

**An RDE assessment of sputtered Ir-Ru-Pt overlayer nanostructured thin film catalysts for protection of PEMFC cathodes against start-up and shut-down: The durability of oxygen reduction activity**

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Electrocatalyst research for PEM FCs traditionally focuses on the oxygen reduction reaction (ORR) catalyzed either by Pt, some alloy of Pt, or some other novel non-precious metal catalyst. However, oxygen evolution electrocatalysts are also of interest to PEM fuel cell researchers striving to improve durability.

The decline of fuel cell performance is primarily caused by the corrosion of carbon components in the fuel cell. The altered morphology and decreased porosity of corroded carbon constricts the access of O<sub>2</sub> to the Pt catalyst. The electrochemical conversion of carbon to CO<sub>2</sub> is caused by the presence of air in the anode during start-up and shut-down (SU/SD) and has been called the called reverse current decay mechanism<sup>1</sup>. The effect of air and hydrogen simultaneously occupying separate regions of the anode flow field is best understood by considering the fuel cell as two electrochemical cells with their electrodes connected. A galvanic “driving” cell, powered by oxygen and hydrogen, provides a voltage to an electrolytic “driven” cell, whose cathodic reaction is oxygen reduction on the fuel cell “anode” and anodic reaction is carbon oxidation on the fuel cell “cathode”<sup>2</sup>. The potential on the driven cell anode during su or sd lies within approximately 1.3 to 1.8 V vs RHE.

Non-carbon catalyst supports, such as 3M’s nano structured thin film (NSTF) offer some protection against carbon corrosion due to SU/SD, but other carbon parts of the fuel cell, specifically the carbon fibre gas diffusion layer, still have been reported to suffer from prolonged high potentials in the range caused by the reverse current decay mechanism<sup>3</sup>. The electrochemical corrosion of carbon, or carbon oxidation reaction (COR), can be mitigated or altogether prevented by improving the oxygen evolution reaction (OER) activity of the fuel cell cathode catalyst.

Ir and Ru are excellent electro-catalysts for oxygen evolution in acidic electrolytes. It is well known that Ru is more active than Ir, but corrodes at potentials higher than 1.4 V vs RHE. In addition, movements of precious metals prices within the past five years have made Ru almost ten times cheaper than Ir. Although Ru is thermodynamically unstable owing to its oxidation to the volatile and slightly soluble RuO<sub>4</sub>, several studies have shown this problem can be resolved by alloying Ru with other transition metals such as Ir and Ta. The effect of Ru has been reported for preparing fuel cell catalysts tolerant to CO, and able to function as electrolyser anodes in addition to fuel cell cathodes (i.e. the so called “unitized regenerative fuel cell”) but no studies on the effect of Ru on fuel cell durability has been reported.

Fuel cell researchers have already shown adding minute amounts of Ir to dispersed Pt on carbon black (Pt/C), can significantly decrease corrosion of carbon in the fuel cell cathode when the fuel cell is held at potentials similar to those experienced during SU/SD (i.e. 1.3 – 1.8 V vs RHE).

However, questions remain as to the impact of OER catalyst coverage on ORR performance

A rotating disk electrode (RDE) study was carried out to determine the effect Ir and Ru has on the ORR performance of underlying Pt when subjected to repeated electrochemically simulated SU/SD conditions. 3M’s NSTF was grown on glassy carbon disks, upon which was sputtered first a base layer of 85ug/cm<sup>2</sup> Pt, followed by varying loadings of Ir and Ru.

Figure 1 shows the initial ORR performance of all disks tested, 35 unique compositions and 65 experiments in all (some experiments were replicated. ORR was defined as the current at 0.94 mV after surface oxide formation was corrected for by subtraction of the Ar CV from the O<sub>2</sub> CV. Figure 2 shows the ORR performance after 200 SU/SD simulations. OER catalyst coverage initially affects ORR but after 200 SU/SD simulations, ORR performance adversely affected by OER catalyst coverage is restored, by up to 0.8 mA cm<sup>-2</sup> for high OER coverage. Ru loading had no significant impact on the lifetime of catalyst compositions, which typically lasted anywhere between 600 and 4000 SU/SD simulations before losing most of their ORR activity. Variations in catalyst lifetime were typically dependant on Ir loading.

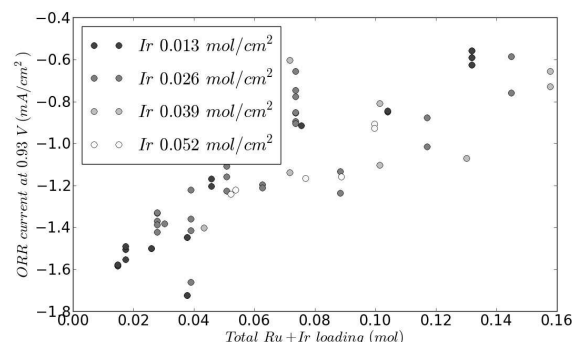


Figure 1: Initial ORR performance of all 65 experiments prior to any SU/SD simulations.

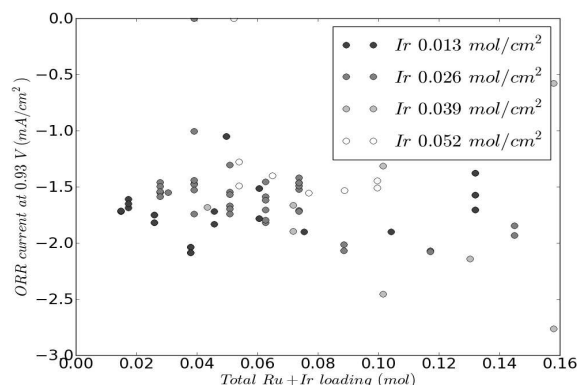


Figure 2: ORR performance of all 65 experiments after 200 SU/SD simulations.

1. C. A. Reiser et al., *Electrochem. Solid-State Lett.*, **8**, A273–A276 (2005).
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3. A. Kongkanand, Z. Liu, I. Dutta, and F. T. Wagner, *J. Electrochem. Soc.*, **158**, B1286–B1291 (2011).