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Influence of counter electrode material during accelerated durability test of non-precious metal electrocatalysts in acidic medium

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ABSTRACT

Significant progress has been made in the development of non-precious metal electrocatalysts (NPMEs) during the past decade. Correspondingly, there is an urgent demand for an appropriate measurement method to be established for the reliable evaluation of NPMEs. In this study, platinum and graphite counter electrodes were used to investigate the impact of counter electrode material on the accelerated durability testing (ADT) of NPMEs in acidic medium. Platinum used as the counter electrode in a traditional three-electrode electrochemical cell was found to dissolve in acidic medium and re-deposit on NPME coated on the working electrode during ADT. Such re-deposition causes the oxygen reduction reaction (ORR) performance of NPMEs to remarkably improve, and thus will seriously mislead our judgment of NPMEs if we are unaware of it. The phenomenon can be avoided using a graphite counter electrode.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have become a focus of intensive research owing to their environmental friendliness and high energy conversion efficiency [1]. In PEMFCs, H_2 fuel is electrochemically oxidized at the anode side and O_2 is electrochemically reduced at the cathode side. The cathode reaction is a slow four-electron transfer reaction, which results in a high overpotential and thus high performance electrocatalysts are required to accelerate the oxygen reduction reaction (ORR). To date, platinum and platinum-based alloy nanoparticles dispersed on carbon supports have been dominantly employed as ORR electrocatalysts [2,3]. The ORR activity and durability of commercial Pt/C and Pt-based electrocatalysts are routinely characterized by casting a thin layer of the electrocatalyst on a rotating disk electrode (RDE) and measuring its ORR performance in acidic medium in a three-electrode electrochemical cell, which is composed of a working electrode, a reference electrode, and a counter electrode [4–9]. It has been shown that the three-electrode electrochemical cell setup can be used to effectively evaluate the performance of electrocatalysts [10]. The performance of commercial Pt/C and Pt-based electrocatalysts is normally measured by cyclic voltammetry (CV) in N_2-saturated electrolyte with ORR polarization on the RDE in the presence of O_2. To assess the durability of an electrocatalyst, accelerated durabil-

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ity testing (ADT) is carried out by potential cycling in the three-electrode system with CV and ORR measurements taken at certain cycle numbers to evaluate the degradation of the electrocatalyst in terms of electrochemical surface area (ECSA) and mass activity (MA) [5,6].

Commercial Pt/C electrocatalysts have been widely accepted as state-of-the-art electrocatalysts for ORR. However, platinum is scarce and expensive, so there is an urgent demand for the replacement of Pt-based electrocatalysts with high performance NPMEs. NPMEs have attracted much attention recently [11–16], and significant progress has been made in the investigation of novel synthetic approaches and the creation of NPME with high performance in acidic media [17–22]. For example, Feng and Müllen [20] reported a hierarchically porous NPME with an almost identical ORR half-wave potential to that of commercial 20 wt% Pt/C under alkaline conditions when the loading of both electrocatalysts was 0.1 mg/cm^2. Liao and co-workers [23] synthesized a graphene-like NPME with a ORR half-wave potential only 60 mV more negative than that of commercial Pt/C in 0.1 mol/L $HClO_4$. The electrochemical characterization of NPMEs has spontaneously inherited the characterization method used for commercial Pt/C, including as the same working electrode, reference electrode, and counter electrode in the three-electrode system, the same CV and ORR measurement sweep rate, and the same ADT conditions. However, the active sites and ORR reaction mechanism of NPMEs are more than likely to be different from those of commercial Pt/C, and therefore the effect of electrochemical characterization parameters on the evaluation of NPMEs should be paid special attention [24–26].

Herein, we focus on the effect of the counter electrode [27,28] on the evaluation of NPMEs using the three-electrode cell in an acidic medium. For the three-electrode measurement system, almost all of the literature has used a platinum counter electrode when evaluating Pt-based electrocatalysts, but different counter electrodes in the case of NPMEs, such as platinum [29], graphite [19], and gold [30]. Only a few studies have addressed the selection of the counter electrode. In this study, we investigated the impact of counter electrode material on the performance of NPMEs during ADT in acidic medium. We found that the platinum counter electrode dissolved in acidic electrolyte and re-deposits on the NPME during ADT, which will seriously interfere with the measurement of the durability of NPMEs. This finding demonstrates that graphite counter electrodes should be used for ADT in acidic medium instead of platinum to allow the reliable judgment of NPME performance.

2. Experimental

2.1. Materials

Two types of electrocatalysts were used in the ORR performance tests. Commercial Pt/C (20 wt% Pt on Vulcan XC-72) was purchased from Johnson Matthey, and a non-precious metal electrocatalyst was prepared in our lab. Nafion perfluorinated resin solution (5 wt% in a mixture of lower aliphatic alcohols and water) was supplied by Sigma-Aldrich. All aqueous solutions were prepared with ultrapure water (18.2 MΩ·cm at 25 °C) from a Millipore water system (Synergy® UV, France).

2.2. Electrode preparation

A 5.0 mm diameter glassy carbon RDE (geometric area of 0.19625 cm^2, Pine Research) was coated with a thin film of electrocatalyst. A slurry of NPME (2 mg/mL) was prepared by blending the electrocatalyst with water, ethanol, and Nafion solution (V_{water}:$V_{ethanol}$:V_{Nafion} = 1:9:0.06) under sonication in a water bath for 2 min. The suspension was pipetted onto the RDE and evaporated in air, resulting in an electrocatalyst loading of 0.6 mg/cm^2. For comparison, commercial 20 wt% Pt/C electrocatalyst ink (1 mg/mL) was prepared in a similar manner, and the Pt/C loading on the resulting RDE was 20 μg_{Pt}/cm^2.

2.3. Electrochemical measurements

All electrochemical measurements were carried out using an Autolab potentiostat/galvanostat (Echo Chemie BV Model PGSTAT-302N, The Netherlands) and a standard three-electrode electrochemical cell with the glassy carbon RDE as the working electrode, platinum mesh or graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode, which was connected to the cell by a salt bridge (agar gel containing saturated KNO_3). All potentials in this study are referenced to that of the reversible hydrogen electrode (RHE).

All of the electrochemical tests were carried out at 25 °C in N_2-saturated or O_2-saturated aqueous 0.1 mol/L $HClO_4$ solution. The CV curves of the electrocatalysts were recorded at a positive scan rate of 100 mV/s. ORR polarization curves collected on the RDE were obtained at a rotation rate of 1600 rpm and a scan rate of 10 mV/s.

The electron transfer number of the electrocatalysts for ORR was determined using the Koutecky-Levich (K-L) equation:

$$1/I_D = 1/I_K + 1/B\omega^{1/2} \quad (1)$$

where I_D is the measured current density at the glassy carbon RDE, I_K is the kinetic current in amperes at a constant potential, ω is the electrode rotation speed (r/min), and B is the reciprocal of the slope, which can be determined from the slope of the K-L plot using the Levich equation:

$$B = 0.62nFAC_0D_0^{2/3}\nu^{-1/6} \quad (2)$$

where n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96485 C/mol), D_0 is the diffusion coefficient of O_2 (1.93×10^{-5} cm^2/s), C_0 is the bulk concentration of O_2 (1.26×10^{-3} mol/cm^3), and ν is the kinematic viscosity of the electrolyte (0.01009 cm^2/s) [21,31].

For ADT, the potential cycling was conducted between 0.6–1.2 V (vs RHE) at a scan rate of 100 mV/s in an O_2-saturated acidic solution that provided a harsh degradation environment. CV curves and ORR polarization curves were collected at certain cycle numbers during the test to monitor the degradation of the electrocatalyst.