RRDE study of oxygen reduction on Pt nanoparticles inside Nafion®: H2O2 production in PEMFC cathode conditions

O. ANTOINE* and R. DURAND
Laboratoire d’Electrochimie et de Physicochimie des Matériaux et des Interfaces (U.M.R. CNRS-INPG 5631 associated to UJF), ENSEEG, BP 75, 38402 Saint Martin d’Heres Cedex, France
(*author for correspondence at Département de Chimie Minérale, Analytique et Appliquée, Sciences II, Université de Genève, 30 quai Ernest-Ansermet, 1211 Genève 4, Switzerland)

Received 15 February 1999; accepted in revised form 30 November 1999

Key words: dihydrogen peroxide, nanoparticle, oxygen reduction reaction, platinum, rotating ring-disc electrode, size effect

Abstract
Dihydrogen peroxide production on platinum particles supported on carbon inside a proton exchange membrane (Nafion®), that is, under the working conditions of PEMFC cathodes, is rather small at the usual oxygen reduction potentials. As on bulk platinum, a four-electron mechanism appears to be the main pathway, with particle size and carbon substrate effects on the H2O2 production. A large increase in the H2O2 contribution takes place at low potentials, that is, at the working potentials of PEMFC anodes.

List of symbols

\[ \begin{align*}
E_D & \quad \text{disc potential (V vs SCE)} \\
d & \quad \text{diameter (nm)} \\
I_D & \quad \text{disc current (A)} \\
I_R & \quad \text{ring current (A)} \\
I_{2e}^- & \quad \text{two-electron disc current (A)} \\
I_{4e}^- & \quad \text{four-electron disc current (A)} \\
I_{2e}^-_{\text{Pt}} & \quad \text{2-electron reduction current of H2O2 (produced on C) by Pt particles in an active layer on the disc (A)} \\
L & \quad \text{active layer thickness (µm)} \\
N & \quad \text{collection efficiency of H2O2 produced on the disc and 'collected' on the ring} \\
n_{2e}^- & \quad \text{average number of exchanged electrons} \\
\%Pt/(Pt+C) & \quad \text{Pt mass ratio}
\end{align*} \]

1. Introduction
The oxygen reduction reaction (ORR) occurs as the cathodic process in numerous energy conversion processes. Therefore, this electrocatalytic reaction has been studied on numerous materials and electrolytes. The rotating ring-disc electrode (RRDE) methodology is commonly used for this study [1–9] since it enables the kinetics and the mechanism of the reaction to be determined. This method is able to quantitatively detect one possible intermediate species: dihydrogen peroxide (H2O2). The ORR takes place on the central disc electrode and the produced H2O2 is either oxidized or reduced on the concentric ring electrode, depending on the potential of this electrode. Several reaction mechanisms reviewed in [6] are proposed on bulk noble metals. They are analysed by Hsueh et al. [4] who define the Damjanovic mechanism [1] as the most realistic on platinum. The mechanism considers that the main reaction is the direct reduction of O2 to H2O (with a four-electron charge transfer), the rate determining step (rds) being O2 protonation which takes place on bare platinum atoms. The secondary reaction is a parallel reduction to H2O with an intermediate species: H2O2 in acidic media. RRDE studies for the ORR [3, 4] allow evaluation of the molar proportion of produced H2O2 on bulk platinum, either in aqueous sulphuric or phosphoric solutions.

The Damjanovic mechanism can be also assumed as valid on platinum nanoparticles in aqueous acidic solution; however no attempt has been made to perform a RRDE study on such particles. A particle size effect on ORR kinetics has been demonstrated [10–15]. The specific activity (SA) decreases with particles size, mainly below 2 nm, and there is a maximum mass activity (MA) between 3 and 4 nm in aqueous sulphuric and phosphoric acids. According to Kinoshita [10], this maximum corresponds to the optimum number of active surface atoms for cubo-octahedric platinum particles. Several studies [13–17] have demonstrated a correlation between the platinum particle size decrease and its increase in degree of surface oxidation for a
given potential (by degree of surface oxidation, we mean degree of surface coverage by intermediate oxygenated species). In accordance with the Damjanovic theory [18], this effect involves a current density decrease. There are very few papers on ORR on platinum particles in Nafion® [13, 14, 19]. From potentiostatic steady-state polarization curves and impedance measurements this mechanism was confirmed as the main reaction on Pt nanoparticles inside Nafion® [20]. But the platinum particle size and degree of surface coverage by intermediate oxygenated species could also influence the secondary reaction of H₂O₂ production. In this paper, an experimental RRDE study of ORR on platinum nanoparticles supported on carbon (in a Pt/C + Nafion® active layer) is proposed in order to clarify the particle size and carbon substrate effects on H₂O₂ production.

2. Experimental details

A glass cell was used. The reference electrodes were two saturated calomel electrodes (SCE), each immersed in an isolated compartment connected to the cell by a Luggin–Haber capillary. These ionic bridges avoid electrolyte contamination by chlorides. Two platinum grids were used as counter electrodes for disc and ring electrodes. The [glassy carbon disc-bulk platinum ring] Pine Instrument electrode (AFDT21 [21]) was used as working electrodes. Disc and ring electrode potentials were respectively controlled by EGG PAR and Tacussel potentiostats and measured versus the SCE reference electrode (AFASRE [21]). The disc and ring currents (I_D and I_R, respectively) were recorded as a function of disc electrode potential from 0.7 V vs SCE and 0 V vs SCE (or −0.3 V vs SCE) at 1 mV s⁻¹, the ring electrode potential being held at 1 V vs SCE in order to obtain the oxidation limiting current of H₂O₂ into O₂. This experiment was performed at 293 K for a series of rotation rates (ω). The rotation rate influence on the collection efficiency (N) and the average number of exchanged electron (n_e) is very small. Therefore, only one rotation rate is reported in this paper (ω = 800 rpm).

Before the RRDE experiments were performed, the electrolyte was saturated with 99.999 pure oxygen for 10 min. The disc electrode potential was then scanned between 0.7 V vs SCE and 0 V vs SCE (or −0.3 V vs SCE) at 1 mV s⁻¹, the ring electrode potential being held at 1 V vs SCE in order to obtain the oxidation limiting current of H₂O₂ into O₂. This experiment was performed at 293 K for a series of rotation rates (ω).

A 0.1 M electrolyte was prepared from Merck suprapur concentrated sulphuric acid diluted with ultrapure water (Millipore SuperQ System, resistivity: 18 MΩ cm). Cyclic voltammograms (10 mV s⁻¹) were recorded under high purity argon gas to verify the electrode and electrolyte cleanliness (no change with cycle number or rotation rate), and to determine the electrochemically-active platinum surface area from hydrogen adsorption–desorption coulometry.

The H₂O₂ electronic and molar proportions decrease when the average number of exchanged electrons increases. A factor 2 between these two proportions is