# Fluorine doped $(Sn,Ru)O_2$ electro-catalysts for oxygen evolution reaction (OER) in PEM based water electrolysis

Karan Kadakia[a], Moni K. Datta[b], Oleg Velikokhatnyi[b] and Prashant N. Kumta[a,b,c,d]

[a]*Department of Chemical and Petroleum Engineering*
[b]*Department of Bioengineering*
[c]*Department of Mechanical Engineering and Materials Science*
[d]*School of Dental Medicine*
*University of Pittsburgh, Pittsburgh, PA 15261*

Hydrogen is considered as the ideal energy carrier and holds the potential to provide a clean, reliable, and affordable energy supply to meet the growing global demands of electric power and transportation fuels. Splitting of water using electricity to produce hydrogen has always been considered a very promising way to produce hydrogen[1]. This involves passage of an electric current through water causing electrochemical splitting of water into hydrogen and oxygen popularly known as electrolysis. It offers virtually no pollution or toxic byproducts if the electric current is generated using renewable energy (wind, solar, geothermal and hydropower) making it a very attractive proposition.

Recently, we have reported that F doping of the solid solution of $IrO_2$ and corrosion resistant oxides such as $SnO_2$, $Nb_2O_5$ and $Ta_2O_5$ shows a drastic improvement in electrochemical activity and durability with significant reduction in the $IrO_2$ content[2,3]. The studies show that this may be due to increase in the electrical conductivity and shifting of the d-band center towards pure $IrO_2$. Exploiting a similar concept, we have studied F doped $(Sn_{0.80}Ru_{0.20})O_2$ for the first time to explore improvement in the electrochemical activity and also demonstrate the performance equivalence to pure $RuO_2$ when the precious metal loading is reduced by almost 80%. In order to demonstrate this remarkable result, a homogeneous solid solution of $SnO_2$:F and $RuO_2$ [(Sn,Ru)$O_2$:F] of nominal compositions $(Sn_{0.8}Ru_{0.2})$:x wt.% F with x = 0, 5, 10 and 15, has been synthesized by thermal decomposition of a mixture of metal salt precursors on Ti foil as a thin film anode electrocatalyst for PEM based electrolysis. In addition, to obtain a better understanding of the fundamental electrochemical activity and long term stability of the (Sn,Ru)$O_2$:F electrocatalyst, first-principles calculations of the total energies and electronic structures of the model systems with chemical compositions similar to those of the above mentioned experimentally synthesized materials have been carried out to complement the present experimental study.

The electrochemical activity of $(Sn_{0.80}Ru_{0.20})O_2$:F accordingly increases with increase in F. Furthermore, the electrochemical performance including the current density, polarization resistance, Tafel slope and stability/durability at an optimal composition of 10wt.% F matches that of pure $RuO_2$. The polarization curve of pure $RuO_2$ and $(Sn_{0.2}Ru_{0.8})O_2$:F thin film before and after ohmic resistance correction is shown in Fig. 1. The current density of (Sn,Ru)$O_2$:10F is similar to that of pure $RuO_2$ making it an excellent choice as an OER electro-catalyst. Theoretical studies comprising first principles calculation of the total energies and electronic structures of the model systems have also been performed to understand the excellent electrochemical activity.

As a result, we conclude that $(Sn_{0.80}Ru_{0.20})O_2$:F doped with ~10 wt% of F is potentially a preferred oxygen evolution electro-catalyst composition for water electrolysis resulting in almost ~80% reduction in noble metal content. Thus we believe that the F doped solid solution of $IrO_2$ and $RuO_2$ system and the composition identified combined with its excellent performance can thus be considered viable for contributing to significant reduction in the overall capital cost of PEM based water electrolyzers.

**References:**

1. Crabtree G.W. et. al., Physics Today 2004; 57: 39.
2. Datta M.K., Kadakia K. et. al., Journal of Materials Chemistry A 2013; 1: 4026.
3. Kadakia K. et. al., Journal of Power Sources 2013; 222: 313.

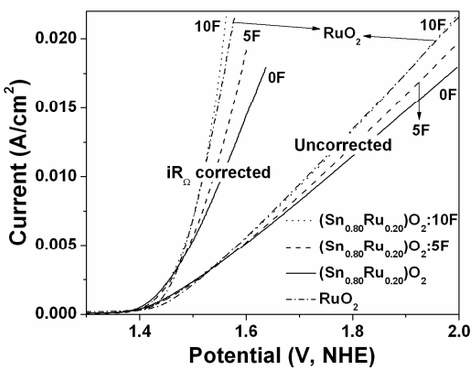


**Fig. 1**: Polarization curves of (Sn,Ru)$O_2$:F thin films in 1N $H_2SO_4$ at 40°C for PEM based water electrolysis.

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