The influence of chloride impurities on Pt/C fuel cell catalyst corrosion

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Introduction

Despite great efforts in the search for viable catalysts during past years, platinum based electrocatalysts supported on carbon remain the most realistic option for the manufacture of low temperature fuel cells. These catalysts can reach high enough activities per unit price; however, a serious concern of platinum stability still retards a wide platinum-based proton exchange membrane fuel cell (PEMFC) commercialization [1,2]. On the other hand, this "instability" can be seen as an opportunity in the process of refining (recycling) of platinum from the used catalysts [3]. To this end, potentiodynamic Pt/C fuel cell catalyst corrosion has been studied.

Materials and Methods

Potentiodynamic Pt/C (cycled from 0.05 V to 1.4 V with 5 mV s⁻¹ in 0.1 M HClO₄) fuel cell catalyst corrosion has been carried out as a function of chloride concentration with an electrochemical flow cell (EFC) coupled with a highly sensitive inductively coupled plasma mass spectrometer (ICP-MS). We chose a commercial catalysts consisting of ca. 3 nm Pt nanoparticles deposited on a high surface area carbon Vulcan XC72 with a metal loading of 28.6 wt% (supplier: De Nora Tecnologie Elettrochomiche S.p.A. (DNTE) (IT)). In continuation all electrode potentials are given relative to the reversible hydrogen electrode (RHE). Using the present special setup EFC-ICP-MS [4,5] the corrosion could be followed with a resolution on the ppb scale (Fig. 1-2).

Results and Discussion



Figure 1. a) Mass of dissolved Pt per cycle vs. Cl⁻ concentrations. Column labels denote increase in Pt dissolution relative to the Cl⁻ free electrolyte; b) Potential-resolved potentiodynamic Pt ICP-MS response plotted against Pt cyclic voltammetry response on Pt/C (3 nm) at different chloride concentrations.

From Fig. 1 and 2 it can be seen that the increase in chloride concentration promotes the overall platinum dissolution. Importantly, even very small amounts of chloride, such as 10^{-6} M (36 ppb), induce a substantial (21%) increase in platinum dissolution (Fig. 1).

Increasing the chloride concentration also markedly lowers the dissolution potential of platinum in 0.1 M HClO₄, as seen from the progressive shift of the curves in Fig. 2b to the left. We have found that the corrosion potential shifts from ca. 1.23 V in chloride-free solution to ca. 1.0 V and 0.82 V at chloride concentrations of 10^{-4} M and 10^{-2} M, respectively.

A closer inspection of Fig. 2a reveals that the rate of anodic corrosion (the left peak) increases much faster with addition of Cl⁻ than cathodic corrosion – the right peak. One might say that whereas the presence of chlorides suppresses to some extent the cathodic corrosion (see also Fig. 1), it at the same time induces another type of Pt corrosion, namely the classical thermodynamic dissolution mechanism (also referred to as the anodic corrosion) which is insignificant in the absence of chlorides.



Figure 2. a) Time-resolved potentiodynamic Pt ICP-MS response at different Cl concentrations vs. time. b) Close-up of start potentials of Pt dissolution.

Significance

It was shown that chloride affects the platinum corrosion in three ways. First, it lowers the platinum dissolution potential. Secondly, it increases the overall amount of dissolved platinum. And thirdly, the presence of chloride changes importantly the dissolution profile: it enhances much more the anodic dissolution than the cathodic corrosion that strongly prevails in the CI⁻ free electrolyte.

References

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