Synthesis and evaluation of a platinum-rare earth alloy catalyst for PEM-fuel cells

Eva Dahlqvist, Rémi Albert, Hazel Ndulue
Supervisor: Björn Lönn
Department of Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden
TRA275 - Fuel Cell Systems

1 Catalyst activity and the ORR reaction

The main kinetic challenge in the PEM fuel cell is the oxygen reduction reaction (ORR). To reach the required efficiency, considerable amounts of platinum is used as a catalyst at the cathode, making up a large part of the cost of the fuel cell. It has already been shown that the activity of the platinum catalyst can be improved by alloying with rare earth metals, something recreated in this work by making Pt_3Y thin films and comparing them to bulk platinum[1].

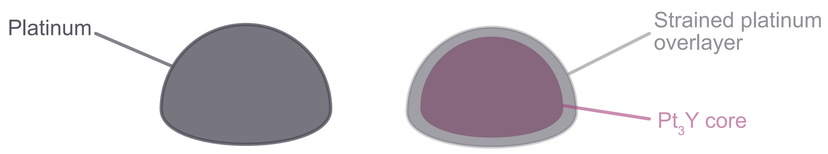

Figure 1, A pure platinum nanoparticle compared with a platinum-yttrium alloyed nanoparticle.

When used, the yttrium of the outermost shell will leach from the particle, leaving behind a strained platinum overlayer, believed to enhance the catalytic ORR activity[1]. This same principle has been shown to work for different ratios of platinum to yttrium alloy thin films, but with Pt_3Y and Pt_7Y_3 alloys obtaining the best results.

3 Results

Cyclic voltammetry allows for exhibiting characteristic electrochemical features. In the present case, we can observe the adsoption/desorption of hydrogen at lower potentials, the double layer capacitance and the Oxidation and Reduction.

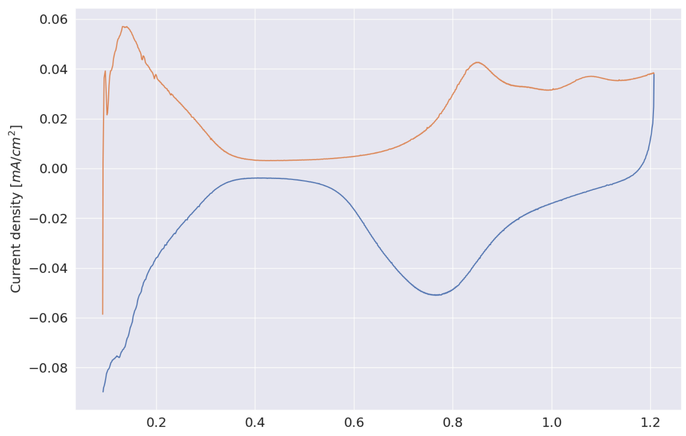

Figure 4, CV of Pt_3Y under argon.

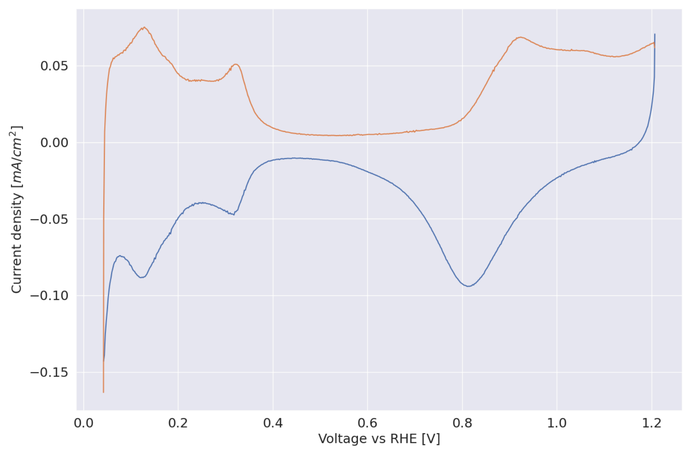

Figure 5, CV of Pt under argon.

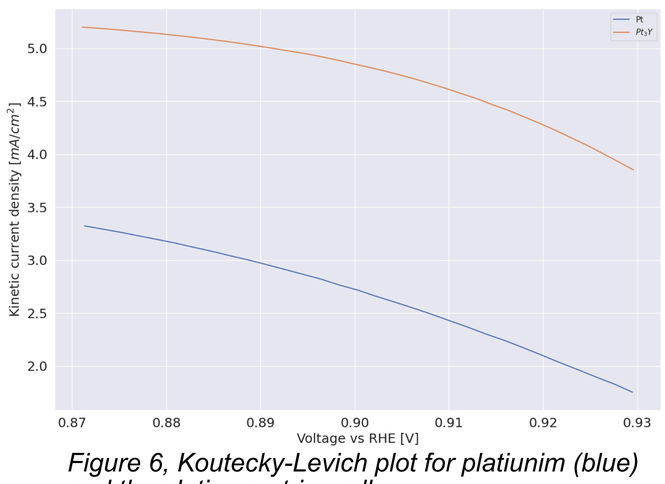

Figure 6, Koutecky-Levich plot for platiunim (blue) and the platinum-ytrium alloy.

2 Methodology

Magnetron sputtering of thin alloy films

Discovered by Chapin in 1974, boasting high speed, low damage and lower temperature sputtering, Magnetron sputtering is a deposition technology involving a gaseous plasma which is generated and confined to a space in close vicinity of the material to be deposited – the 'target'. The surface of the target is eroded by high-energy ions within the plasma, and the liberated atoms travel through the vacuum environment and deposit onto a substrate to form a thin film.

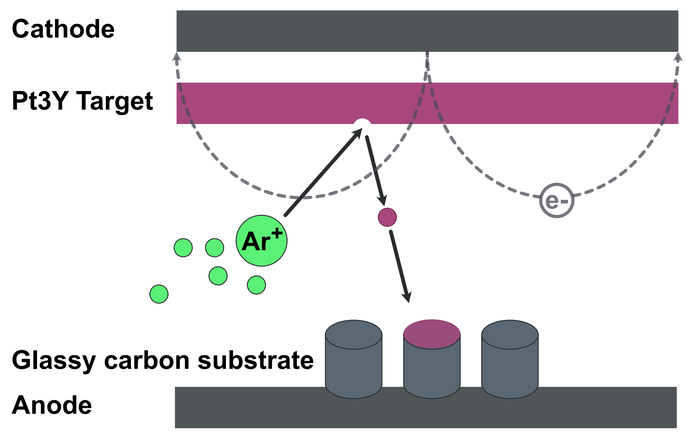

Figure 2, A schematic of the how magnetron sputtering of thin film works.

How does it work? By introducing a closed magnetic field over the target surface the likelihood of collision between electrons and argon atoms is increased, plasma generation efficiency is enhanced, resulting in rapid target erosion and high-density thin film deposition onto substrates. The employment of lower voltage and high current discharge, make it a great coating process among other sputtering techniques.

Rotating disk electrode

RDE is a technique used to investigate electrode reaction mechanisms and kinetics. The RDE technique is used to control and determine the transportation of reactants near the electrode surface and its impact on electron-transfer kinetics.Two processes are crucial:

- Convection, which influences the thickness of the diffusion layer
- Diffusion, which governs the transport rate of the reactant through the diffusion layer.

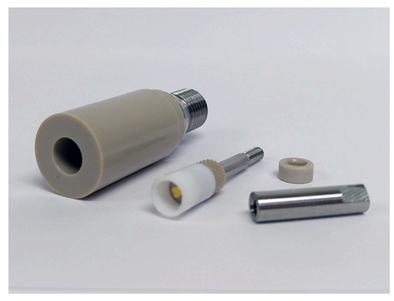

Figure 3, A picture of an RDE sample holder.

The kinetic current density, I_k, relate to the catalytic activity of a reaction. It can be extracted using the Koutecky-Levich relation,

$$\frac{1}{I_m} = \frac{1}{I_k} + \frac{1}{I_{MT}}$$

The Platinum-Yttrium alloy catalyst demonstrates a significantly higher kinetic current density, with the performance gap widening as the potential increases, reaching up to twice as performant as the bulk Pt. This suggests that Pt_3Y has superior catalytic activity for ORR compared to pure Pt.

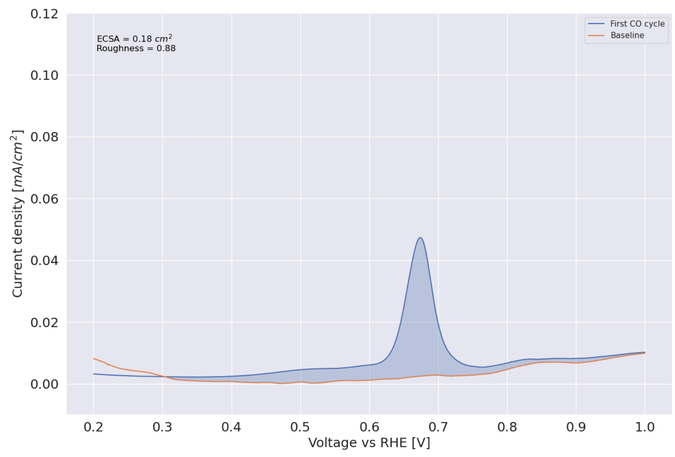

Figure 7, partial CV plot of CO-stripping for Pt_3Y, using the first and second cycle.

CO stripping can be used to quantify the ECSA of the catalyst by adsorbing CO onto the catalyst surface to form a monolayer, then "stripping" it off by applying a potential that oxidizes the CO to CO_2. The area under the CO stripping peak, after correcting for the baseline, can be integrated to find the charge required to oxidize the adsorbed CO. This charge is then used to calculate the ECSA by using the known charge required to oxidize a monolayer of CO on a smooth platinum surface (420 μC/cm²).

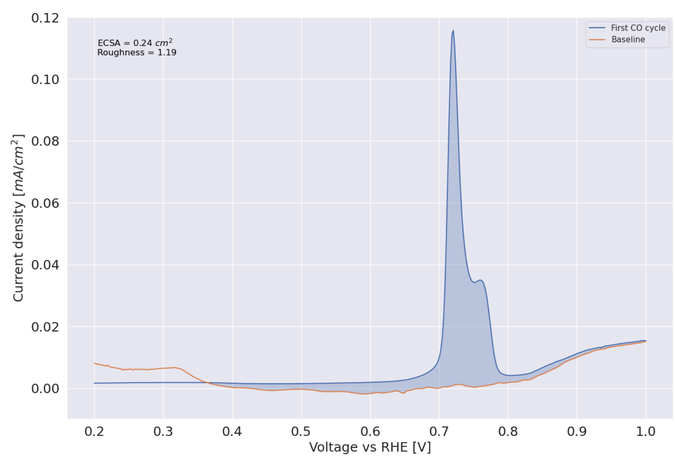

Figure 8, partial CV plot of CO-stripping for Pt, using the first and second cycle.

4 Conclusions

Analysis of the experimentations revealed distinct electrochemical surface area (ECSA) results for Pt3Y and Pt, with Pt3Y exhibiting a lower peak in CO-stripping experiments (0.18 cm² vs. 0.24 cm² for Pt). However, Pt3Y demonstrated a higher kinetic current density, indicating superior catalytic activity for the oxygen reduction reaction compared to Pt.

Reference
[1]N. Lindahl, E. Zamburlini, L. Feng, H. Grönbeck, M. Escudero-Escribano, I. E. L. Stephens, I. Chorkendorff, C. Langhammer, B. Wickman, Adv. Mater. Interfaces 2017, 4, 1700311.