Surface Oxide Growth on Platinum Electrode in Aqueous CF$_3$SO$_3$H

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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 Pt in MEA, thus its surface area should be the largest possible. Since in the case of Pt, the interfacial structure giving rise to a modification of the surface electronic properties.

Experimental

We study the surface oxide growth on Pt in 0.1 M aq. CF$_3$SO$_3$H at $E_p$ values (1.1 $\leq E_p \leq 1.5$ V vs RHE), for various $t_p$ values (10$^{-6}$ $\leq t_p \leq 10^{-3}$ s), and at several temperatures (273 $\leq T \leq 333$ K). Cyclic-voltammetry (CV) oxide-reduction profiles obtained at a scan rate of $s = 50$ mV s$^{-1}$ show one feature (OCI peak) that is assigned to the reduction of POI (not PI(OH)) [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$^{2+}$ and O$_{aq}^{2-}$ ($q_{ox}$ $\leq$ 1 ML, $\approx 440 \mu C cm^{-2}$) 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 $t_p$.

$$\ln \left( \frac{dR \xi \Delta E_p}{kN_2 \beta \mu} \right) + \frac{2N \beta \mu}{dRT} = \ln \left( t_p + \tau \right)$$

(1)

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

$$\frac{d}{dt} \frac{q_{ox}}{\Delta V} = \frac{H + U}{\Delta V} \ln \left( t_p + \tau \right)$$

(2)

In this contribution, we report on the surface oxide growth behavior. 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.

If the components of the electrode/electrolyte interface are changed, the surface dipole moment $\mu$ of the Pt$^{2+}$--O$_{aq}^{2-}$ 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/CF$_3$SO$_3$H 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 $\leq E_p \leq 1.5$ 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$^{2+}$--O$_{aq}^{2-}$ species is consistently $\mu = 1.05 \pm 0.1$ D. This value is smaller than that obtained in H$_2$SO$_4$ ($\mu = 1.1 \pm 0.1$ D) [8]. Fig. 2 shows oxide growth plots at $T = 298$ K expressed as $U_{qox}$ 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 CF$_3$SO$_3$H, the slope is ca. twice of that for H$_2$SO$_4$. 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 $\leq E_p \leq 1.5$ 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.

Reference