

Surface Oxide Growth on Platinum Electrode in Aqueous CF₃SO₃H

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Introduction

Cost reduction is the main challenge for the commercialization of fuel cell electric vehicles (FCEVs). In order to reduce the fabrication cost of FCEVs, it is vital to reduce the amount of platinum (Pt) in membrane electrode assembly (MEA) and to increase its lifetime and stability. Platinum needs to be utilized effectively to reduce the amount of Pt in MEA, thus its surface area should be the largest possible. Since in the case of automotive applications fuel cells operate in a high potential range, Pt surface is at least partially oxidized and the Pt surface oxide can undergo electro-dissolution. Platinum surface sites can also be occupied by adsorbed anions (sulfonic acid group) originating from the Nafion[®] ionomer in catalyst layer [1]. These adsorbed species can influence the oxygen reduction reaction (ORR) kinetics and the durability of MEAs [2,3]. Although numerous studied report on the Pt oxide growth in aq.H₂SO₄, HClO₄ and NaOH, there are very few studied on the surface oxide growth on Pt electrodes in CF₃SO₃H [4,5].

In this contribution, we report on the surface oxide growth on Pt electrodes in aq. CF₃SO₃H (the smallest fluorinated sulfonic acid) and examined the influence of temperature (*T*), polarization potential (*E_p*) and polarization time (*t_p*) on the oxide growth behavior. We provide a molecular-level understanding of the oxide growth on Pt using oxide-growth theories and compare the results to those obtained in aq. H₂SO₄.

Experimental

We study the surface oxide growth on Pt in 0.1 M aq. CF₃SO₃H at *E_p* values (1.1 ≤ *E_p* ≤ 1.50 V vs RHE), for various *t_p* values (10⁰ ≤ *t_p* ≤ 10⁴ s), and at several temperatures (273 ≤ *T* ≤ 333 K). Cyclic-voltammetry (CV) oxide-reduction profiles obtained at a scan rate of *s* = 50 mV s⁻¹ show one feature (OC1 peak) that is assigned to the reduction of PtO (not PtOH) [5]; their integration provides the oxide charge density (*q_{ox}*) values.

Oxide growth theories are applied to identify the growth mechanisms and to analyze the oxide thickness in relation to *E_p*, *t_p* and *T* [6,7]. In the initial stage, Pt oxide growth is limited by the *place-exchange* between Pt^{δ+} and O_{ads}^{δ-} (*q_{ox}* < 1 ML = 440 μC cm⁻²) and the relationship between *q_{ox}* and *t_p* is given by Eq. (1) [6]. The equation indicates that *q_{ox}* should increase upon extending *t_p*.

$$\ln\left(\frac{dRTA}{kN_A^2\beta\mu^2}\frac{\varepsilon_0}{\varepsilon_0}\right) + \frac{2N_A^2\beta\mu^2}{dRTF}\frac{\varepsilon_0}{\varepsilon_0}q_{ox}$$

$$= \frac{2(\chi_0 - \Delta\phi)\beta\mu}{dRT} + \ln(t_p + \tau') \quad (1)$$

In the case of 1 < *q_{ox}* < 2 ML, the escape of the Pt²⁺ cation from the metal into the oxide at the inner metal-oxide interface is the rate-determined step [7] and the relationship between 1/*q_{ox}* and *t_p* is given by Eq. (2).

$$\frac{1}{d} = \frac{k_B T}{qbV} \ln\left(\frac{qbV}{k_B T d_L^2}\right) - \frac{H_i + U}{qbV} + \frac{k_B T}{qbV} \ln t_p \quad (2)$$

If the components of the electrode/electrolyte interface are changed, the surface dipole moment μ of the Pt^{δ+}-O_{ads}^{δ-} surface species (Eq. (1)) and the potential drop across the oxide layer *V* (Eq. (2)) can be changed. In this study, we report on these molecular-level parameters of the Pt/CF₃SO₃H interface.

Results and Discussion

Fig. 1 shows Pt oxide growth plots at *T* = 298 K expressed as *q_{ox}* vs. log *t_p* for 1.1 ≤ *E_p* ≤ 1.5 V vs RHE. Since the results show that the *q_{ox}* vs. log *t_p* relations are linear for lower *E_p* values (*q_{ox}* < 1 ML), the results can be explained using Eq. (1). The surface dipole moment of the Pt^{δ+}-O_{ads}^{δ-} species is consistently $\mu = 1.05 \pm 0.1$ D. This value is smaller than that obtained in H₂SO₄ ($\mu = 1.1 \pm 0.1$ D) [8]. Fig. 2 shows oxide growth plots at *T* = 298 K expressed as 1/*q_{ox}* vs. log *t_p* for one value of *E_p*, namely *E_p* = 1.4 V. The oxide thickness is in the 1 < *q_{ox}* < 2 ML range. In the case of CF₃SO₃H, the slope is ca. twice of that for H₂SO₄. The results suggest that the potential drop across the oxide layer *V* is affected by the electrolyte nature. Anion which can be adsorbed on the Pt surface is likely to influence the interfacial structure giving rise to a modification of the surface electronic properties.

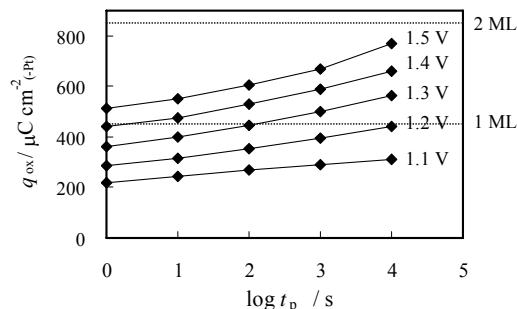


Fig. 1 Pt oxide growth plots at *T* = 298 K expressed as *q_{ox}* vs. log *t_p* for 1.1 ≤ *E_p* ≤ 1.5 V vs RHE.

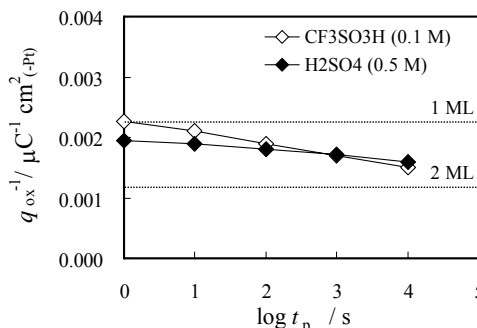


Fig. 2 Pt oxide growth plots at *T* = 298 K expressed as 1/*q_{ox}* versus log *t_p* in the *E_p* = 1.4 V vs RHE.

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