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Abstract

„Inorganic-based electrocatalysts for electrochemical oxygen evolution reaction"

As the society primary source of energy for the past several decades, fossil fuels have played an important role. Nevertheless, the use of fossil fuels has a significant negative impact on the environment. Consequently, new, renewable energy systems, such as solar, wind, and tidal, have gained popularity. However, due to their ineffective energy storage and production dependent on external factors, the applications of these systems are limited. Therefore, the development of new, sustainable, and source-independent energy systems is crucial for the future economy and environment. Hydrogen has gained attractiveness to be used as a fuel, due to its high energy density, low environmental impact, and purity. It can be generated form water during the process called water splitting, which involves to half-reactions: hydrogen evolution reaction (HER) and oxygen-evolution reaction (OER). Despite numerous of research, there is still a need to develop and discover a catalyst, which will be effective, stable, and based on earth-abundant elements.

In this thesis, the water splitting process with particular emphasis on the oxygen evolution reaction (OER) has been explored. Commonly employed catalysts together with several strategies to improve electrocatalysts properties have been analyzed. The main objective of this work was to develop effective inorganic-based OER electrocatalysts. To optimize the efficiency of electrocatalysts, attention has been focused on preparing the substrate for further modifications with nanoparticles. The research encompasses the preparation of substrates based on two types of materials: cellulose fibers and borophene.

In the first part of the work, cellulose fibers are subjected to a carbonization and activation process to obtain a carbon material with a developed surface. The influence of carbonization temperature on the physicochemical properties of the obtained materials was investigated. All obtained materials were characterized using techniques such as TEM, XRD, Raman spectroscopy, and specific surface area measurements. It was found that carbonization at a temperature of 850°C produces a sample with the smallest number of defects in the structure

(I_D/I_G ratio calculated from Raman spectra). This results in a material with a very high specific surface area obtained after the activation process ($SSA_{cel\_carb\_850\_act}$=3 164 m^2/g), containing graphene-like structures. For this reason, the cel_carb_850_act sample was used in further research as a substrate for further modifications.

Further, a method was developed for the synthesis of nickel phosphide with various crystalline phases (NiP_x) deposited on carbon material derived from cellulose. The influence of the reduction method on the electrochemical properties of the material was analyzed. The reduction of nickel phosphides was carried out in two atmospheres: hydrogen and vacuum. Studies have shown that reduction in hydrogen for NiP_x and reduction in vacuum for NiP_x_cel result in the formation of nanoparticles with a smaller diameter, inducing the lowest overpotential value - η_{NiPx_H2}=330 mV (6.7% less compared to RuO_2) and $\eta_{NiPx+cel\_vac}$=339 mV (4.2% less compared to RuO_2).

The next part of the research concerned the single-phase structure of nickel phosphide: Ni_2P on carbon material derived from cellulose. For this purpose, materials with differed mass ratios of Ni_2P to carbonized cellulose were prepared: 100:1, 10:1, 1:1, and 100:1. A physicochemical analysis of the obtained materials was carried out using techniques such as TEM, XRD, and Raman spectroscopy, and a detailed analysis of their electrochemical properties in terms of the OER reaction was carried out. The obtained data prove that the lowest overpotential (315 mV) was obtained for the cel_Ni_2P_100:1 sample, and the lowest Tafel coefficient of 54.3 mV/dec was obtained for the cel_Ni_2P_1:10 sample. Moreover, the most promising sample showed better stability compared to the mixed-phase nickel phosphide sample.

The second part of the thesis concerned research on a new, two-dimensional (2D) material - borophene - and its use as a platform for an efficient OER electrocatalyst. Much attention has been paid to the development of synthesis methods that result in the creation of multi-layer borophene sheets. For this purpose, research was carried out on two methods of obtaining borophene: (i) electrochemical exfoliation and (ii) the modified Hummers method.

The electrochemical exfoliation process - the influence of two electrolytes on the morphology of the obtained material was investigated: (i) Li^+/DMSO and (ii) SO_4^{2-}/H_2O. To carry out the process, boron was pressed into metal meshes (nickel or copper). It was found that, depending on the current applied and the mesh used, material with different phases was

obtained. By selecting an appropriate metal mesh as a boron carrier and optimizing the applied current, it is possible to produce multi-layer borophene of controlled quality. Moreover, electrochemical exfoliation of boron has been successfully reported for the first time.

Next, by applying the modified Hummers method, few-layer derivatives of borophene oxide were produced. The process was then followed by heating the samples at high temperatures in a hydrogen atmosphere. Using techniques such as TEM, XRD, FTIR, and XPS, the influence of hydrogen treatment at higher temperatures on the structure and chemical composition of the samples was demonstrated. The study of electrochemical properties showed that the sample treated with hydrogen at a temperature of 600 °C shows the lowest overpotential value, the lowest Tafel coefficient value, and the best stability.

Finally, the electrocatalytic properties of borophene were boosted using single-phase nickel phosphide nanoparticles. The influence of the nickel phosphide to borophene ratio on the OER activity of the catalysts was investigated. The results indicate a significant impact of the content on the final parameters, with the sample having the most favorable properties borofen-Ni_2P_1:1 with a low overpotential value of 299 mV and a low Tafel slope, which proves that the most effective electrocatalyst demonstrated in this doctoral thesis is the borofen_Ni_2P_1:1 sample. Additionally, in order to determine the reaction mechanism, XRD, TEM, and XPS tests were performed after the LSV process.

In conclusion, the impact of the design electrocatalyst on the OER was revealed by performing electrochemical tests, such as linear sweep voltammetry (LSV), Tafel tests, electrochemical impendence spectroscopy (EIS), chronopotentiometry test, and electrochemical surface area determination. The discussion about the influence of modifications to electrocatalytic properties was carried out throughout the entire work. Ultimately, the PhD thesis describes the routes of optimization to obtain a sample that is characterized by outstanding properties, such as low overpotential (η=299 mV), low Tafel slope (53.6 mV/dec), and overall stability. Developing efficient and durable electrocatalysts is made possible by these discoveries, which contribute to the advancement of sustainable energy technologies.

Keywords: electrochemical water splitting, oxygen evolution reaction, cellulose fibers, borophene, nickel phosphides