Activity and Stability of RuO$_x$ Based Electrocatalysts for the Oxygen Evolution Reaction - DTU Orbit (22/08/2019)

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The focus of this Ph.D. thesis is on the electrocatalytic oxygen evolution reaction (OER) in acidic media for Proton Exchange Membrane (PEM) Electrolyser applications. This technology is an attractive alternative for storage of renewable energy, such as from solar and wind power, in small scale delocalized hydrogen refueling stations. The sluggish kinetics of OER and the high costs of the materials represent some of the biggest technological challenges for PEM electrolysers.

The current technology relies on Pt group based materials and in particular ruthenium and iridium are the most active and stable OER catalysts. To contain costs and precious metals supply, the mass activity should be maximized. However, in order to define the properties of a catalyst, knowing the distinction between geometric and electronic effects is fundamental.

It is not trivial to determine the intrinsic catalytic activity on oxides and studies on well-defined surfaces are required. Notably, industrial applications demand maximized surface-to-bulk ratio, hence fabrication of catalysts in nanoparticulate form. In this perspective, this project aimed at investigating well-defined mass-selected ruthenium and ruthenium dioxide nanoparticles (NPs) in the technological relevant size range of 2-9 nm. The objectives were to estimate the intrinsic catalytic activity of ruthenium and to identify any particle size effects. The results show that activity and stability are strongly influenced by the surface pre-treatment. Furthermore, these RuO$_2$ NPs exhibit over an order of magnitude improvement in activity and turnover frequency in comparison to the current state-of-the-art, and a tentative maximum at around 3-5 nm.

Although high activity is essential for an efficient catalyst, stability should be also considered, in particular under the harsh acidic and oxidizing conditions for a PEM electrolyser. Standardised protocols for assessing the stability have not been established for the oxygen evolution reaction. Hence, this thesis focuses on providing guidelines for quantifying the corrosion rate of an OER catalyst. By coupling Electrochemical Quartz Crystal Microbalance (EQCM) measurements with Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analyses of the electrolyte, we emphasize the importance of monitoring the mass loss.

Finally, the thesis focuses on improving the stability of ruthenium dioxide under OER conditions, by sub-monolayer addition of iridium oxide. The approach was inspired by theoretical calculations, which suggested that iridium would impede Ru corrosion by migrating to the undercoordinated sites at the surface, such as step and kink sites, which are the most prone to corrosion. Preliminary results show that an improvement of stability can be obtained, slightly decreasing the activity as well. Unfortunately, a drastic enhancement, as hoped, was not detected. Instead the results serve as a starting point from which the strategy and method for stability improvements can be further developed.

**General information**
- Publication status: Published
- Organisations: Department of Physics, Experimental Surface and Nanomaterials Physics
- Contributors: Paoli, E. A.
- Number of pages: 219
- Publication date: 2014

**Publication information**
- Place of publication: Kgs. Lyngby
- Publisher: Technical University of Denmark (DTU)
- Original language: English