Abstract of PhD thesis

author: **Karolina Kordek-Khalil**

title: "Modified carbon fibre cloth as a material for high performance self-supported electrocatalytic water splitting electrodes"

Currently, the large-scale application of water electrolysis is limited by high cost of noble metal-based electrocatalysts of both hydrogen (HER) and oxygen evolution reactions (OER). Attractive alternative materials, investigated as their possible replacements, are the non-noble metal compounds, carbon materials, and composites of both of them. Nonetheless, presently investigated electrocatalyst are often prepared by complicated, multi-step techniques and are generally in the form of powders, that for application as electrocatalysts must be attached to the electrode surfaces, usually using polymer binders which may block the catalytically active sites or increase the electrode resistance.

In this doctoral dissertation, different noble metal-free electrocatalytic materials were prepared by direct modifications of surfaces of two types of commercial carbon fibre cloths, in order to obtain free-standing electrodes, which can directly be applied in electrochemical devices. Various material modification techniques were applied and optimised, resulting in the development of preparation procedures of high-performance HER and OER electrocatalysts. Moreover, different obtained series of electrodes were characterised in terms of physicochemical properties and electrocatalytic performances, enabling indications of the material features possessing the greatest influence on the HER and/or OER activity of materials in alkaline medium. The investigated materials included fully metal-free flexible electrodes, prepared by mild oxidation of carbon cloth, and noble-metal free composite electrodes composed of modified carbon cloth phase and metal-based film. Methods of electrocatalytic film deposition included electrodeposition and pulsed laser deposition. Both methods were used to obtain cobalt-based films, and electrodeposition was also applied to prepare bimetallic cobalt/nickel-based electrodes.

As a result of performed optimisations of one-step electrodeposition process, a bimetallic, Co,Ni-based composite electrode preparation procedure was elaborated. The material is composed of three phases: carbonaceous, metallic and mixed hydroxide $Co,Ni(OH)_2$. The electrode possesses low HER overpotential of 150 mV (at the current density 10 mA cm^{-2}), and high-performance stability. Both the material activity and stability are significantly higher than that of corresponding monometallic electrodes.

Also, a two-step carbon cloth oxidation procedure was elaborated, which has given as a product highly active bifunctional oxygen evolution/reduction electrode, which is composed of only carbon, hydrogen and oxygen atoms. The low OER overpotential of 360 mV (at the current density of 10 mA cm^{-2}), is achieved thanks to mild oxidation which introduced surface oxygen functional groups and structural defects in constituent fibres, but does not affect their high electric conductivity. It was shown that only the combination of two optimised steps of modification lead to formation of such highly active electrode.

A method of simple and quick electrochemical oxidation of poorly oxidised carbon cloth was also presented. It was shown that, the oxidation performed prior to film deposition increases significantly the electrocatalytic activity of thus obtained composite electrodes, irrespective of the film deposition technique applied.

The results presented in this dissertation demonstrate new pathways of preparation of highly active free-standing electrocatalytic electrodes and contribute to understanding of the origins of electrocatalytic activity of metal-free and composite electrocatalytic materials.