New insight into platinum dissolution from nanoparticulate Pt-based electrocatalysts using highly sensitive in-situ concentration measurements

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Introduction

In PEM fuel cells, the activity has not only reached but even markedly surpassed the DOE 2015 targets. Now the challenge remains to increase their stability^[1]. In this respect understanding the dominant mechanisms of electrochemical surface area loss such as electrochemical dissolution of platinum or alloy nanoparticles is of vital importance ^[2]. We here present a new method for the investigation corrosion of Pt and Pt alloy nanoparticles under potentiodynamic regime by coupling an electrochemical flow cell to inductively coupled plasma mass spectrometry (ICP-MS). This new method provides remarkable sensitivity and new insights in to Pt dissolution.

Materials and Methods

Electrochemical flow cell was coupled with an ICP-MS instrument for in-situ concentration measurements. Three samples were investigated: two commercial Pt nanoparticulate samples (with average particle size about 3 and 30 nm and an in-house produced highly active nanoparticulate PtCu alloy system (particle size between 5 and 50 nm). The catalyst thin films were prepared by drop casting the suspension of well-dispersed catalyst on glassy carbon electrodes ^[4].

Results and Discussion

Fig. 1 shows the results of basic experiments using the coupled technique on nanoparticulate Pt-based material. The main features are similar to those found on polycrystalline $Pt^{[3]}$. If the upper potential in a CV experiment is gradually raised from 0.9 V to 1.6 V vs. RHE, an increasing platinum dissolution can be observed (Figure 1a). With increasing the upper potential two peaks can be observed (Figure 1a), the smaller one evolving in the anodic and the bigger one in the cathodic scan (Figure 2). A direct comparison of CVs and platinum dissolution profile (Figure 1c) shows that cathodic corrosion peak appears during reduction of irreversibly formed oxide, a process which presumably weakens the Pt-Pt bonds by roughening the surface causing Pt to detach ^[3]. A comparison of samples with different particle size reveals that Pt dissolution is increasing with decreasing particle size (Figure 2). It seems as if the particle size determines decisively not only the extent of Pt dissolution in the cathodic scan but also the potential at which this dissolution a prograd PtCu alloy with a broad particle size distribution (5–50 nm); in this sample the Pt dissolution peak seems to reveal combined features of those seen in the 3-nm and the 30-nm Pt samples.



Figure 1. An experimental regime used on all samples, b is a magnification at the upper potential limit of 1.6 Vvs. RHE (revesible hydrogen electrode).



Figure 2. ICP-MS responses with corresponding cyclic voltammograms at the potential upper limit of 1.6 V for all three types of catalyst. Black dashed vertical line shows the position of maximum of dissolution profile for polycrystalline Pt from ref [3].

Significance

The highly sensitive and accurate results obtained by ICP-MS clearly indicate that Pt corrosion depends markedly on particle size. This findings together with new insights accessible with the method used in our work will trigger vigourous research of the actual mechanism of Pt-based and other catalysts. This will have a profound impact for a rational design of low temperature fuel cell.

References

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