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A comparative study of ORR at the Pt electrode in ammonium ion-contaminated H_2SO_4 and $HClO_4$ solutions

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HIGHLIGHTS

► Poisoning of the Pt electrode by low concentration NH_4^+ ion was investigated in H_2SO_4 and $HClO_4$ solutions.
► Significant poisoning was observed in H_2SO_4 solution.
► An extraordinary recovery of the poisoned electrode was achieved in $HClO_4$ solution.
► The Tafel slopes were affected by NH_4^+ ion in H_2SO_4 but not in $HClO_4$ solution.

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ABSTRACT

Poisoning of the poly-Pt electrode by low concentration ammonium ion was investigated in H_2SO_4 and $HClO_4$ solutions and a significant poisoning was observed in H_2SO_4 solution. An extraordinary recovery of the poisoned electrode was achieved in $HClO_4$ solution by cycling the electrode potential between the onset potentials of the hydrogen and oxygen evolution. The extent of recovery was marked using the oxygen reduction reaction (ORR) as a probing reaction. Ammonium ion poisoning of the electrodes in H_2SO_4 caused a significant contribution of the two-electron reduction of O_2 to hydrogen peroxide, as indicated by the rotating ring-disk voltammetry. The Tafel slopes at the low and high current densities were also affected by the presence of ammonium ion in H_2SO_4 solution and an increase in the Tafel slope was recognized with increasing the concentration of ammonium ion. However, the Tafel slopes at the low and high current densities were hardly affected by the ammonium ion in $HClO_4$ solution.

1. Introduction

In recent years, proton exchange membrane fuel cells (PEMFCs), in which electrochemical oxygen reduction reaction (ORR) is the prime reaction, have become a subject of considerable interest because it may add promising advances in the energy conversion technology [1–7]. During fuel cell operation, polarization at the cathode (oxygen reduction) is highly significant compared to that at the anode and thus much efforts have been devoted to the study of the factors affecting the cathodic reaction including the adsorption of several poisoning species. Common air-borne poisons (e.g., sulphur dioxide (SO_2), nitrogen dioxide (NO_2)), and other contaminants (e.g., ammonium (NH_4^+) ion) have deleterious effects on PEMFC performance [8–13]. The poisoning effect of the adsorbed SO_2 on the polycrystalline platinum (poly-Pt) electrode has been studied extensively [11,14–24]. However, a little attention has been paid to the poisoning effect of NH_4^+ ion on the poly-Pt electrode towards ORR [25,26]. Although various studies have demonstrated that NH_4^+ ion has a negative effect on PEMFC performance, especially the major poisoning effect of NH_4^+ ion at the anode [27,28], studies of phosphoric acid FCs have revealed that there is a significant effect of NH_4^+ ion on the ORR [29].

The aim of the present work is to explore the effects of the low concentration NH_4^+ ion poisoning on the ORR at the poly-Pt electrodes in sulphuric (H_2SO_4) and perchloric ($HClO_4$) acid solutions at ambient temperature (25 °C). H_2SO_4 and $HClO_4$ are often used as electrolyte solutions in the electrochemical studies for developing PEMFCs, especially the fundamental electrocatalysis of their electrocatalysts, while in PEMFCs Nafion® is typically used as polymer

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electrolyte membrane. It is noteworthy to mention here that $HClO_4$ solution is usually used for the study of the electrochemical behaviour of ORR because the perchlorate is nonadsorbable anion, similar to the solid acid (Nafion®), while the adsorption of bisulphate and sulphate anions is evident on the Pt surface [30,31]. Recovery of the poisoned electrodes is examined by cycling the electrode potential (starting from the open circuit potential towards either cathodic or anodic direction of potential) between 0.06 and 1.56 V vs. RHE for 10 cycles at 100 mV s^{-1} in NH_4^+ ion-free H_2SO_4 or $HClO_4$ solutions. In addition, the effect of the adsorbed NH_4^+ on the mechanism of the ORR is elucidated using rotating ring-disk electrode (RRDE) methodology [32,33]. The rotating disk measurements permit a correction for diffusion limitations of the oxygen gas (O_2) in solution at high potentials, allowing isolation of the ORR kinetics. The additional ring, which surrounds the central disk with the electrocatalyst, is used to oxidize any hydrogen peroxide (H_2O_2) that forms at the disk-electrocatalyst. With this approach, we can resolve whether a trace of adsorbed NH_4^+ ion changes the mechanism of the oxygen reduction from four-electron pathway to two-electron pathway forming H_2O_2 or not. Similar experiments have also been performed at the pre-oxidized and pre-reduced poly-Pt electrodes in the presence of various concentrations of NH_4^+ ion. Although the present cases are not exactly the real one, the comparative study may help to provide better understanding of NH_4^+ ion-poisoning effects and recovery approaches that may be used in the recovery of PEMFC performance.

2. Experimental

All the electrochemical measurements were performed and recorded using a computer-controlled ALS CHI-760D electrochemical analyser, driven with a general-purpose electrochemical system software (BAS). Steady-state voltammograms were obtained at the RRDE using a rotary system from Nikko Keisoku, Japan. A conventional three-electrode cell of around 20 cm^3 was used for the cyclic voltammetric measurements, while in the case of hydrodynamic voltammetric measurements the working electrode compartment was 200 cm^3 to eliminate any possible changes in the O_2 concentration during the measurements. Poly-Pt electrode of 1.6 mm in diameter was employed for the cyclic voltammetric measurements while steady-state voltammograms were measured using the RRDE with Pt-disk (6.0 mm in diameter) and Pt-ring. A spiral Pt wire and an Ag|AgCl|KCl (sat.) were used as counter and reference electrodes, respectively. All the potential values in the text and figures are mentioned with respect to a reversible hydrogen electrode (RHE). Prior to use, the poly-Pt electrode was polished first with no. 2000 emery paper, then with aqueous slurries of successively finer alumina powder (particle size down to 0.06 mm) with the help of a polishing microcloth. The electrode was then sonicated for 10 min in milli-Q water followed by potential cycling between the onset potentials of the hydrogen and oxygen evolution until the voltammetric characteristic of clean Pt electrode was obtained. The Pt disk–Pt ring RRDE was cleaned in the same manner as the poly-Pt electrode. The potential of the Pt-disk was held for 10 min at 1.06 V or 0.06 V vs. RHE to obtain pre-oxidized or pre-reduced electrodes, respectively. No such pre-treatment was performed for the Pt-ring electrode.

NH_4^+ ion-poisoned solution was prepared by introducing a specific volume of 30% NH_3 solution in either 0.1 M H_2SO_4 or 0.1 M $HClO_4$ solution giving a desired concentration of the NH_4^+ ion. Prior to each experiment, either N_2 or O_2 gas was bubbled directly into the cell for 30 min to obtain either N_2 or O_2 saturated solution and electrochemical measurements were carried out under either of these two gases according to the requirement. All the measurements were accomplished at room temperature (25 ± 1 °C). All of the reagents (of analytical grade) used in this study were purchased from either Kanto Chemicals Co. Ltd. (Tokyo, Japan) or Wako Pure Chemicals Industries Ltd. (Osaka, Japan) and used without further purification. All the solutions were prepared with Milli-Q (18 MΩ cm) deionized water.

3. Results and discussion

The characteristic current–potential (I–E) curves at the poly-Pt electrode in deoxygenated (i.e., N_2-saturated) 0.1 M H_2SO_4 and 0.1 M $HClO_4$ solutions are shown in Fig. 1(A) and (B), respectively (black lines). In the presence of 1 ppm NH_4^+ ion, in the anodic potential scan, the charge for the hydrogen desorption peaks was noticed to be decreased in both electrolytic media. It decreased further with increasing the concentration of NH_4^+ ion. The Pt oxide layer formation region was also affected. The current of the onset of the oxide layer formation (at 0.86 V vs. RHE) was found to decrease with increasing the NH_4^+ ion concentration. There was also a slightly higher oxidation current at potentials above 1.16 V vs. RHE

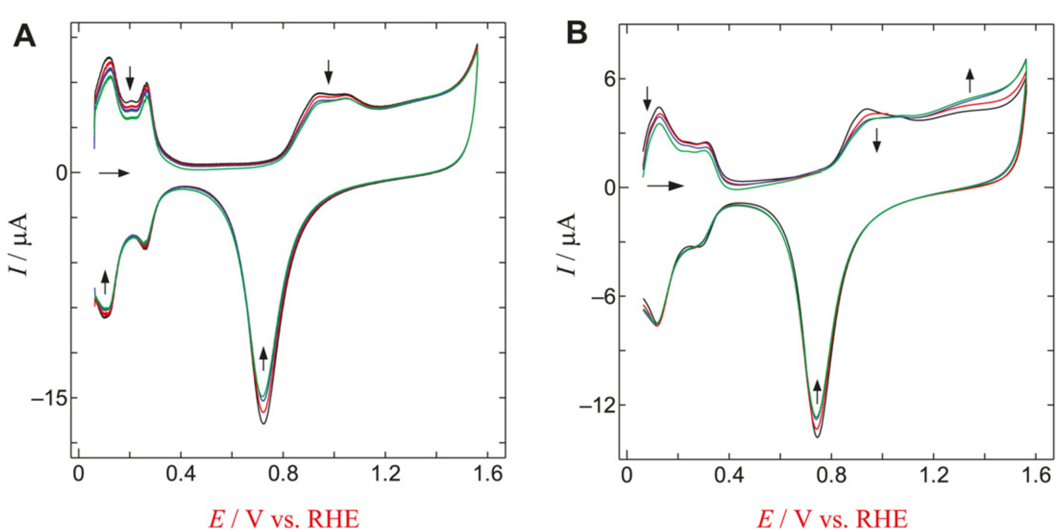

Fig. 1. CVs obtained at the poly-Pt electrode in N_2-saturated 0.1 M H_2SO_4 (A) and 0.1 M $HClO_4$ (B) solutions containing 0 (Black), 1 (Red), 10 (Blue) and 100 (Green) ppm NH_4^+ ion. Scan rate: 100 mV s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)