Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting information

Highly Corrosion Resistant Platinum - Niobium Oxide - Carbon Nanotube Electrodes for the Oxygen Reduction in PEM Fuel Cells

Li Zhang [*a,b], Liya Wang [c,d], Chris M. B. Holt [a,b], Beniamin Zahiri [a,b], Kourosh Malek[c], Titichai Navessin[c], Michael H. Eikerling [c,d] and David Mitlin [*a,b]

[a]*Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB, T6G 2V4, Canada*

[b]*National Institute for Nanotechnology, 11421 Saskatchewan Drive, Edmonton, AB, T6G 2M9, Canada*

[c]*NRC Institute for Fuel Cell Innovation, 4250 Wesbrook Mall, Vancouver, BC, V6T 1W5, Canada*

[d]*Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, V5A 1S6, Canada*

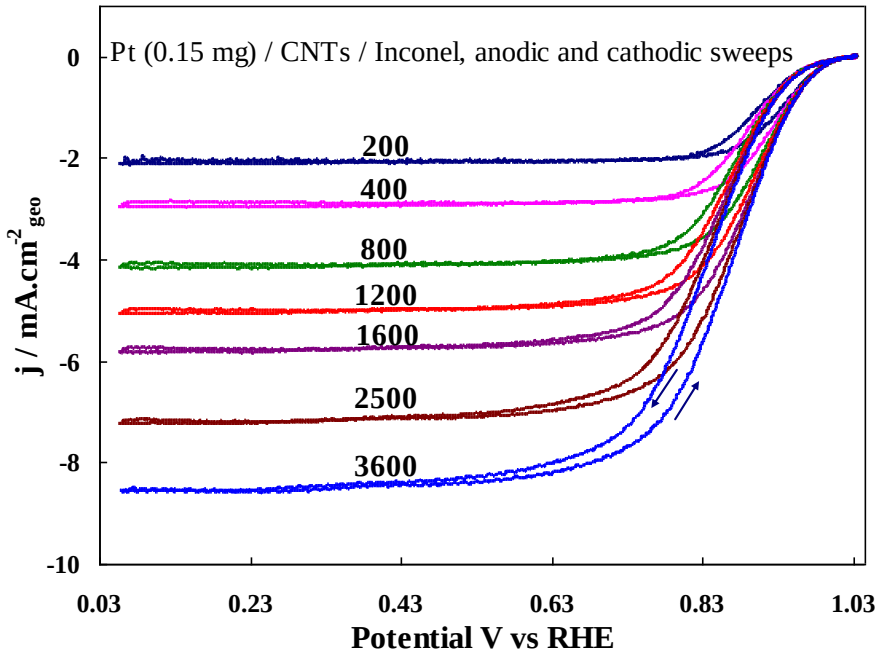

Figure 1S. Oxygen reduction curve of Pt (0.15mg)/CNTs/Inconel in oxygen-saturated 0.1 M $HClO_4$. Sweep rate: 2 mV / s. Disk electrode area: 1cm^2.

In this work, only positive-going (anodic) sweeps were presented and analyzed. We followed the guidelines described by H. A. Gasteiger et al., Applied Catalysis B: Environmental 56 (2005) 9–35, and K. J. J. Mayrhofer et al., Electrochimica Acta 53 (2008) 3181–3188, which are the "standard texts" for RDE ORR testing. However we do possess both the cathodic and the anodic sweep data. For example, the whole ORR curve for the Pt (0.15mg)/CNT electrode, including the anodic and cathodic scans, is shown in Figure 1S. The observed hysteresis between the anodic and the cathodic scans is related to the asymmetry in oxide removal versus growth and is quite small.

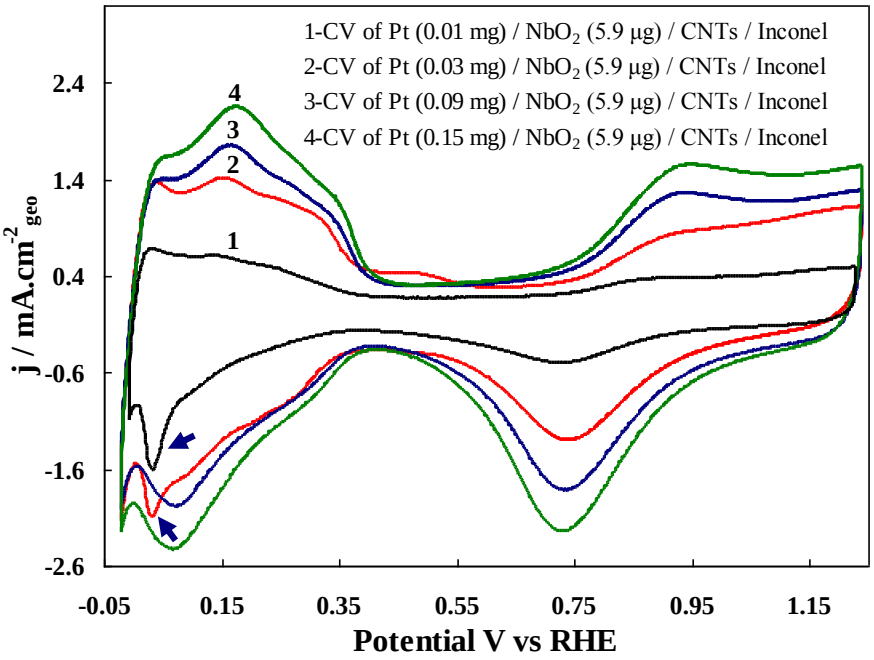

Figure 2S. Cyclic voltammograms of $Pt/NbO_2/CNT$ with different Pt mass loadings. Scan rate: 100 mV/s. Arrows point to the hydrogen adsorption peaks that are observed when there is Pt with Nb_2O_5 underneath.

We previously demonstrated that unprotected NbO_2 almost entirely oxidizes into the equilibrium Nb_2O_5 phase within the first anodic CV scan. [34] We also showed that hydrogen adsorption peaks occur at differing potentials on bare Pt versus for Pt with Nb_2O_5 underneath. Figure 2S now demonstrates that depending on the Pt mass loading there are two distinct sets of behaviors. At the lower loadings of 0.01 and 0.03 mg (as shown in Curve 1 and 2), the $Pt/NbO_2/CNT$ system shows hydrogen adsorption behavior analogous to the case of planar Pt/Nb_2O_5 samples. In other words the low Pt loadings do not offer sufficient protection for NbO_2 oxidation. At the higher Pt loading of 0.09 and 0.15 mg (as shown

in Curve 3 and 4), the Pt/NbO_2/CNT samples possess hydrogen adsorption peaks analogous to that of Pt on glassy carbon. This indicates that the Pt loading is sufficient to protect the underlying NbO_2 from oxidizing. It is expected that NbO_2 would preferentially wet any defective sites in the CNT due to their higher surface energy. Therefore even if the wetting of the CNTs by the NbO_2 is not 100% over the entire CNT surface, the relevant corrosion initiation sites would be protected.