

Rafał Roszak

Abstract of the PhD thesis entitled: "Adsorption and catalytic properties of functionalized carbon nanomaterials - theoretical study"

The aim of the study was to design new carbon-based materials that could be used for hydrogen adsorption storage and as catalysts for the electrochemical reduction of oxygen. Both of these issues are closely interrelated and occur in fuel cell cars powered by hydrogen. To popularize such vehicles and make their mass production cost effective it is necessary to solve the problem of on-board hydrogen storage and its effective oxidation in low-cost highly durable and efficient fuel cells.

Pure carbon materials are not suitable for hydrogen storage at ambient temperatures due to the low adsorption energy of H_2 . Therefore, the first aim of this work was to propose modified carbon structures which have a higher interaction energy with hydrogen what means greater adsorption capacity at room temperature. The research was focused on beryllium-doped carbon-based structures.

The second aim of the thesis was to determine the mechanism of oxygen reduction on carbon materials with a quaternary nitrogen. This information is necessary to design optimal structure of the catalyst. Although the reaction mechanism has been described in the literature there is no consensus on the reduction mechanism on the carbons neighboring to the quaternary nitrogen. The following mechanisms for electrochemical oxygen reduction were proposed: two-electron process (less efficient, in an alkaline environment proceeding according to the equation: $O_2 + H_2O + 2e \rightarrow OOH^- + OH^-$) and four-electron (more efficient in alkaline medium leads to the direct reduction of oxygen to hydroxyl anions: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$) as well as a coexistence of both. The discrepancies between proposed mechanisms can be caused by different hydration models used in theoretical calculations. Therefore the effects of the solvent on the mechanism of oxygen reduction, as well as the hydration of reaction products were also a matter of investigations. Good understanding of this mechanism is necessary to design efficient and selective carbon-based catalysts for oxygen reduction reaction which is also an aim of this dissertation.

Obtained results in the field of the carbon-doped beryllium showed that the dimer Be_2 can replace a carbon atom in the structure of carbon materials (including the chemical compounds wherein the carbon have sp^2 hybridization). Such moiety can adsorb one hydrogen molecule with energy of 5-6 kcal/mol. Further functionalization of such structures with hydrogen bond acceptor in the vicinity of Be_2 causes an increase of hydrogen adsorption energy up to two times. Adsorption in such system is

based on the interactions of hydrogen molecule with the metal and at the same time with hydrogen bond acceptor. Such mechanism has not been previously described in the literature and it represents a third method of hydrogen physisorption. The new mechanism of hydrogen adsorption can be used not only in materials with Be_2 fragment but also in the materials doped with other metals. The study showed that appropriate selection of the hydrogen bond acceptor can increase the hydrogen adsorption energy by 50% on lithium centers and by 300 % on magnesium centers.

Investigation on oxygen reduction reaction showed that the mechanism of the process is not particularly sensitive to adopted hydration model (in contrast to what has been postulated in the literature). Described in the literature discrepancies of the oxygen reduction mechanism (two or four electron process) can be explained by the fact that both paths have low energy barriers, and relative energies in both paths are similar. Results presented in the thesis indicate that in the case of carbon materials with quaternary nitrogen even minor changes in hydration model change the reaction barriers. Therefore it is not possible to reliably determine which path would be preferred.

Selectivity of oxygen reduction depends on whether OOH^- or OH^- anion will be dissociated from COOH group attached to the carbon material. Performed calculations lead to the conclusion that selectivity of the process depends not only on the dopant type but also on the conformation of OOH group. The highest selectivity to the desired direct process is obtained on material in which the carbon atom which is bonded to the oxygen (and the group OOH) is connected with two boron atoms and one nitrogen atom.