

Abstract

In the future, low-temperature proton exchange membrane fuel cells (PEMFC) are expected to compete and eventually replace conventional internal combustion engines in the automotive industry. However, the most vital part of PEMFC - the electrocatalyst - still contains too high quantities of the critical raw material, *i.e.* platinum (Pt). The state-of-the-art approach of lowering the need for Pt as well as improving the sluggish oxygen reduction reaction (ORR) can be achieved by alloying it with other transition metals (preparation of Pt-M; M = Cu, Ni, Co...).

In the first part of the Dissertation, we firstly tackle the stability issue of our previous generation of the PtCu₃/C electrocatalyst *via* doping the crystal structure with gold (Au). In order to bridge the gap between laboratory scale evaluation using thin film rotating disk electrode (TF-RDE) and the industrial membrane electrode assembly (MEA), we have developed a novel approach towards the well-known galvanic displacement (GD) method using so-called “double passivation” mechanism. The method enables preparation of large quantities of high-performance supported Pt-M electrocatalysts which is crucial for faster development and commercialization of PEMFCs. The method is facile, green, energy efficient and highly reproducible. In addition, it offers great flexibility over the catalyst design such as the choice of the sacrificial metal (M), variation of the chemical composition of (Pt:M) alloy, variation of total metal loading (Pt+M) on carbon support or even variation of the carbon support itself.

In the second part, we try to improve the understanding of the developed PtCu₃/C electrocatalyst using advanced characterization tools. For instance, using *in-situ* transmission electron microscopy (TEM) heating, we show that a better understanding of the thermal annealing process can be achieved. On the other hand, using the electrochemical flow cell connected to inductively coupled plasma mass spectrometry (EFC-ICP-MS), one can gain understanding of the similarities and differences of dissolution of metals constituting the alloy (Pt and M). Using the obtained knowledge, we demonstrate a development of a CO-assisted *ex-situ* chemical activation (*ex-situ* CA) method in order to activate the PtCu₃/C electrocatalyst prior to incorporation in the MEA. Lastly, we show that the optimized binary PtCu₃/C electrocatalyst can exhibit a better performance than the conventional Pt/C reference cathode material also in the PEMFC relevant environment.

Keywords: proton exchange membrane fuel cell (PEMFC), oxygen reduction reaction (ORR), Pt-alloys (Pt-M), double passivation, *ex-situ* chemical activation (*ex-situ* CA)