Durability of carbon-supported electrocatalysts in alkaline electrolytes for fuel cell applications

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Alkaline fuel cells (AFC) may compete with proton-exchange membrane fuel cells (PEMFC) for stationary or portable applications.[1] The intrinsic stability of many metals and metal oxides at high pH[2] led the scientific community to admit that AFC electrocatalysts should be more stable than PEMFC ones, but it is not the case for carbon-supported Pt and Pd nanoparticles (NPs) aged in liquid alkaline environment: severe electrochemical surface area losses are observed upon mild accelerated stress tests in 0.1 M NaOH[3,4] (Figure). Pronounced detachment of the Pt (and Pd) NPs from the carbon support occurs, but minor degradation of the metal NPs and of the carbon support are observed by identical-location transmission electron microscopy (ILTEM). Additional experiments performed in various alkaline electrolytes (LiOH, NaOH, KOH, CsOH) coupled with in situ Fourier-transform infrared spectroscopy linked this detachment to the formation of solid carbonates at the interface between the Pt (Pd) NPs via carbon support corrosion: in essence, the Pt (Pd) NPs do locally catalyze the carbon support corrosion (firstly carbon surface oxides groups are formed, then evolve into CO2, which leads to the formation of carbonate anions in alkaline environment and finally to metal carbonate precipitation, M2CO3, M = Li, Na, K or Cs).[5]

The loss of Pt NPs is mitigated for solid alkaline electrolytes (anion-exchange membrane), because the counter-cation of the OH- species are immobilized on the polymer backbone and cannot lead to precipitation into M2CO3, which happens in MOH aqueous electrolytes. This minor degradation of the Pt/C NPs in AEM electrolytes does not mean that no degradation processes are at stake, though: Ostwald ripening and Pt redeposition are observed. This means that the nature of the predominant mechanisms of degradation differ in solid versus liquid alkaline environment, which had also been demonstrated for solid versus liquid acidic electrolytes.[6,7] Finally, it will be shown that these degradations are not unavoidable; non-noble electrocatalysts (e.g. Ni-based) prove much more resistant to corrosion in alkaline environments,[8] and should therefore be more durable in AFC applications.

References