

Electrochemical investigation of Pt model electrodes for application in polymer electrolyte fuel cells (PEFCs)

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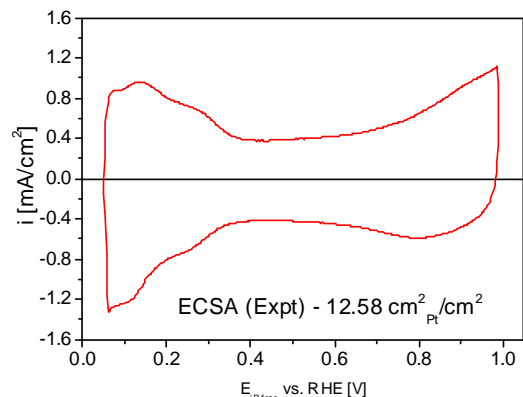
Polymer electrolyte fuel cells (PEFCs) are electrochemical devices converting chemical energy of hydrogen and oxygen (or air) into electrical energy with relatively high efficiencies and low emissions. For these reasons they have attracted much attention as promising power sources for small stationary, mobile, and portable applications. About two-thirds of the overall voltage losses of a PEFC at high current density are due to the slow oxygen reduction reaction (ORR) kinetics at the positive electrode, and therefore large efforts are currently devoted to search for more active catalysts. However, at present Pt-based catalysts are still recognized as the materials of choice for the ORR in acidic environments.[1,2]

To minimize the amount of Pt required for a given level of activity, the Pt catalyst is generally dispersed as small particles on high surface area carbon supports (Pt/C) which allows higher Pt dispersion and hence larger catalyst surface area compared to unsupported Pt-black. However, it was proposed from by several authors that there is a variation of Pt/C activity with Pt particle size, i.e. for Pt particles in the range of 1-12 nm, the highest mass activity was obtained for Pt particles of about 3 nm.[3] A different non-carbon catalyst support developed by 3M is based on an oriented array of organic whiskers coated with Pt by physical vapor deposition.[4] These nanostructured thin film (NSTF) catalysts present significantly lower electrochemical surface area compared to conventional Pt/C catalysts for the same catalyst loading, but 10 times higher area specific activity and 2 times higher mass activity than conventional Pt/C. The aforementioned studies make it clear that it is of utmost importance to have a thorough understanding of the influence of the Pt surface and particle size on the ORR activity and reaction mechanism.

In this study, we have developed model electrodes to gain a better understanding of the difference between extended surface catalysts (i.e. continuous platinum surfaces as in the NSTF catalysts) and discontinuous platinum surfaces (i.e. Pt nanoparticles supported on high surface area carbon). Particularly, model electrodes were fabricated by sputtering various Pt loadings between 2 and 100  $\mu\text{gPt}/\text{cm}^2$  on high surface area carbon (Vulcan XC72), according to the procedure reported in reference.[5]

The model electrodes were characterized in a three electrode compartment electrochemical cell in 0.1 M HClO<sub>4</sub> using a hydrogen reference electrode and a Pt-mesh as the counter electrode. The Cyclic voltammetry (CV) measurement in Ar-saturated electrolyte for the model electrode with Pt loading of 100  $\mu\text{gPt}/\text{cm}^2$  is shown in Figure 1. The so-called hydrogen underpotential deposition (Hupd) in Ar saturated electrolyte was used to determine the electrochemical surface area (ECSA) of the Pt model electrodes. For the calculation of the Pt surface

area, a specific charge of 210  $\mu\text{C}/\text{cm}^2_{\text{Pt}}$  was used as the adsorption of a monolayer of hydrogen on an atomically flat polycrystalline Pt electrode. The model Pt electrode surface area was also measured by CO-stripping method (Figure 2); in this case the electrochemically active surface area is determined through the oxidation of a monolayer of CO species adsorbed on the Pt surface (normalization factor of 420  $\mu\text{C}/\text{cm}^2_{\text{Pt}}$ ). Generally, slightly larger values of ECSA were obtained using CO-stripping compared to those determined by the Hupd method. The model electrode activity towards ORR was measured by rotating ring disk electrode (RRDE) measurements in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> electrolyte. A decrease in surface specific activity measured at a constant electrode potential of 0.90 V (RHE) was observed with decreasing Pt loadings in the model electrodes.



Figure

1: Cyclic voltammetry curves for sputtered model electrodes with Pt loading of 100  $\mu\text{gPt}/\text{cm}^2$  in Ar saturated 0.1 M HClO<sub>4</sub> solution. Sweep rate 50 mV/s at room temperature and ambient pressure.

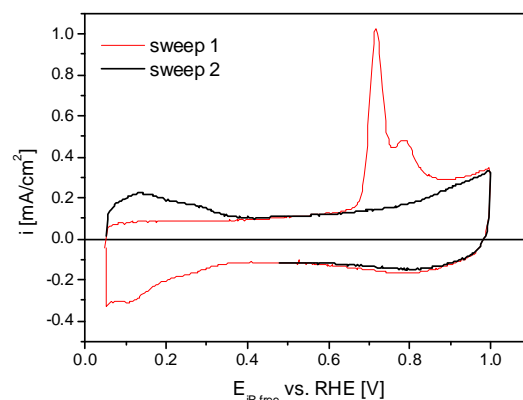


Figure 1: Cyclic voltammetry curves for sputtered model electrodes with Pt loadings of 100  $\mu\text{gPt}/\text{cm}^2$  in Ar saturated 0.1 M HClO<sub>4</sub> solution after holding the electrode potential at 0.1 V (RHE) for 15 min in CO-saturated electrolyte. Sweep rate 10 mV/s at room temperature and ambient pressure

#### References

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