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Active oxygen evolution catalyst in PEMFCs cathode

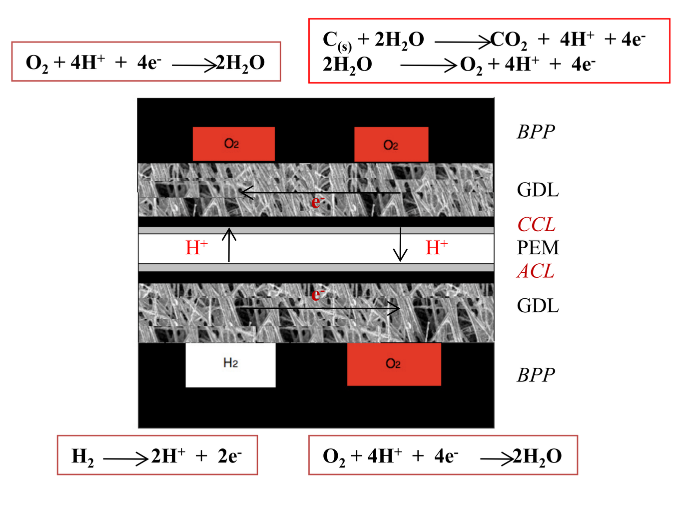
Reduced carbon corrosion during Start Up/Shut Down

Background

Considerable attention has been focused on the corrosion of the catalyst support in PEMFC electrodes, due to the large negative impact it has on the performance.

Under fuel starvation conditions or during start-ups and shut-downs, H_2 and O_2 unavoidably coexist at the anode. It has been shown that under these conditions the cathode may reach high enough potentials to induce severe carbon corrosion of the cathode

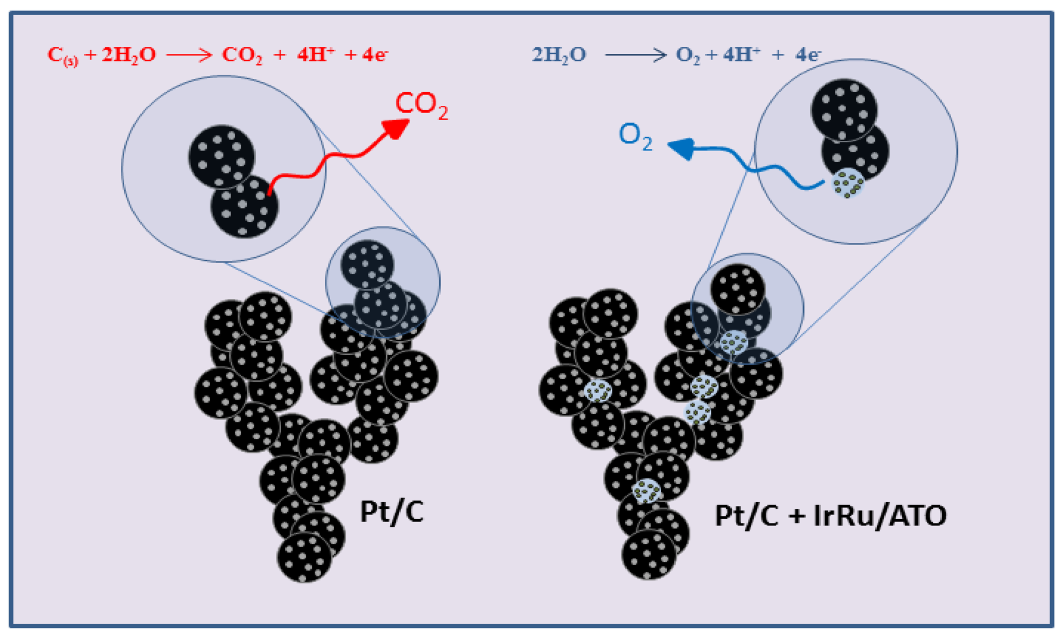
Reversed decay mechanisms



[C. A. Reiser et al., Electrochemical and Solid-State Letters, 8 (2005)A273-A276]

Abstract

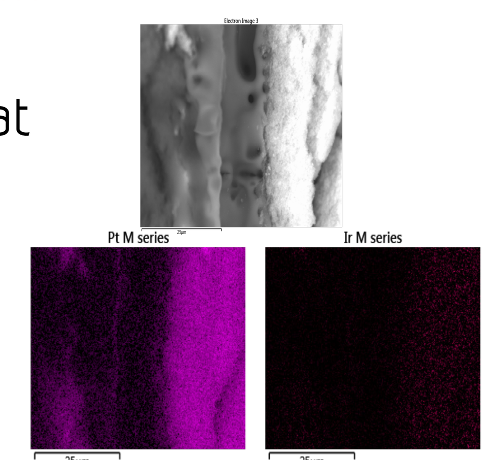
A very active oxygen evolution catalyst (21 wt% $Ir_{0.86}Ru_{0.14}O_2$ supported on $Sn_{(1-x)}Sb_xO_2$ (ATO)) was added to a Pt/C (30wt% Pt) cathode of a PEMFC. The aim of the study was to investigate the effectiveness of such catalyst to protect the cathode catalyst layer during prolonged start-ups and shut-downs (SU/SD). It is shown that only very small amounts of IrRu/ATO is needed to provide considerable protection against carbon corrosion.



Electrode composition

The Pt/C + IrRu/ATO electrode contains only small amounts of the oxygen evolution catalyst (5 wt% with respect to Pt); high amounts of Ru has been shown to negatively affect the ORR.

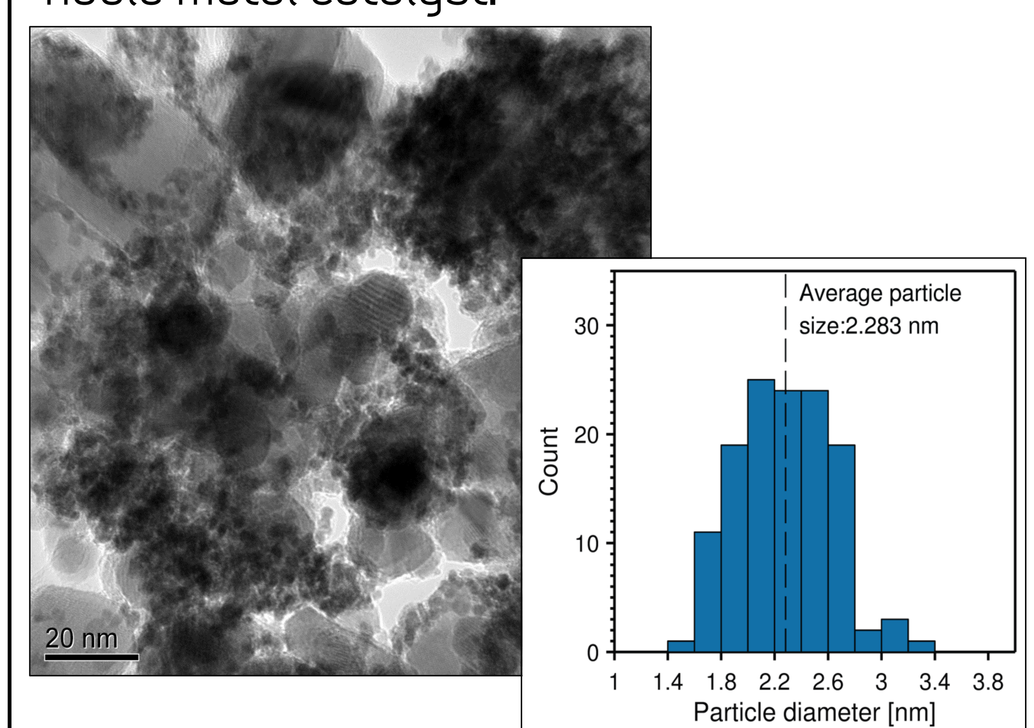
EDS analysis of the cathode shows that Ir is well dispersed in small quantities



Electrode	Nafion ($mgcm^{-2}$)	Pt ($mgcm^{-2}$)	Carbon ($mgcm^{-2}$)	IrRu ($mgcm^{-2}$)	ATO ($mgcm^{-2}$)
Pt/C	0,32	0,261	0,61	0	0
Pt/C+IrRu/ATO	0,39	0,32	0,75	0,0165	0,063

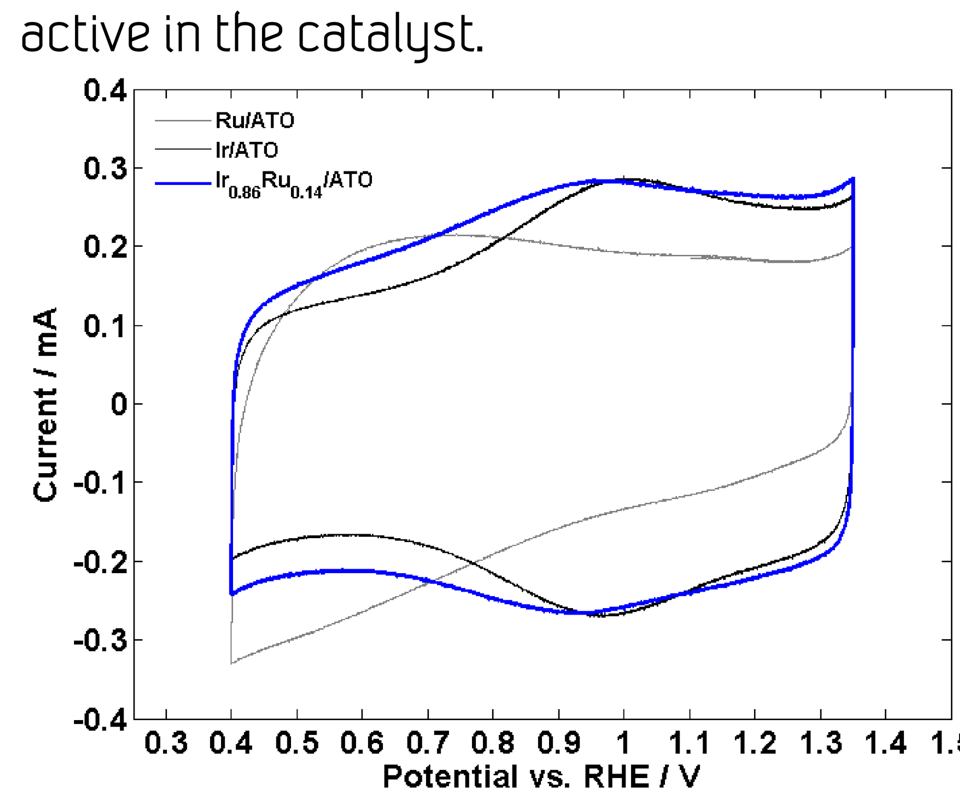
Novel oxygen evolution catalysts

Catalysts with very high activity for oxygen evolution have been made by a microwave polyol method. Nanoparticles of Ir, Ru and IrRu-oxides (2-3 nm), are supported on $Sn_{(1-x)}Sb_xO_2$ giving a very high utilization of the noble metal catalyst.



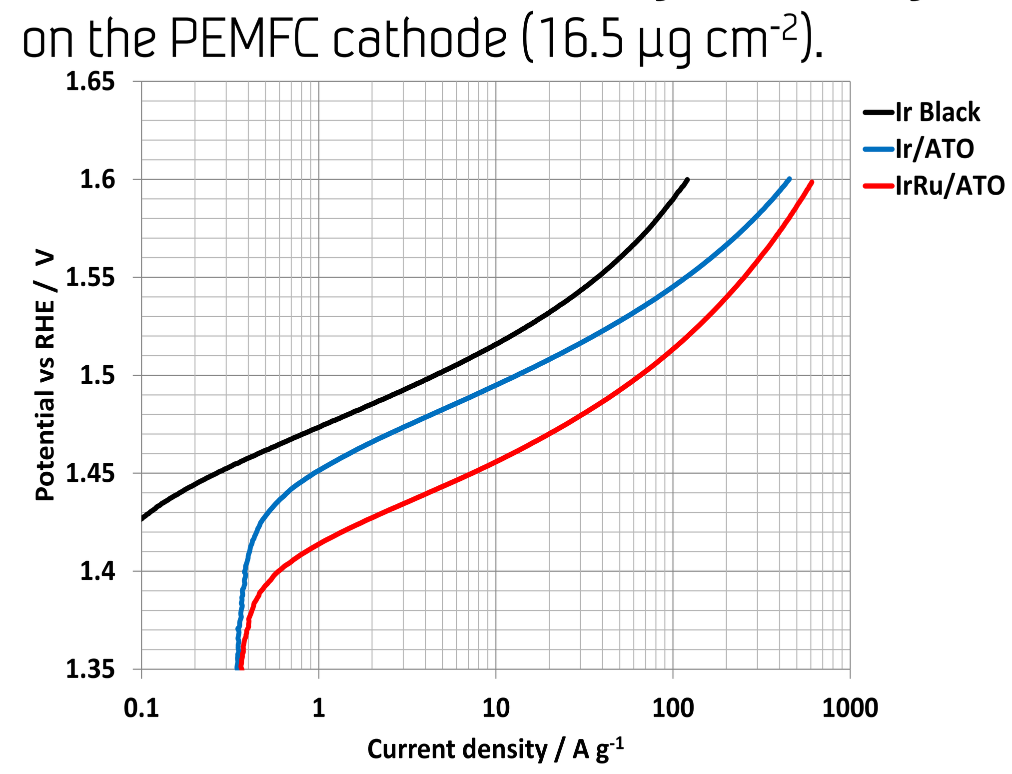
Cyclic voltammetry

The IrRu catalyst shows a combination of the redox behaviour of the pure Ru and Ir catalysts, validating that both elements are active in the catalyst.

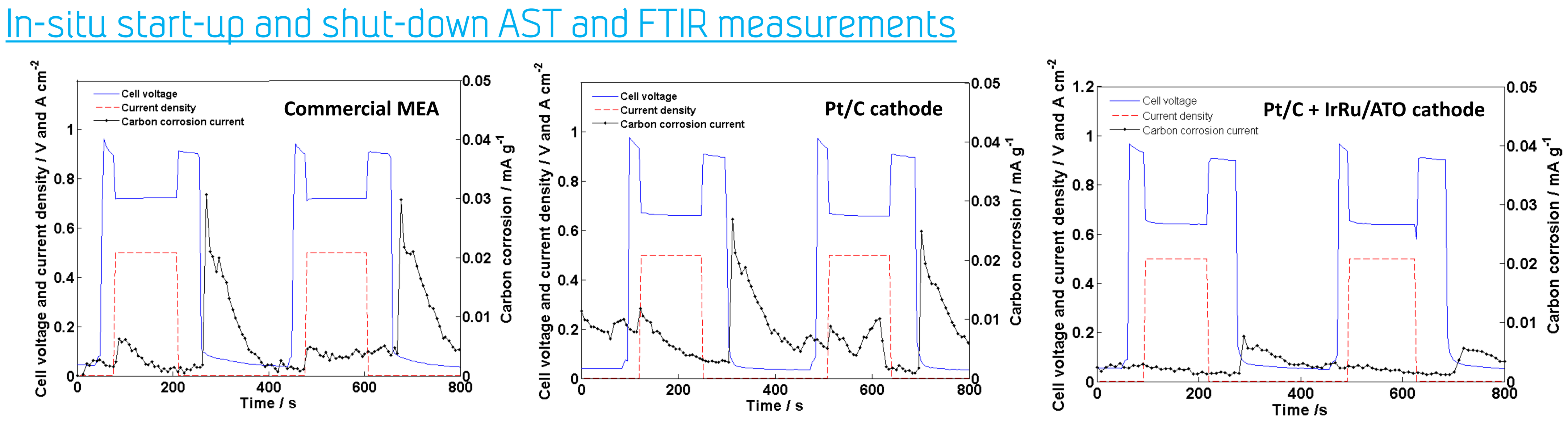


Increased activity

The catalyst have more than 25 times the catalytic activity of a commercial Ir-black catalyst. (7.6 A g^{-1} at 1.45 V, 1 M H_2SO_4, 25 ºC), and no dissolution of Ru is observed. This allows for the use of very low loading on the PEMFC cathode (16.5 µg cm^{-2}).

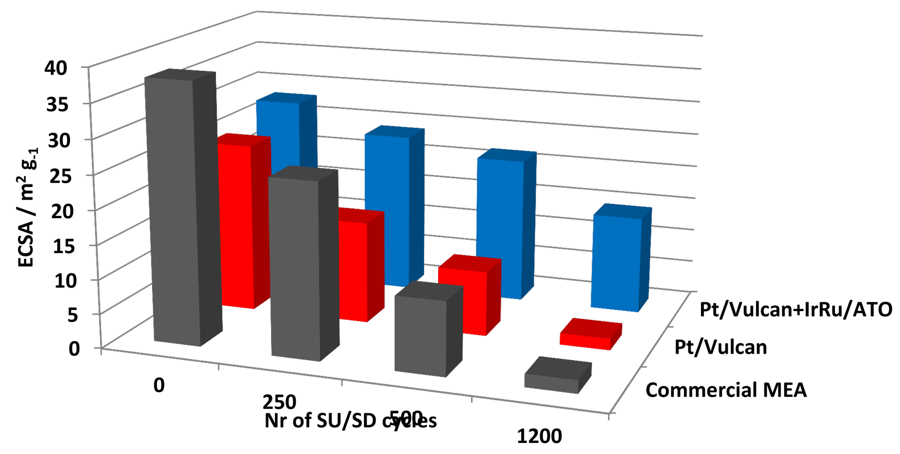


In-situ start-up and shut-down AST and FTIR measurements

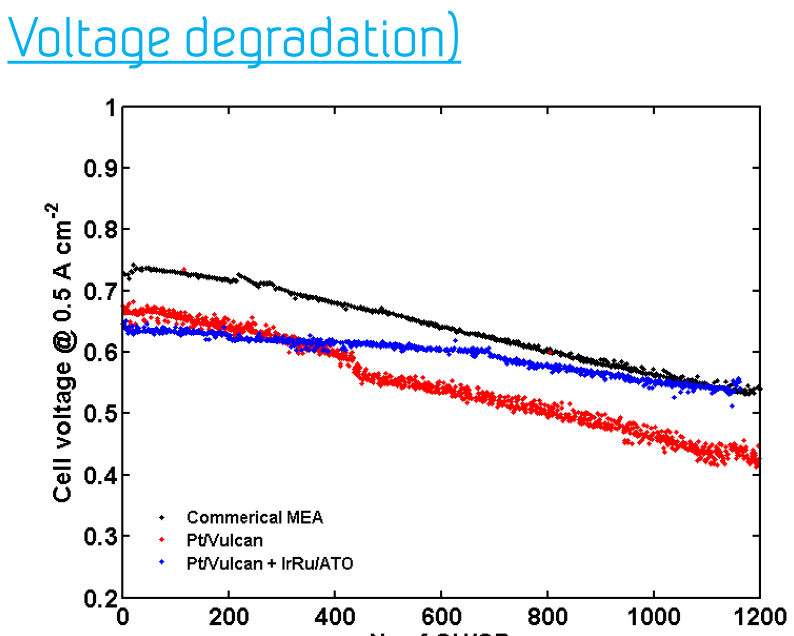


The AST consists in current cycling between 0 and 0.5 A cm^{-2}, at 70 ºC and using fully humidified gases. For each cycle the fuel cell is shut-down by purging the anode side of the fuel cell with air in order to removed t remaining hydrogen. FTIR measurements show that the hydrogen/air front at the anode induces carbon corrosion at the cathode. FTIR also shows that evolved CO_2 is considerably lower in magnitude for the IrRu containing electrode.

Electrochemically active surface area (ECSA)



Voltage degradation)



The IrRu containing Pt/C cathode shows considerably lower degradation rates, e. g. lower degradation of the ECSA and an overall lower voltage decrease, compared to the Pt/C electrode. For comparison, the same was performed with a state-of-the-art commercial MEA.

Conclusions

The addition of 16.5 µg cm^{-2} IrRu catalyst into a conventional Pt/C-based PEMFC cathode results in a significant increase of the durability of the electrode. The small amounts of Ir and Ru not only limits the negative effects it may have on the ORR, but also makes this method an cost-effective mitigation strategy against carbon corrosion during SU/SD.

Acknowledgements

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