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On the nature of platinum oxides on carbon-supported catalysts

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ABSTRACT

In fuel cells, the formation of platinum oxides on the Pt surface interferes with the Oxygen Reduction Reaction (ORR). The chemical composition of Pt oxides formed on carbon-supported Pt nanoparticles has been postulated for the first time to be hydroxylated platinum PtOH and hydroxylated platinous $PtOH^+$ species. The thermodynamics of electrocapillary was applied to determine the charge number for Pt oxidation in various pH under a constant ionic strength perchlorate solutions. The charge number of the Pt oxide increased with the holding potential from −0.9 up to −1.5 electrons/H^+ at 0.765 and 0.89 V vs. SHE, respectively. This indicates the coexistence of multi oxides, where PtOH is initially formed and is further converted at higher potentials to $PtOH^+$. The charge number for H adsorption was measured as expected to be +1, increasing the confidence in the technique. The charge number allows the calculation of individual oxide coverages, explaining the previously intriguing reports that the fraction coverage was larger than 1 under the simplified assumption of one-electron transfer per Pt atom and without the need to assume a place-exchange mechanism. It is concluded that under increasing holding potential the coverage of $PtOH^+$ increases while that of PtOH decreases. The formation of both oxides can be periodically reversed by a short switch to lower potentials, $E < 0.6$ V vs. SHE. The reduction of the oxides and consequently the recovery of Pt activity are found to be relatively fast.

1. Introduction

Oxygen Reduction Reaction (ORR) is one of the most important electrochemical reactions in nature and technology. It is a highly sluggish reaction in need of catalysis and therefore represents the rate determining step in H_2–O_2 fuel cells [1–3] and metal–air batteries [4,5]. It is a well studied reaction [6–11], yet its slow mechanism [12] is far from being well understood due to its complexity and the multiple electron transfer involved [13–15]. Platinum and Pt-based catalysts remain the best catalysts for use in H_2–O_2 proton exchange membrane fuel cells (PEMFC), however the high cost of platinum requires a better understanding in order to minimize the amount of catalyst. Furthermore, the catalytic activity of Pt is complicated by the formation of oxides at high potentials [16]. These oxides progressively cover the Pt surface at high potentials (>0.74 V vs. SHE) thus reducing the fraction of the Pt surface available for ORR. The oxide coverage of Pt at high potentials have been determined and well discussed, however due to experimental difficulties the exact nature and the chemical composition of these oxides have not been determined. Furthermore, it has been observed that the amount and nature of the oxides are determined by the history of the Pt and the time the Pt electrode has been held at a positive potential.

The mechanism of Pt oxides formation and growth has been studied extensively [4–10]. It has been shown that Pt oxides are formed at positive potentials upon exposure to water, while surprisingly dissolved molecular oxygen has little effect [17,18]. Reaction schemes have been suggested by different studies [19–21]. The following one electron reaction has been proposed

$$Pt + H_2O \rightarrow PtOH + H^+ + e^- \quad (1)$$

to be followed by the possible reaction:

$$PtOH \rightarrow PtO + H^+ + e^- \quad (2)$$

This mechanism is characterized by a charge number of −1 electron per H^+. The purpose of the present work is to challenge this mechanism by experimentally determining the charge number and identifying the oxide species.

The tendency at positive potentials toward the formation of Pt oxides results in a temporal decay of ORR activity [16]. Proper

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Nomenclature

γ	surface energy (J/m^2_{Pt})
q	charge density ($\mu C/cm^2_{Pt}$)
E	electric potential (V vs. SHE)
Γ_{OH}	Gibbs excess of adsorbed oxide species (mol/m^2_{Pt})
R	ideal gas constant (8.31 J/mol/K)
T	temperature (298.15 K)
$C_{H_3O^+}$	hydronium ion concentration (mol/L)
n	charge number at constant chemical potential (electron/hydronium ion)
Γ_H	Gibbs excess of adsorbed H (mol/m^2_{Pt})

modeling of the reaction requires the knowledge of the actual charge transfer associated with oxide formation or the nature of the oxides and their coverage [22–27]. Substantial effort has been devoted to understanding the mechanism of Pt oxide formation and growth [19], and to identifying oxide species and their coverage [18], but these have been partially frustrated by the difficulty of detecting such species in situ. A logarithmic time growth of oxide [20,28,29], multiple Pt oxides [30,31] and their coverage have been reported [32,33], however, these results were limited to continuous Pt films [18,28,32], transient-state measurements [31,33] and under an unsupported assumption of one-electron transfer per Pt [16,17,24]. These experiments would not necessarily reflect the practical case of carbon-supported Pt nano-particles under high potentials, as in PEM fuel cells [1].

It is commonly assumed that one electron transfer occurs per Pt atom [16,17,33]. This assumption might be valid only for a short-time oxide growth and is obviously inappropriate for a long-time oxide growth, where oxide fractional coverage was calculated to be significantly greater than 1 [16]. By applying electrocapillary to a solid Pt(1 1 1) electrode, Mostany et al. [34] obtained a charge number of about -1 per oxide which suggests that the oxide species is indeed PtOH. However, the measurements were restricted to a single crystal Pt(1 1 1) and to a potential window over which the cyclic voltammogram shows a reversible behavior of adsorbed oxygen species. It is expected however that the charge number would be different for carbon-supported Pt nanoparticles at large potentials due to different surface states and the polycrystalline structure of the C-supported Pt nanoparticles.

In this paper, we determined for the first time the equilibrium charge number of Pt oxides formed during a long time potential hold of C-supported Pt nanoparticles. Electrocapillary theory is used to measure the charge density on Pt particles in various pH solutions $(0.1-x)$ M $HClO_4 + x$ M $NaClO_4$ under a constant ionic strength. The identity of the oxides (PtOH and $PtOH^+$) and their coverage are determined as a function of the held potential. The analysis was validated for the reversible H adsorption where the charge number as expected was determined to be 1.

2. Experimental

2.1. Preparation of working electrode

We used a commercially available catalyst: 50 wt.% Pt supported on Vulcan carbon black (Tanaka Kikinzoku, Japan). A mixed solution of ultrapure water (Milli-Q® system, Millipore, MA USA), isopropanol (HPLC grade, Sigma–Aldrich, USA) and a 5.37 wt.% Nafion® solution (Sigma–Aldrich, USA) with a volume ratio of 200:50:1, mixed with an appropriate amount of catalyst, was prepared and sonicated for 5 min. Ten microliters of this ink was then transferred onto the glassy carbon surface with a geometric area of $0.196\ cm^2$ to achieve Pt loading of $22\ \mu g/cm^2$. The electrode was dried in air for 5 h before measurement.

2.2. Electrochemical measurements

Electrochemical measurements were performed by the rotating-disk electrode (RDE) (Pine Research Instrumentation) technique using a glassy carbon rotating disk electrode in a 3-electrode electrochemical cell setup with a PGZ421 potentiostat (Princeton Applied Research). An Ag/AgCl electrode, connected to the working electrode compartment by a salt bridge, served as a reference. The counter electrode was a large-area Pt foil. Electrolytes were $(0.1-x)$ M $HClO_4$ (Veritas® doubly distilled, GFS Chemicals, OH, USA) + x M $NaClO_4$ (97 + %, Sigma–Aldrich, USA) with $x = 0, 5\times10^{-2}, 7.5\times10^{-2}$, or 9.5×10^{-2}, all diluted using Millipore ultrapure water. Care was made, by boiling glasswares in de-ionized water and using double-junction electrolyte to prevent chloride contamination from the reference electrode. The potential difference measured between Ag/AgCl and RHE in 0.1 M $HClO_4$ was 290 mV. Potential differences between Ag/AgCl and RHE in electrolyte with other proton concentrations were calculated using the following equation:

$$\Delta E = 0.29 + \frac{RT}{F}\ln\left(\frac{0.1}{C_{H_3O^+}}\right)V \qquad (3)$$

Electrode potentials in this paper are reported vs. the standard hydrogen electrode (SHE) with unit hydrogen-ion activity. RHE was converted onto SHE by the following formula:

$$E(\text{vs. SHE}) = E(\text{vs. RHE}) + \frac{RT}{F}\ln C_{H_3O^+} \qquad (4)$$

As electrolyte solutions used in this study are relatively dilute solutions, activity coefficient is approximately 1 and thus, not included in the equations above.

CVs were measured in a N_2-saturated electrolyte at a sweep rate of 20 mV/s. The charge density was determined by integrating the oxide reduction area. In detail, the oxide reduction area was obtained by holding the electrode at several specific potentials for up to 2 h followed by a potential sweep back to 0.02 V vs. RHE at a rate of 20 mV/s (N_2-saturated). The charge density of H was determined by integrating H adsorption area in regular CVs directly. All measurements were carried out at room temperature, and N_2 atmosphere was maintained throughout the duration of the experiments.

3. Results and discussion

3.1. CVs and charge densities

Our approach is based on charge densities integrated from CVs in a series of solutions $(0.1-x)$ M $HClO_4 + x$ M $NaClO_4$ with a constant ionic strength. Fig. 1a shows CVs in an electrolyte of 0.025 M $HClO_4$ + 0.075 M $NaClO_4$. Before CV scanning, the C-supported Pt catalyst was held at various potentials from 0.74 to 0.89 V vs. SHE for extended periods of time (up to 2 h) in order to approach an equilibrium state for oxide coverage. This is because oxide