Surface Oxide Growth on Platinum Electrode in Aqueous CF$_3$SO$_3$H
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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. 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 oxidation can undergo electro-dissolution. Platinum surface sites can also be occupied by adsorbed anions (sulfonic acid group) originating from the Nafion$^b$ 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. H$_2$SO$_4$, HClO$_4$ and NaOH, there are very few studied on the surface oxide growth on Pt electrodes in CF$_3$SO$_3$H [4,5].

In this contribution, we report on the surface oxide growth on Pt electrodes in aq. CF$_3$SO$_3$H (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. H$_2$SO$_4$.

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 ≤ $E_p$ ≤ 1.50 V vs RHE), for various $t_p$ values (10$^0$ ≤ $t_p$ ≤ 10$^5$ 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 (OCl-I peak) that is assigned to the reduction of PO (not PiOH) [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 phase-exchange between Pt$^{2+}$ and O$_{ads}$ ($q_{ox}$ < 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 $t_p$.

$$\ln \left( \frac{dRT}{kN_\Lambda 2βμ} \right) + 2N_Zβμ \frac{q_{ox}}{dRT} = \ln (E_p - Δφ) + \ln (t_p + τ)$$

(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-determined step [7] and the relationship between $q_{ox}$ and $t_p$ is given by Eq. (2).

$$\frac{d}{dt} \ln t_p = \frac{k_f}{k_b} \left( \frac{q_{ox}}{k_b T \Lambda} \right) \frac{H + U}{q_{ox}} \frac{k_f T}{k_b} \ln t_p$$

(2)

If the components of the electrode/electrolyte interface are changed, the surface dipole moment $μ$ of the Pt$^{2+}$-O$_{ads}$$^+$ 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 ≤ $E_p$ ≤ 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$^{2+}$-O$_{ads}$$^+$ species is consistently $μ = 1.05$ ± 0.1 D. This value is smaller than that obtained in H$_2$SO$_4$ ($μ = 1.1$ ± 0.1 D) [8]. Fig. 2 shows oxide growth plots at $T = 298$ K expressed as $V_{iq}$ 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 that of 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 ≤ $E_p$ ≤ 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.

Reference

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