ABSTRACT

The presented doctoral dissertation highlights the importance of the durability of state-of-the-art carbon-supported binary platinum (Pt)-nanoalloy electrocatalysts, used to accelerate a generally sluggish cathodic oxygen reduction reaction (ORR) in a low-temperature proton exchange membrane fuel cell (PEMFC), which is particularly used for the operation of hydrogen-powered vehicles and energy devices. The main focus of the dissertation is the stability of metallic (alloy) nanoparticles (NPs), specifically the stability of Pt and less noble 3d transition metal (M). Using advanced electrochemical characterisation techniques, such as an electrochemical flow cell system coupled to an inductively coupled plasma mass spectrometry (EFC-ICP-MS) and a high-temperature disc-electrode (HT-DE) system, special attention was paid to a fundamental understanding of the metal dissolution phenomena and correlated mechanisms (such as Pt oxide formation/reduction and Pt redeposition) depending on both the operating conditions of the PEMFC and the intrinsic properties of the electrocatalyst itself.

By simulating operating conditions of the PEMFC (i.e. using a temperature of 75 °C and potential windows that simulate both 'operating' voltage window as well as less usual – wider – voltage window of the PEMFC), we first have demonstrated that both temperature and potential/voltage window have a significant impact on the stability of metal NPs of Pt-nanoalloy-based electrocatalysts. In particular, we have shown that the dissolution of the M from Pt-alloy NPs increases with increasing temperature. In addition, we have made an important observation that the rate of Pt redeposition back to the electrocatalyst layer also increases with increasing temperature, thus concealing the actual amount of dissolved Pt. Furthermore, it has been shown that the stability of metal NPs deteriorates more significantly with the widening of the potential window at the close-to-real operating temperature, due to an increased dissolution of both Pt and M. These results have prompted further research aimed at improving the stability of Pt-nanoalloy electrocatalysts under aggressive PEMFC operating conditions by adjusting (i) the operating conditions of the PEMFC as well as (ii) the intrinsic properties, particularly composition and structure of the Pt-nanoalloy electrocatalyst.

Therefore, in continuation, by simulating typical operation of the PEMFC, it has been demonstrated that by narrowing the potential window from 0.6–0.95 V_{RHE} (still mostly used potential/voltage window for the simulation of the electrocatalyst degradation during PEMFC operation) to 0.7–0.85 V_{RHE}, i.e. by adjusting both potential limits, the losses of electrochemically active surface area and specific activity of the electrocatalyst can be significantly reduced. Additionally, whereas the metal dissolution mechanism at both potential windows remained unchanged, narrowing potential window also resulted in a decrease in dissolution of both metals (Pt and M). Furthermore, it has also been demonstrated that the hold time at the upper potential limit (UPL) also has a significant impact on the dissolution of metals from Pt nanoalloys. Namely, it has been shown that a longer hold time at the UPL increases the dissolution of Pt and M due to prolonged formation of Pt oxide, i.e. due to a larger amount of formed oxide. On the other hand, the hold time at the lower potential limit (LPL) has proved to have no significant impact on the dissolution mechanisms of both metals.

Finally, emphasis has been placed on the design of state-of-the-art carbon-supported binary Pt-nanoalloy electrocatalysts. In particular, the effect of crystal structure in correlation with the chemical composition (atomic ratio of Pt to M) on the stability of metallic NPs has been investigated. In this regard, it has been confirmed that enrichment of the crystal structure with an M can improve the electrocatalyst properties (i.e. its intrinsic activity towards ORR) at the beginning of its life, whereas the properties of such an electrocatalyst significantly deteriorate after an accelerated degradation test that simulates PEMFC operating conditions. Nevertheless, it has been further observed that a compromise between activity and stability of a Pt-nanoalloy electrocatalyst rich in an M can be achieved by adjusting the crystal structure. In other words, we have demonstrated that an optimal Pt-to-Co composition, with the presence of a specific ordered intermetallic phase, particularly tetragonal $L1_0$–Pt-Co, can improve the stability of a cobalt-rich Pt-nanoalloy electrocatalyst.

Keywords: *proton exchange membrane fuel cell, oxygen reduction reaction, durability of platinum nanoalloys, operating conditions, intrinsic properties*