Abstract of the PhD thesis by mgr inż. Wojciech Kukułka, entitled: "Electrochemical and sorption properties of carbonized metal–organic frameworks and their composites"

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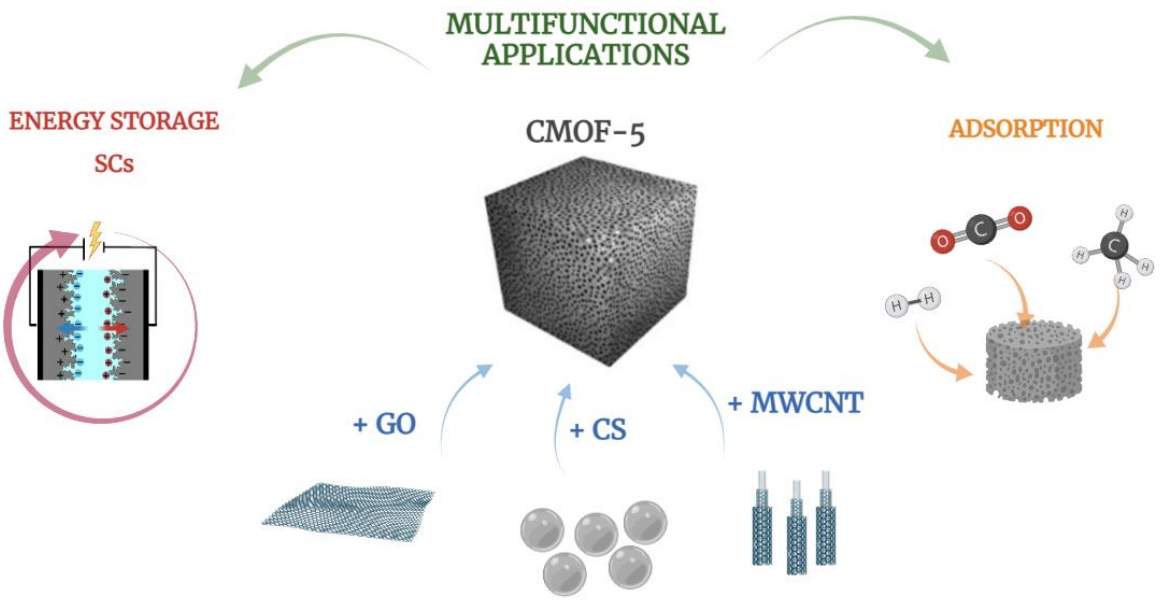
The PhD thesis concerns the preparation of carbonized metal-organic frameworks and their composites and the examination of their physicochemical, electrochemical and sorption properties. The focus was on an metal-organic structure based on zinc (MOF-5) and its use as an active material in the electrodes of supercapacitors and as an adsorbent for carbon dioxide, methane and hydrogen.

The work has a classic layout and is divided into two parts: theoretical and experimental. The theoretical part begins with an introduction to metal-organic frameworks - their structure, methods of synthesis, potential applications and design of the components of these structures, i.e. metal centers and organic ligands. Then, the derivatives of these structures (including carbonized structures) are described - methods of their preparation, design and potential application, with particular emphasis on the use of their electrochemical and sorption properties. Additionally, composites with the participation of metal-organic frameworks are discussed, as well as a specific representative of this group - the zinc-based structure (MOF-5) and its carbonized version. The last chapter of the theoretical part discusses the most important methods of characterization of the obtained materials: transmission (TEM) and scanning (SEM) electron microscopy, X-ray diffraction (XRD), Raman spectroscopy, thermogravimetric analysis (TGA) and all methods used to determine electrochemical and sorption properties.

The experimental part began with the description of the synthesis of a carbonized structure based on zinc (CMOF-5), its physicochemical, electrochemical and sorption properties. The influence of the composition parameters of the measuring electrode on the results of electrochemical properties and the possibility of reducing the environmental impact by recycling used electrodes after measurement and their reuse as well as the synthesis of metal-organic frameworks from recycled substrates were also investigated. A supercapacitor made of electrodes containing CMOF-5 and PVDF in the ratio 80:20 showed a specific capacity of 218 F/g at a current density of 1 A/g, CMOF-5 also has very good sorption properties. Its CO_2 adsorption capacity was 2.43 mmol/g (at 25 °C and 1 bar pressure). The adsorption capacity towards CO^2 in the temperature range up to 100 °C and pressure up to 40 bar, as well as the adsorption capacity towards methane and hydrogen (at the temperature of 25 °C and the pressure of 1 bar) were also tested.

The next chapter describes the research on the synthesis and properties of composites composed of carbonized metal-organic frameworks and three different carbon nanoadditives - graphene oxide (GO), multi-wall carbon nanotubes (MWCNT) and carbon spheres (CS). The physicochemical, electrochemical and sorption properties of all obtained composites were checked. In the case of physicochemical and electrochemical properties, composites obtained in two ways were tested - as a result of physical mixing and in situ during MOF-5 synthesis (chemical mixing). The introduction of carbon nanoadditives resulted in improved stability along with an increase in the current density and the number of charge/discharge cycles, but also with a decrease in the value of the specific capacitance. The specific capacitance results measured at 1 A/g current density were 195.4, 143.5, and 78.7 F / g for CMOF-5_GO, CMOF-5_CS, and CMOF-5_MWCNT, respectively.
The introduction of carbon nanoadditives also resulted in a general deterioration of sorption properties for all three gases. In the last chapter, CMOF-5 and composites with carbon nanoadditives obtained in situ were further functionalized with furfuryl alcohol. In the case of electrochemical properties, the stability was again improved with increasing current density at the cost of a significant loss of specific capacitance. In the case of sorption properties, the results were again worse than CMOF-5.



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