

Iridium-Ruthenium Mixed Oxide for Oxygen Evolution Reaction Prepared by Pechini Synthesis

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In acidic water electrolysis noble metals are commonly used as catalysts for the oxygen evolution reaction (OER)^[1]. Ruthenium oxide is the most active catalyst for OER, however it lacks the required stability for long-term operation. Iridium oxide possesses activity similar to ruthenium oxide but is more stable. Ruthenium-iridium mixed oxide is therefore studied extensively to further enhance the activity and thermodynamic stability.^[2]

Production of $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ can be carried out using various techniques. Oxide films can be produced by sputtering^[3] and powders by hydrolysis and Adams' fusion method^[1]. The electrochemical behavior of the bimetallic oxide has proven to vary with the preparation method of choice. In the work by Kötzt and Stucki^[3] it was shown that sputtered films of mixed iridium and ruthenium rutile possessed an activity which did not correlate to the linear combination of the properties of the two single oxides, and therefore showed a synergetic effect between ruthenium and iridium. Higher activity of the bimetallic oxide was obtained than what one would expect from simply adding the individual activities of the pure oxides. However, the $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ powders made by hydrolysis method by Owe et al.^[1] showed coinciding behavior with a system having properties composed of a linear combination of the pure individual oxides. The synthesis method is therefore of great importance and can be decisive for whether interaction in bimetallic, rutile structured oxides are present or not, and should be investigated further. The outcome of such a study would be determining for the direction one would choose to proceed in the further work to obtain catalyst with higher activity towards OER, and which methods that must be employed in order to produce these catalyst. In this work iridium-ruthenium oxide powders have been synthesized by the Pechini synthesis with the objective to investigate whether or not a synergistic behavior could be observed for mixed iridium-ruthenium oxide produced by this method of synthesis.

Experimental

$\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ of $x=0, 2.5, 0.5, 0.75$ and 1 were synthesized by a Pechini synthesis method, three parallels for each composition. The powders were synthesized as described in the work by Mamaca et al.^[4], with some modifications. The powders were characterized by use of XRD and a range of conventional electrochemical methods.

Results and Discussion

The structural characterization of the powders obtained with XRD showed presence of metallic iridium in the pure IrO_2 and the $x=0.75$ samples. It was however possible to further oxidize this metal electrochemically by repetitive potential cycling between the onset of hydrogen and oxygen evolution. The observed oxide peaks in the voltammogram were growing with increasing cycle number (Fig. 1), similar to what has been observed when metallic iridium is oxidized by potential cycling during

growth of AIROF ^[5]. 150 cycles were carried out before slow-sweep polarization curves were recorded. As the final CV, cycle 150, demonstrates iridium oxide behavior it is believed that the outer layer of the catalyst consist of oxide when polarization curves were recorded.

The potential at which the charged normalized current of $10\text{mA}\text{C}^{-1}$ was obtained during polarization has been plotted as a function of nominal ruthenium fraction in Fig. 2. The solid line included in the figure represents the potential for OER at constant current density of $10\text{mA}\text{C}^{-1}$ under the assumption that the current density is a linear superposition of contributions from pure IrO_2 and RuO_2 . The dashed line represents the type of behavior reported by Kötzt and Stucki^[3]. As can be seen in Fig. 2, the potential points of the $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ series synthesized by Pechini method lie close to the solid line, and therefore follow the trend of activity being a linear combination of the pure oxides rather than demonstrating a synergistic effect.

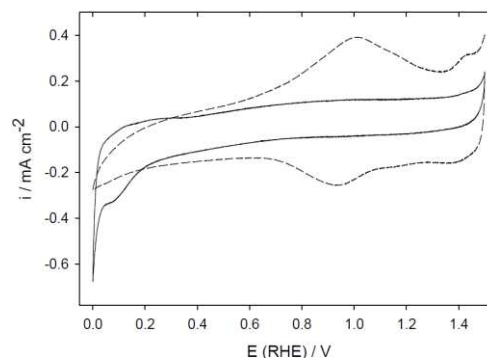


Figure 1 Cycle 1 (solid line) and cycle 150 (dashed line) of cycling of IrO_2 , $x=1$.

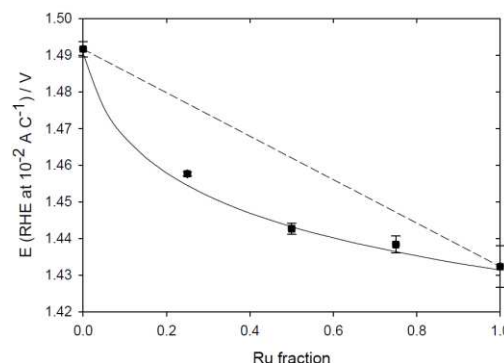


Figure 2 Potential for OER at $10\text{mA}\text{C}^{-1}$ as function of nominal ruthenium fraction. Potential calculated assuming linear combination of properties of IrO_2 and RuO_2 shown with solid line, dashed line represents behavior seen in Ref. 3.

References

1. L.-E Owe, M. Tsyppkin, K. S. Wallwork, R. G. Haverkamp, S. Sunde, *Electrochimica Acta* **70** (2012) 158-164
2. S. Park, Y. Shao, J. Liu, Y. Wang, *Energy Environmental Science* **5** (2012) 9331-9344
3. R. Kötzt, S. Stucki. *Electrochimica Acta* **31** (10) (1986) 1311-1316
4. N. Mamaca, E. Mayousse, S. Arrii-Clacens, T.W. Napporn, K. Servat, N. Guillet, K.B. Kokoh, *Applied Catalysis B: Environmental* **111-112** (2012) 376-380
5. H. Elzanowska, E. Miasek, V.I. Birss, *Electrochimica Acta* **53** (2008) 2706-2715