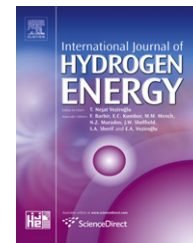


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Oxygen reduction reaction on a Pt/carbon fuel cell catalyst in the presence of trace quantities of ammonium ions: An RRDE study

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ARTICLE INFO

Article history:

Received 21 October 2011

Received in revised form

3 December 2011

Accepted 6 December 2011

Available online 11 January 2012

Keywords:

ORR kinetics

Ammonia

Contaminant

PEMFCs

ABSTRACT

The effect of trace quantities of ammonia on oxygen reduction reaction (ORR) on carbon-supported platinum catalysts in perchloric acid solutions is assessed using rotating ring disk electrode (RRDE) technique. The study demonstrates that ammonia has detrimental effects on ORR. The most significant effect takes place in the potential region above 0.7 V vs RHE. The effect is explained by the electrochemical oxidation of ammonia, which blocks Pt active sites and increases the formation of H₂O₂. This leads to losses in the disk currents and increments in the ring currents. The apparent losses in ORR currents may occur in two ways, namely, through the blocking of the active sites for ORR as well as by generating a small anodic current, which is believed to have a lower contribution. In addition, a detrimental effect of sodium cations in the potential range below 0.75 V vs RHE was demonstrated. This effect is most likely due to the co-adsorption of sodium cations and perchlorate anions on the Pt surface.

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1. Introduction

Abundance of inexpensive clean energy is one of the most important conditions of sustainability in the highly developed world. In order to fulfill this condition, contemporary power sources must be inexpensive, durable and generate little or no pollution.

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) have commonly been regarded as the most promising energy conversion devices for a sustainable world. In the last two decades, they have been studied extensively and developed to the point of being close to entering the mass market. PEMFCs

are already used in a limited number of commercial power systems for specific applications. Two most notable examples of such systems are those developed by Smart Fuel Cell (Brunnthal, Germany) and ReliOn (Spokane, WA, USA). While the first system has been designed for rather low auxiliary power applications in recreational vehicles and yachts, the latter is a several kilowatt hydrogen-fueled system for backup power applications. These two examples illustrate yet another advantage of PEMFCs, i.e., they can be designed to satisfy wide power requirements 10⁰–10⁵ W.

In spite of the successful commercialization of the Smart Fuel Cell and ReliOn systems, the widespread

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doi:10.1016/j.ijhydene.2011.12.040

commercialization of PEMFCs is hampered by the relatively high cost and limited durability of the cell components. There are many degradation and failure mechanisms of a PEMFC system [1]. One of the factors that may lead to a premature cell failure are impurities, which can enter the cell together with the feeding gases and affect functioning of the vital cell components, such as the catalysts or the membrane.

Ammonia is a common gas impurity that can contaminate both the cathode and anode gas streams. Beyond carbon monoxide and hydrogen sulfide, ammonia is a typical contaminant of hydrogen from fuel reforming processes [2], where elevated temperatures facilitate the reduction of nitrogen present in the air by the product hydrogen. Ammonia is also a product of decomposition of organic matter and can easily contaminate the air fed to the PEMFC cathode in some environments, e.g., near farms. Ammonia can undergo two different processes in hydrogen-air PEMFCs [3]. It can react with water or protons from the Nafion™ membrane and produce ammonium cation [4]. It can also be oxidized over Pt/C catalyst [4,5], commonly used in state of the art PEMFCs.

The protonation of ammonia reduces ionic conductivity and proton activity (pH shift) of Nafion™ in both membrane and catalyst layers. On the other hand, ammonia or the products of its oxidation may poison the catalyst surface [4,6,7] and thus increase charge transfer overpotentials of the half-cell reactions.

Only a limited number of studies have addressed the effects of exposure of fuel cells to ammonia [3,6–12]. The results obtained for high concentrations of ammonia demonstrated the severity of ammonia effects on the cell performance. However, no work has explored the effects of traces of NH_4^+ on ORR, which are more likely to be the actual quantities present in a fuel cell. Consequently, we decided to focus on the effects of trace quantities of ammonia/ammonium on the oxygen reduction reaction (ORR). In order to obtain quantitative results, the experiments were performed in a glass cell using liquid electrolytes containing known trace quantities of ammonia.

2. Experimental

A 0.1 mol L⁻¹ perchloric acid solution was used as a background electrolyte. The respective stock solution was obtained by dilution of 70% HClO_4 (99.999% trace metals basis, purified by redistillation) from Aldrich with Millipore water (18.2 MΩ cm). Ammonium and sodium perchlorate stock solutions were prepared using the respective salts (99.999% purity on the trace metals basis) from Aldrich. The corresponding molar fractions of ammonium or sodium in the studied solutions are expressed in this work in a part per million scale. Unless otherwise stated, all experiments were performed at 30 °C, controlled using a recirculating water bath.

The catalyst used was a carbon-supported platinum (20% by weight) from E-TEK/BASF Fuel Cell. An aqueous dispersion of the catalyst (1 mg mL⁻¹) was prepared by adding 50 mg of the catalyst to 50 mL of DI-water and ultrasonically dispersing the resultant mixture until the catalyst particles were uniformly distributed in the entire volume. In order to prepare

the working electrode, 20 μL of this dispersion (1 mg mL⁻¹) was deposited onto the disk and dried overnight. The procedure produced a uniform ~2 μm thick catalyst film with the nominal Pt loading of 20 μg cm⁻². As the present work was focused on the effects of ammonium on ORR, Nafion was applied neither in the catalyst ink nor as an overcoating of the catalyst layer in order to avoid the potential effects of the contaminant on the catalyst layer resistance [4].

A glass cell for rotating electrodes with water jacket was used together with a Rotating Ring Disk Electrode (RRDE) equipped with E6 series ChangeDisk tips (Pine Research Instruments). The nominal collection efficiency of the glassy carbon disk (0.196 cm²) and polycrystalline platinum ring combination used was 22%.

A platinum mesh was used as the counter electrode, while an Ag/AgCl electrode in 3 mol L⁻¹ NaCl was used as the reference electrode. In order to avoid the contamination of the studied solutions with chlorides, the reference electrode was isolated from the main cell compartment by two Vycor frits. All potentials in this paper are referred to the Reversible Hydrogen Electrode (RHE). A digital potentiostat (CH Instruments) connected to a desktop PC computer was used for experiment control and data acquisition.

In order to determine the electrochemically active surface area of the catalyst deposited onto the RRDE disk, cyclic voltammograms in absence of oxygen were recorded before each experiment. The charge of adsorbed hydrogen was determined from the voltammograms using known procedures [13]. Catalyst active surface area was always checked after the experiments and no changes were observed.

After the determination of the electrochemically active surface area of the catalyst on the disk, the solution was saturated with oxygen and oxygen reduction voltammograms recorded. The corresponding Tafel plot (not shown) was obtained using a standard mass transport correction [14,15]. The data agreed with those reported in the literature for a very comparable loading of an identical E-TEK catalyst [14,15].

The effects of trace quantities of ammonium on ORR were studied using standard RRDE technique adding different trace quantities of ammonium perchlorate (NH_4ClO_4) to an oxygen saturated 0.1 mol L⁻¹ perchloric acid (HClO_4) aqueous solution. The effect of the addition of NH_4^+ on ORR was quantified as current changes relative to the currents recorded in oxygen saturated 0.1 mol L⁻¹ perchloric acid aqueous solution in absence of ammonium (NH_4^+) for both disk and ring currents as described in Eqs. (2.1) and (2.2).

$$\Delta j_{\text{disk}} = -\left(j_{\text{disk}}^{\text{NH}_4^+} - j_{\text{disk}}\right) \quad (2.1)$$

$$\Delta j_{\text{ring}} = j_{\text{ring}}^{\text{NH}_4^+} - j_{\text{ring}} \quad (2.2)$$

The molar fractions of hydrogen peroxide generated by ORR were calculated using a well-known formula shown in Eq. (2.3) [14],

$$X_{\text{H}_2\text{O}_2} (\%) = 100 \cdot \left(\frac{2i_{\text{ring}}/N}{i_{\text{disk}} + i_{\text{ring}}/N}\right) \quad (2.3)$$

The ring potential was kept at 1.2 V vs RHE during the experiments.

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