Electrocatalysts for Oxygen (and Chlorine) Evolution Reaction

Renewable energy sources are good candidates for supplying the world energetic needs but only if it is possible to store the produced energy in a carrier which could allow its usage after its production. One of the most promising energy vectors is hydrogen, even if several issues due to its low (volumetric) energy density and difficult storage have still to be solved. However, nowadays hydrogen is mostly produced from fossil fuels (principally CH₄) by steam reforming, but this process produces CO₂ emissions into the atmosphere.

It is possible to obtain hydrogen from water by water splitting. This is one of the most promising techniques due to the abundance of the raw material. It is an up-hill reaction, non-spontaneous in standard conditions (ΔG°>0), which therefore requires an energy supply in order to take place. If combined with a photovoltaic panel or a wind turbine, it is possible to produce zero-emission hydrogen. The reaction is composed by the following two half reactions:

At the anode (+): 2H₂O → O₂ + 4e⁻ + 4H⁺ \[ E^0 = 1.23 \text{ V} \]

At the cathode (-): 2e⁻ + 2H⁺ → H₂ \[ E^0 = 0 \text{ V} \]

Due to the losses that inevitably occur, the required voltage for the reaction is higher than predicted. More in details, the anodic overpotentials are predominant because of the involvement of 4 protons and 4 electrons which slows down the reaction kinetics. The development of an active, stable and resistant catalyst for the anodic compartment is therefore crucial in order to increase the competitiveness of this process. Among them, DSA® anodes have been revealed among the most active for this reaction and are the only ones which can work in an acidic environment as well. They typically consist in a solid solution of RuO₂ (or IrO₂) and TiO₂ ¹; the first is the active phase while the latter enhances the stability of the electrode. When tested in seawater electrolysis, even if thermodynamically the Oxygen Evolution Reaction (OER) should be favorable, the main reaction which takes place is the Chlorine Evolution Reaction, due its faster kinetics. It is however possible to tune the selectivity towards one reaction or another adding an additional layer on the surface of the electrodes (eg: manganese oxide, which enhances the selectivity towards the OER ²,³).

The project will be mainly focused on:
- Synthesis, characterization and electrochemical tests of TiO₂ - RuO₂ anodes. Different techniques will be used for the preparation (dip coating, spin coating, electrodeposition), characterization (XRD, XPS, SEM, Raman) and tests (Cyclic Voltammetry, Linear Scan Voltammetry, Chronoamperometry) of the catalysts.
- Studying the selectivity of the catalysts towards the OER or CER during seawater electrolysis. The addition of a transition metal layer on the surface of the anode allows to tune the selectivity towards one reaction respect to the other. Understanding the factors which determine this selectivity will be a main goal of the project.
- Exploring the surface modifications of the anodes which take place during electrolysis, both in freshwater and seawater. The use of advanced spectroscopic techniques, such as Near-Ambient Pressure XPS, will be used to achieve this task.

For further information:
Marco Etzi (Helix, STW 3.49), Tel 4195, m.etzi.collier.pascuzzi@tue.nl
Jan Philipp Hofmann (Helix, STW 3.48), Tel 3466, j.p.hofmann@tue.nl