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Short communication

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

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HIGHLIGHTS

- A novel electrochemical half-cell setup design.
- ORR catalyst evaluation in concentrated phosphoric acid at elevated temperatures.
- The effect of catalyst layer thickness on the catalyst utilization explored.
- High catalyst utilization and efficient mass transport achieved.
- Indication of the possible performance enhancement of fuel cells.

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ABSTRACT

Phosphoric acid is the common electrolyte for high-temperature polymer electrolyte fuel cells (HT-PEMFCs) that have 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 to measure the intrinsic activities of catalysts towards the oxygen reduction reaction (ORR) in conditions close to HT-PEMFC cathodes. 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.

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 have 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 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, by immersing the catalyst layer in an O₂ saturated acidic solution, almost all catalyst particles have good access to the reactants,

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i.e., oxygen, protons, and electrons [17]. The challenge is the big mass transport resistance from the low solubility of molecular O_2 and its small diffusion coefficient in aqueous solutions [18]. But this O_2 diffusion 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, 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 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

The structure of the half-cell setup is illustrated in Fig. 1. The cell had an oil heating jacket and a polytetrafluoroethylene (PTFE) lid. 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. A platinum mesh placed facing the WE was used as the counter electrode (CE). The electrolyte was 85 wt% H_3PO_4 (from VMR[®], ACS reagent grade) or lower concentrations diluted from it with Millipore water. The WE consisted of a catalyst layer, a microporous carbon layer (MPL) and a gas diffusion layer (GDL), as illustrated in Fig. 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,

which also defined the active surface area of the electrode (i.e., 0.385 cm^2). 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. It is a well-studied standard Pt catalyst and has the activity similar to high-performing non-Pt catalysts, paving the way for this approach to be used in the future to study both Pt and non-Pt catalysts. The electrodes for tests in concentrated H_3PO_4 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. 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. We have prepared and tested six electrodes to investigate the effect of catalyst layer thickness on the catalyst performance, which had the same PTFE content (i.e., 10 wt%) but different catalyst loadings, including 22.4, 46.6, 67.2, 107.5, 138.7, and 273.0 $\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$. For the tests in 5.0 M H_3PO_4 , 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 the 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 half-cell measurements were conducted by using a potentiostat (Versa STAT4, Princeton Applied Research). Tests with O_2 at the flow rate of about 20 mL min^{-1} (corresponding to the stoichiometry of around 20 at 0.6 V for the typical measurements) were first conducted. 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. After measurements with O_2 , the gas flow was switched to N_2 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 between the WE and RE. The half-cell measurements were done with an upper-temperature limit of 140 °C to limit dehydration of the phosphoric acid over time. More details of the half cell tests can be found in Supporting Information. For comparison, we also tested the same catalyst at room temperature by the rotating disk electrode (RDE) approach and at 140 °C in a fuel cell, the experimental details of which are shown in Supporting Information.

3. Results and discussion

We first evaluated the feasibility of the RDE approach for ORR catalyst evaluation in concentrated H_3PO_4 . Fig. 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

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