Synthesis of carbon nanostructures with encapsulated metal nanoparticles and their application as bifunctional oxygen reduction and evolution electrocatalysts

In recent years, we observe rapid development of ubiquitous electronic devices, which must fulfill increasing user requirements, including multifunctionality, wifelessness, and flexibility. Nonetheless, their functionalities are often limited by the properties of available energy sources, i.e. batteries. Zinc-air batteries (Zn-air batteries) are a promising category of energy sources that possess a half-open structure enabling oxygen uptake from the air during discharge and its emission during charge. Therefore, their theoretical capacities are higher than those of lithium-ion batteries. Furthermore, their construction enables the application of flexible air electrodes and solid-state electrolyte, and consequently the formation of flexible Zn-air batteries for application in e.g. wearable electronics.

The bottlenecks in the development of Zn-air batteries are the sluggish electrode reactions that occur during their use. During charge, the oxygen reduction reaction (ORR) occurs, while the oxygen evolution reaction (OER) takes place during discharge. The reactions can be accelerated by application of proper electrode materials, i.e. electrocatalysts, which must exhibit electrocatalytic activity in both ORR and OER. Therefore, currently extensive research efforts are employed to develop a bifunctional electrocatalyst with high activity toward both reactions that will also maintain high performance under working conditions and will be obtained from possibly low-cost raw materials. The research focuses on non-noble metal-based materials, including transition metals: oxides, hydroxides, sulfides, and nitrides. Nevertheless, their application is connected with the risk of material degradation under strongly oxidizing conditions of battery charge, as a result of oxidation of metal species. This fact encouraged interest in considering metal-free materials for this use, particularly carbon materials.

Carbon nanotubes (CNTs) are of particular interest for this application because of their developed surface area, assuring plenty of catalytically active centers, combined with high electrical conductivity. However, recent studies have shown that the exceptional electrocatalytic properties of CNTs might arise from another factor. Their synthesis is usually performed using metal catalysts, residues of which may be present in product materials in the form of metal nanoparticles encapsulated in carbon nanostructures (with concentrations below 1wt%). Both theoretical and experimental studies have shown that metal nanoparticles encapsulated in carbon nanostructures, even at trace concentrations, effectively induce charge redistribution in carbon material, thus forming electrocatalytically active spots and increasing material activity. Furthermore, the carbonaceous capsule prevents leaching of metal nanoparticles, increasing the electrocatalyst stability during battery performance.

Using the effect described above, we intend to obtain bifunctional electrodes for ORR and OER with high electrocatalytic activity, by direct synthesis of CNTs on a flexible carbon cloth support, using different catalysts. The catalysts are expected to perform in a dual role, i.e. conditioning the growth of CNTs with given properties and intentionally becoming an encapsulated species in the obtained CNTs. Due to the application of different catalyst precursors, we expect the formation of CNTs with different physicochemical characteristics (sizes, chemical compositions and structures), as well as encapsulated nanoparticles with different features (sizes, shapes and chemical compositions). Because the CNTs will be directly deposited on the flexible carbon cloth electrode surface, we expect the obtained material to possess excellent electrode-reactants electron transfer and good attachment between the deposited CNTs and carbon cloth. The latter feature is especially crucial in the flexible battery application.

We expect that the studies will enable evaluation of physicochemical properties of both CNTs and encapsulated metal nanoparticles that govern the electrocatalytic performance of obtained electrodes. Furthermore, we hope that the research will lead to better understanding of ORR and OER electrocatalytic phenomena.