility of molecular O₂ and its small diffusion coefficient in aqueous solutions. In 0.1 M HClO₄ at room temperature, for example, they have values of $1.26 \times 10^{-3} \text{ mol L}^{-1}$ and $1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively. [18] But this resistance can be corrected by applying the *Koutecký-Levich* analysis,

a major reason for the wide application of this technique. In hot concentrated phosphoric acid, however, the RDE technique meets greater challenges. The oxygen solubility in concentrated phosphoric acid is much lower, e.g., $3.8 \times 10^{-4} \text{ mol L}^{-1}$ in 90 wt% H_3PO_4 at 100 °C and $2.8 \times 10^{-4} \text{ mol L}^{-1}$ at 150 °C.[19] And the viscosity of concentrated H_3PO_4 is two orders of magnitude higher than that of dilute acid solutions.[20-22] Consequently, oxygen transport is limited and the recorded ORR limiting current is very small. The O_2 diffusion resistance within the diffusion and catalyst layer is so significant that it can no longer be compensated by the *Koutecký-Levich* equation. Fleige et al. have skillfully developed a pressurized RDE setup to increase the oxygen solubility and diffusion rate in electrolytes, which was an effective strategy but it increased the complexity of the measurement and met the issue of unstable reference electrode potentials under the pressurized environment.[23] Construction of an RDE setup operational at temperatures above 100 °C is another challenge. The tightness of the joint of the electrode disk and the surrounding plastic body is always an issue at elevated temperatures. Few reports are available on RDE tests of catalysts in hot concentrated acid. [22, 24]

A fuel cell gas diffusion electrode is a porous structure with optimized pore size distribution and wetting characteristics. This also applies to gas diffusion electrodes in half cells. Using gas diffusion electrodes in electrochemical half-cells is attractive for the characterization of the catalyst activity under practical conditions closer to fuel cell operation.[25-31] Zalitis *et al.*[30] introduced a floating electrode design with a thin catalyst layer, whereby the catalyst activity was measured with efficient mass transport in 4.0 M HClO_4 . Pinaud *et al.* [27] showed a half-cell design with a graphite flow field and the catalyst activity could be accurately measured in 1.0 M HClO_4 . In order to increase the mass transport and catalyst utilization in gas diffusion electrodes, optimum distribution of electrolyte throughout the catalyst layer is the key. Several mathematical models have been proposed to understand structures of gas diffusion electrodes, which, to some extent, showed good correlation with experimental results.[32, 33]

In this work, we designed and tested an electrochemical half-cell setup for catalyst evaluation in concentrated phosphoric acid at elevated temperatures. By optimization of the hydrophobic characteristics of the electrode and application of a thin catalyst layer, ORR activities of typical

highly porous catalysts can be measured under conditions of efficient high mass-transport. With a commercial Pt/C catalyst as a reference, the obtained activity results by the half-cell setup are comparable with those from the RDE measurements at room temperature and from fuel cell tests at high temperatures, demonstrating the feasibility of this method for catalyst performance evaluation under HT-PEMFC conditions.

2. Experimental

2.1 Half-cell construction and electrochemical test protocols

The structure of the half-cell setup is illustrated in Figure 1. The cell body was made from a low thermal expansion borosilicate glass (Pyrex®), which is resistant to concentrated phosphoric acid till 200 °C.[34] The cell had an oil heating jacket and a polytetrafluoroethylene (PTFE) lid. The jacket was heated by circulating silicone oil through a thermostatic oil bath (JULABO® H10) equipped with a temperature controller (HUBER® Pilot One 202 C). The local temperature close to the working electrode was monitored by a separate thermocouple. A three-electrode configuration was used in the setup. The reference electrode (RE) was a reversible hydrogen electrode (RHE) with a freshly cleaned platinum wire soaked in the same electrolyte as in the main compartment with constant hydrogen bubbling. The distance between the Luggin capillary tip and the working electrode (WE) surface was about 5 mm to avoid the shielding effect. [35] A platinum mesh placed facing the WE was used as the counter electrode (CE). The electrolyte was 85 wt% H₃PO₄ (from VMR®, ACS reagent grade) or lower concentrations diluted from it with Millipore water. All glassware was thoroughly cleaned by using Piranha solution and rinsed with hot Millipore water several times before use.

The WE consisted of a catalyst layer, a microporous carbon layer (MPL) and a gas diffusion layer (GDL), as illustrated in Figure 1. It was embedded into a specially designed PTFE holder. A commercial MPL/GDL assembly (Freudenberg® H23C2) was chosen and used for the electrode preparation after preliminary tests of different MPL and GDL combinations. A PTFE O-ring with an inner diameter of 7 mm was used as sealing. This also defined the active surface area of the electrode (i.e., 0.385 cm²). On the back side of the GDL, a stainless steel current collector with separate gas

inlet- and outlet- openings was used to achieve good electronic contact. A low platinum load Pt/C catalyst (20 wt% Pt/C from Johnson Matthey) was selected as the reference material for all measurements since a major motivation for this work is potentially for evaluation of non-platinum catalysts, which often contain high carbon contents. The working electrode was tilted to an angle of 45°, instead of being placed vertically, so that the possible accumulation of purging gas bubbles on the WE surface could be avoided. The electrodes for tests in concentrated H₃PO₄ were prepared with hydrophobic characteristics. The catalyst ink was first prepared by mixing a specific amount of 20 wt% Pt/C in a mixture of 5 wt% PTFE dispersion and isopropanol. It was then sprayed onto the MPL/GDL substrate kept at 110 °C. The electrode was eventually heated and kept at 360 °C in Ar flow for 20 min to remove the surfactant of the PTFE dispersion and sinter the PTFE in the catalyst layer. Addition of PTFE in the catalyst layer is a necessity for constructing a hydrophobic network, though at expense of blocking some catalytic sites. After preliminary efforts to optimize the PTFE content in the catalyst layer, 10 wt% PTFE in the catalyst layer (PTFE/PTFE+catalyst) was chosen and used throughout the work. A high accuracy balance with the resolution of 0.001 mg was used to precisely determine the actual catalyst loading. For the tests in 5.0 M H₃PO₄, a catalyst layer with no addition of PTFE was attempted. In that case, the catalyst layer was prepared by directly depositing a specific amount of catalyst ink (10 mg 20 wt% Pt/C catalyst in 100 µL Milli-Q water and 5.0 mL isopropanol) onto the MPL and dried in air. The catalyst loading for each test would be specified in the discussion section. Scanning electron microcopy was conducted on a Zeiss EVO MA10 and electrode cross sections were made by a Hitachi E-3500 ion mill.

The half-cell measurements were conducted by using a potentiostat (Versa STAT4, Princeton Applied Research). Tests with O₂ at the flow rate of about 20 mL min⁻¹ was first conducted. At higher flows, the gas might diffuse through the electrode and form bubble in the electrolyte, which was visible and should be avoided during the measurements. Potential cycling between 0 and 1.0 V at a scanning rate of 50 mV S⁻¹ was initially used to activate the catalyst layer until the stable performance was achieved. A linear sweep voltammogram at 5 mV s⁻¹ from the open circuit voltage (OCV) to 0.2 V was subsequently recorded. The solution resistance between the RE and WE was determined by conducting electrochemical impedance spectra (EIS) measurements at OCV. It was 1~1.5 Ω for different tests in 85 wt% H₃PO₄ at 140 °C. After measurements with saturated O₂, the

gas flow was switched to N₂ and the double-layer capacitance current of the electrode was recorded at 5 mV s⁻¹. The recorded ORR currents in all figures have been corrected for the capacitance current and solution resistance. The half-cell measurements were done with an upper-temperature limit of 140 °C (in contrast to a usual working temperature of a HT-PEMFC of 160 °C) to limit dehydration of the phosphoric acid over time.

2.2 RDE tests.

For comparison, standard RDE tests were conducted at room temperature. The electrolytes were 0.1 M HClO₄ (prepared from 70 wt% HClO₄, Aldrich, 99.999% trace metals basis) and H₃PO₄ solutions of different concentrations (prepared from 85 wt% H₃PO₄, VMR®, ACS reagent grade). The electrode was prepared by depositing 10 µL of well-dispersed catalyst ink (5 mg 20 wt% Pt/C in the mixture of 40 µL Milli-Q water, 2460 µL formic acid, and 50 µL 5wt% Nafion solution) on an RDE (0.196 cm², Pine Research Instrumentation) and dried in air. This gave the catalyst loading of 20 µg_{Pt} cm⁻². The RE and CE were a reversible hydrogen electrode and a graphite rod (99.995% trace metals basis), respectively.

2.3 Fuel cell tests

Fuel cell tests with the same ORR catalyst (20 wt% Pt/C from Johnson Matthey) with a platinum loading of 50.0 µg_{Pt} cm⁻² were also conducted. The anode was a commercial gas diffusion electrode with a platinum loading of 1.6 mg_{Pt} cm⁻², supplied from Danish Power Systems®. The used membrane was cast from polybenzimidazole of a molecular weight ca. 78000 and doped in 85 wt% H₃PO₄ for a week, reaching an acid doping level of about 10 H₃PO₄ per repeat unit of the polymer. The membrane electrode assemblies (MEAs) were constructed by sandwiching the membrane between the cathode and anode without pre-hot pressing. The active area of the MEA was 9 cm². The test was conducted using in-house hardware and fuel cell test setup. Polarization curves were obtained by a current step potentiometry from OCV to 0.2 V with the steady state potential recorded 2 min after each current was set. EIS measurements at OCV was conducted to measure the fuel cell resistance for the iR-correction. The measurement was carried out at ambient pressure and 140 °C with hydrogen and oxygen (H₂/O₂) and no humidification.

3. Results and discussion

We first evaluated the feasibility of the RDE approach for ORR catalyst evaluation in concentrated H_3PO_4 . Figure 2 shows the ORR polarization curves of a Pt/C coated RDE electrode at room temperature in 0.1 M HClO_4 and H_3PO_4 solutions of different concentrations. The strong effect of phosphate adsorption on the catalyst can be visualized by the negative shift of the kinetic region of ORR curves with switching from the dilute perchloric acid to 0.5 M H_3PO_4 and with further increase in the H_3PO_4 concentration. Meanwhile, the limiting current decreased significantly due to the decrease in oxygen solubility and diffusion coefficient in concentrated H_3PO_4 . When tested in 14.8 M (i.e. 85 wt%) H_3PO_4 the electrode exhibited a limiting current of only $0.08 \text{ mA cm}_{\text{geo}}^{-2}$, which was even smaller than the double-layer capacitance current of the carbon support. In this case, the mass transport resistance in the catalyst layer was so significant that the *Koutecký-Levich* equation derived from the flat RDE could no longer be applied anymore.

The half-cell approach was then investigated. The key to a successful catalyst evaluation using the gas diffusion electrode is to achieve fast mass transport and high, if not full, catalyst utilization. Besides the optimization of electrode structures, the catalyst layer thickness is another factor. Figure 1c shows the cross-section SEM image of a typical working electrode with the catalyst loading of $35.4 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ and the mean thickness of $3.4 \mu\text{m}$. During RDE tests, the O_2 diffusion distance is a function of the thickness of the catalyst layer and the static boundary layer adjacent to it, which alone is estimated to be about $15.4 \mu\text{m}$ for the condition of 0.1 M HClO_4 , 1600 rpm, and room temperature.[15, 36] In case of gas diffusion electrodes, the O_2 diffusion in the gas phase is much faster than that of dissolved molecules in aqueous solutions, and hence the resistance primarily originates from the diffusion through the electrolyte film distributed within the catalyst layer. In concentrated phosphoric acid, this film can be as thin as about 100 nm.[33] Therefore, the mass transport in gas diffusion electrodes is much more efficient than that in RDE measurements. In the followings, we will compare the results from the half-cell tests with those from the RDE and fuel cell tests.

The first comparison was made for RDE and half-cell tests in 5.0 M H₃PO₄ at room temperature. In this condition, the RDE approach is still feasible and serve as a reference. [37] The same amount of Pt/C catalyst (19.6 μg catalyst or 3.92 μg Pt) was deposited on the RDE and the half-cell electrode. As shown in Figure 3a, a standard ORR polarization curve was obtained from the RDE test with an onset potential (at 1.0 mA mg_{Pt}⁻²) of 0.95 V and a half-wave potential of 0.80 V. After correction of the mass-transport resistance by the Koutecky-Levich analysis, the obtained RDE kinetic current for the ORR was very close to that directly measured in the half-cell test. This result verifies the reliability of the half-cell approach for catalyst evaluation in this condition, as also shown in other reports.[27, 30]

The second comparison was made between two gas diffusion electrodes tested in 85 % H₃PO₄ at 140 °C, one having a platinum loading of 10 μg_{Pt} cm⁻² with no PTFE and the other having a thicker catalyst layer (22 μg_{Pt} cm⁻²) with 10 wt% PTFE. For the electrode without PTFE, the catalyst was severely flooded. As shown in Figure 3b, a peak current of about 2 A mg_{Pt}⁻¹ is observed at 0.5 V, indicating significant mass transport limitation of the dissolved oxygen through the concentrated phosphoric acid. Addition of PTFE in the catalyst layer improved the hydrophobicity and the electrode performance was much enhanced, despite the thicker catalyst layer. At the loading of 22 μg_{Pt} cm⁻² with 10 wt% PTFE, the electrode did not exhibit any limiting current in the tested interval.

Further investigations were made for electrodes at a constant PTFE content but varied catalyst loadings or catalyst layer thicknesses in 85 wt% H₃PO₄ at 140 °C. The results are shown in Figure 4a. As the catalyst loading decreased from 270 μg_{Pt} cm⁻² to 20 μg_{Pt} cm⁻², corresponding to a catalyst layer thickness from about 26 to 2 μm, the mass-specific activity of the catalyst (at 0.8 V) increased steadily from 40 mA mg_{Pt}⁻¹ to 133 mA mg_{Pt}⁻¹(Figure 4b), indicating the improved mass transport as well as catalyst utilization in thinner catalyst layers. We expected a steady activity of the catalyst when the catalyst loading was falling in a sufficiently low range where appropriate mass transport and high catalyst utilization were achieved. However, this was not realized. When the catalyst loading was decreased from 47 to 22 μg_{Pt} cm⁻², the measured activity still showed a further increase by 20%. That means even lower catalyst loadings need to be investigated. These are, however, very challenging to

1 achieve with uniform catalyst dispersion and accurate loading determination. Alternatively,
2 other catalysts with a higher platinum-to-carbon ratio should be used. With the 20 wt% Pt/C
3 catalysts, a loading in the range of 20-40 $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ gave a qualitative evaluation of the
4 catalytic activity. At the loading of 22 $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$, the mass-specific activity of the 20 wt%
5 Pt/C in 85 wt% H_3PO_4 at 140 °C, was 33 and 133 $\text{mA mg}_{\text{Pt}}^{-1}$ at 0.85 V and 0.80 V,
6 respectively. These values cannot be compared to values obtained in HClO_4 due to the strong
7 phosphate adsorption.
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10 For ORR measurements in hot concentrated H_3PO_4 , a fuel cell test is another appropriate
11 reference. We conducted both the half-cell and fuel cell tests at the same temperature with
12 similar catalyst loadings, with the result shown in Figure 4c. At 0.75 and 0.70 V, the catalyst
13 activity determined from the fuel cell test were 133 and 311 $\text{mA mg}_{\text{Pt}}^{-1}$, while those from the
14 half-cell test were 315 and 836 $\text{mA mg}_{\text{Pt}}^{-1}$, respectively, i.e. about 2.4 times higher. Given the
15 similar conditions in both tests, the enhanced performance is assumed to originate from
16 increased catalyst utilization. It has been estimated that the catalyst utilization in fuel cell
17 electrodes is in some cases only about 20-40% [38-40]. The observed higher catalytic activity
18 in the half-cell test indicates the possibility of further improvement of the electrode
19 performance in fuel cells.
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22 It should be remarked that to further determine the intrinsic activity of a catalyst, in terms of
23 area-specific or mass-specific activities, it is vital to quantify the electrochemical surface area
24 (ECSA) or the exact catalyst utilization in the catalyst layer. Unfortunately, we haven't found
25 an effective way to fulfill this task. We explored the conventional hydrogen adsorption
26 method and tested the electrode in both 85% H_3PO_4 at 140 °C and 0.1 M HClO_4 at room
27 temperature. The test in H_3PO_4 revealed depressed hydrogen adsorption peaks, apparently
28 because of the strongly adsorbed phosphate anions and the temperature dependent feature of
29 hydrogen adsorption on Pt. [41, 42] In 0.1 M HClO_4 , the electrode was too hydrophobic for
30 this condition and the measured current was extremely small. CO stripping might be a better
31 choice for this task, as Engl *et al.* [43] have proposed, though factors such as the side reaction
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currents may add challenging to determine the actual CO oxidation current. Such tests were not carried out in this study.

Apart from the test at 140 °C, the setup developed can also be used to evaluate the catalyst in a wide temperature range. Figure 4d shows ORR curves of an electrode ($35 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ of 20 wt% Pt/C) at temperatures from 28 to 140 °C. The trend of enhanced ORR kinetics is seen with increasing temperature. Once the ECSA or the catalyst utilization can be measured for each temperature, this provides a means to determine the activation energy of ORR over a wide temperature range.

4. Conclusions

Evaluation of ORR electrocatalysts in concentrated phosphoric acid at elevated temperatures by means of the rotating disk electrode technique was shown unsuitable because of the significant mass transport limitation due to the low solubility and diffusion coefficient of oxygen. An electrochemical half-cell setup was designed and constructed for the ORR activity measurement. Gas diffusion electrodes were optimized with respects to the hydrophobic characteristics and catalyst layer thicknesses, allowing a fast evaluation of the catalytic activity of ORR catalysts. Compared with fuel cell electrodes with the same Pt/C catalyst, the half-cell electrode showed about two times higher mass-specific current densities at low overpotentials. This demonstrates the feasibility of the half-cell technique for catalyst evaluation with electrolytes of varied concentration in a wide range of temperatures. The observed higher catalytic activity in the half-cell test indicates the potential for further improvement of the fuel cell electrode performance.

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Figure 1: Schematic illustration of the half-cell setup: (a) the overall cross-sectional view, and (b) the structure of the working electrode and the holder. The working electrode comprises a catalyst layer (red), a microporous carbon layer (black) and a supporting carbon cloth. The structure of the current collector was omitted in (b) for clarification. (c) Cross-section SEM image of a typical working electrode, where the catalyst layer consists of $35.4 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ of 20 wt% Pt/C and 10 wt% PTFE.

Figure 2: ORR polarization curves of 20 wt% Pt/C by RDE tests at room temperature in different electrolytes. The catalyst loading was $20 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$. The RDE rotation speed was 1600 rpm. All curves have been corrected for the double-layer capacitance current and solution resistance.

Figure 3: (a) ORR polarization curves of 20 wt% Pt/C in 5.0 M H_3PO_4 solution at room temperature by RDE and half-cell tests. The same amount of catalyst was used for both the RDE and the half-cell tests, i.e. $19.6 \mu\text{g}$ catalyst ($3.92 \mu\text{g}$ Pt). The RDE rotation speed was 1600 rpm. “RDE” and “RDE-kinetic” refer to the measured ORR current by the RDE test and the mass-transport corrected ORR current by *Koutecky–Levich* analysis, respectively. (b) ORR polarization curves of two gas diffusion electrodes with or without PFTE from half-cell tests in 85 % H_3PO_4 at 140 °C.

Figure 4: (a) ORR polarization curves of 20 wt% Pt/C electrodes with different catalyst loadings by half-cell testing in 85% H₃PO₄ at 140 °C. The PTFE content was 10 wt% in all electrodes. (b) The ORR activities of the electrodes reported in (a) at 0.8 V. (c) Comparison of the fuel cell and half-cell test results of the same catalyst (i.e. 20 wt% Pt/C) under similar conditions (85% H₃PO₄, 140 °C, ~ 50 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$). (d) ORR polarization curves of an electrode consisting of 35.4 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ of 20 wt% Pt/C and 10 wt% PTFE at different temperatures.

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