ELECTROCATALYSIS FOR ENERGY PRODUCTION AND STORAGE

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ABSTRACT

The world's system of production and exploitation of fossil fuels is reaching a breaking point: finiteness, pollution and geopolitical problems mean that an energy economy based on these resources is no longer "sustainable". The development of a new energy strategy is now a priority and renewable energies are the main candidates for replacing fossil fuels, especially for electrical energy production.

Solar energy is the most abundant and easily available renewable source but it is neither constant nor distributed equally over the surface of the globe. Hydrogen and biofuels, like bioethanol, have the potential, as solar energy storage vectors, to play a fundamental role in the development of a new energy era based on renewable sources. There are two electrochemical devices, which will be fundamental for the realization of such an energy system. Firstly, fuel cells, which are devices that can convert cleanly the chemical energy stored in hydrogen or bioalcohols into electrical energy and secondly, electrolyzers, which are the best candidates for storing electric energy produced from renewable sources as hydrogen.

The focus of this thesis is the development of innovative anodic electrocatalysts for three energy-related devices: a) Direct Alcohol Fuel Cells (DAFCs), b) H_2/O_2 fed Anion Exchange Membrane Fuel Cells (AMFCs) and c) anion exchange membrane alcohol electroreformers. Catalysts have been synthesized and characterized for their morphology and electrochemical activity, both in half-cell and in the complete cell systems. An anion exchange membrane is used in all devices because thealkaline environment is the most promising way to overcome the problems that hinder the development of fuel cells and electrolyzers that belong to the state of the art. For example, in alkaline media, alcohol oxidation kinetics are faster compared the traditional proton exchange membrane based devices. In Chapter 2 a description of the state of the art of fuel cells and

electrolyzers is provided and describes the advantages in replacing the traditional proton exchange membrane electrolytes with anion exchange membranes.

Chapter 3 introduces the OrganoMetallic Fuel Cell (OMFC), which employs a rhodium complex as anodic electrocatalyst. In contrast to established technologies based on metal nanoparticles, in OMFCs every single metal atom is catalytically active and thereby reduces the metal loading of fuel cell electrodes by several orders of magnitude. Because the performance of the metal complexes can be optimized based on established methods of synthetic organometallic and coordination chemistry, the approach via OMFC's – though in its infancies – should allow to truly design electrodes which in principle can operate with earth-abundant, inexpensive metals. Organometallic fuel cells catalyse the selective electrooxidation of renewable diols, simultaneously providing high power densities and chemicals of industrial importance. It is shown that the unique organometallic complex $[Rh(OTf)(trop_2NH)(PPh_3)]$, employed as molecular active site in an anode of an OMFC, selectively oxidizes a number of renewable diols, such as ethylene glycol (EG), 1,2-propanediol (1,2-P), 1,3-propanediol (1,3-P), and 1,4-butanediol (1,4-B) to their corresponding mono-carboxylates. The electrochemical performance of this molecular catalyst is discussed, with the aim to achieve cogeneration of electricity and valuable chemicals in a highly selective electrooxidation from diol precursors.

Removal of platinum from polymer electrolyte membrane fuel cells is one of the most commonly cited objectives for researchers in this field.

In Chapter 4 is described a platinum free anion exchange membrane fuel cell (AEM-FC) that employs nanostructured Pd anode and Fe-Co cathode electrocatalysts. AEM-FC tests run on dry hydrogen and pure air show peak power densities of more than 200 mW cm^{-2}. Such high power output is shown to be due to a nanoparticle Pd anode catalyst with a composite Vulcan XC-72 carbon-CeO_2 support that exhibits enhanced kinetics for hydrogen oxidation in alkaline media.

In chapter 5, a nanostructured anodic electrocatalyst (Au@Pd supported on Vulcan XC-72) is employed in an alkaline alcohol electroreformer, which provides a net energy saving for hydrogen production compared to traditional water electrolysis. In addition, hydrogen production is coupled with the contemporaneous conversion of a bioalcohol into valuable chemicals, for example lactate and glycolate, which are industrially relevant feedstock. Traditional nanostructured palladium based anodic electrocatalysts are not selective in the oxidation of renewable polyols to carboxylic compounds. Modifying the nanoparticle architecture is a way to increase this selectivity. In addition, the energy consumption for hydrogen production by electrolysis was lowered from the 50-60 kWh $kg_{H_2}^{-1}$ of a traditional electrolyzer to ca. 20 kWh $kg_{H_2}^{-1}$.

Chapter 6 summarizes the conclusions of this thesis. The results of this research clearly demonstrate that the architecture of the anodic electrocatalyst plays a fundamental role in the enhancement of the electrochemical performances of devices such as OMFCs, AMFCs and alcohol electroreformers. In addition, the anodic catalyst architecture has the important role for driving the selectivity of the alcohol oxidation reaction towards carboxylic compounds in OMFCs and electroreformers. These devices produce chemicals of industrial relevance with a contemporaneous release of energy or hydrogen at low temperature and atmospheric pressure, matching several principles of sustainable “green chemistry”.