

Impact of Sulfate Adsorption on the Kinetics of Oxygen Reduction Reaction

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Pt or Pt-alloys are used in proton exchange membrane fuel cell (PEMFC) as oxygen reduction reaction (ORR) catalyst. It is well known that anions such as sulfate, when adsorbed on catalyst surface, can significantly impede the ORR.¹ The impact of (bi)sulfate adsorption on ORR kinetics has been reported on both well characterized Pt single crystal surfaces, as well as on supported Pt/C catalyst in aqueous electrochemical cell. Furthermore, the reversible performance loss induced by membrane chemical degradation observed in PEM fuel cells is ascribed to adsorption of sulfate on Pt or Pt-alloy catalyst.²⁻³ The performance loss will become more significant at reduced Pt loading, which is desired to enable PEMFC-powered electric vehicles to be cost competitive. Therefore, a thorough understanding of sulfate adsorption on ORR is much needed.

The interaction of (bi)sulfate anions with Pt electrocatalyst surface in electrolyte solution have been well documented. It is generally agreed that (bi)sulfate adsorbs on Pt(111) via the 3-fold oxygen sites. Auger electron spectroscopy (AES), coulometry, and radiotracer method have been employed by Wieckowski and co-workers to quantify the amount of adsorbed sulfate on Pt(111) electrode exposed to dilute sulfuric acid solution.⁴ It was observed that the sulfate surface coverage depends on potential and sulfuric acid concentration.

Although the impact of sulfate adsorption on ORR has been extensively reported, majority of the previous work have been qualitative. Quantitative studies were very rare in the literature. Therefore, in the present work we attempt to establish the correlation between the ORR activity and sulfate concentration in the solution through the surface coverage of sulfate anion on the catalyst.

The mass activity (in unit of A/mg_{Pt}) of 30% wt. PtCo/HSC catalyst was measured in a three-electrode electrochemical cell using RDE (Pine Instrument Co., USA). A silver/silver chloride electrode was employed as reference electrode which was separated from the working electrode compartment by a salt bridge. However, the potential reported in this work refers to that of the reversible hydrogen electrode (RHE).

The ORR activity of the Pt-alloy catalyst was measured in 0.1 M HClO₄ free of H₂SO₄ and in 0.1 M HClO₄ solutions doped with various concentration of H₂SO₄ ranging from 0.001 to 0.05 mM. The anodic sweep was recorded in O₂-saturated electrolyte at a rotation speed of 1600rpm and a sweep rate of 5 mV/s. All measurements were conducted at room temperature. The mass activity measured at 0.9V (vs. RHE) is shown in Figure 1 (diamonds and solid black line in the figure). The ORR activity drops from 0.39 A/mg_{Pt} to 0.33 A/mg_{Pt} in the presence of 0.001 mM H₂SO₄, and further decreases with the increase of sulfate concentration.

The correlation between sulfate coverage on the

catalyst surface and sulfate concentration in the electrolyte solution was obtained from ref. 4, assuming the adsorption of sulfate on PtCo nanoparticles follows that of the Pt(111) single crystal (Fig. 2). (Bi)sulfate surface coverage increases with bulk sulfuric acid concentration following a semi-logarithmic isotherm.

Finally, a simple kinetic model was used to calculate the impact of sulfate surface coverage on ORR activity. These results will be presented.

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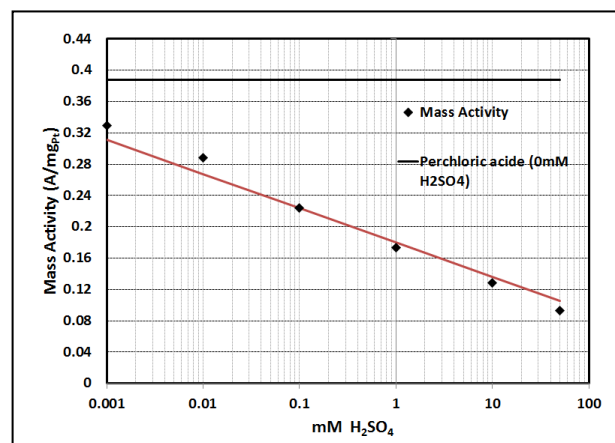


Fig. 1: ORR activity of 30% wt. PtCo/HSC in HClO₄ (black solid line) and various concentration of H₂SO₄ in the electrolyte solution (black diamond). The red solid line is calculation result from kinetic model. Room temperature; Potential scan rate: 5 mV/s; Rotation rate: 1600 rpm.

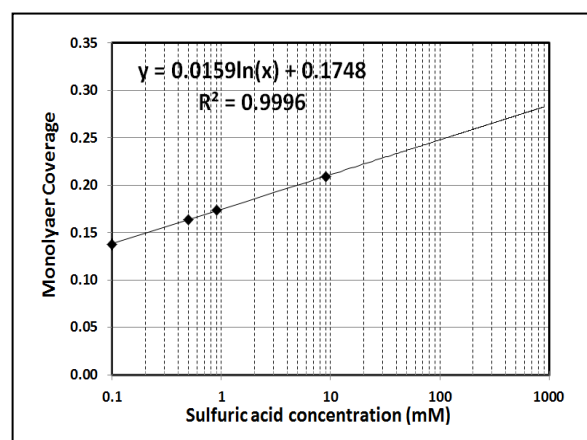


Fig. 2: Sulfate surface coverage on Pt(111) at 0.71V (vs. RHE) at room temperature and in various concentrations of sulfuric acid in solution. (data reproduced from ref. 4).