On-Line ICP-MS in Electrocatalysis Research: Platinum Dissolution Studies

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Abstract. The degradation of electrocatalysts as a consequence of their dissolution in the operating conditions of fuel cells and electrolyzers remains one of the main challenges in electrochemical energy conversion. In order to investigate and predict the kinetics of dissolution of electrocatalysts in real conditions, the electrochemical on-line inductively coupled mass spectrometry (ICP-MS) technique was developed. This approach is employed in electrocatalysis research as a tool for enabling the detection of dissolved elements in the electrolyte going down to the parts-per-trillion (ppt) range and providing at the same time multielement analysis and a wide linear dynamic range of quantification. In this way, on-line ICP-MS has been successfully applied for fundamental studies of noble metal dissolution, and the previous works related to the particular case of platinum are revised in the present chapter.

Keywords: Dissolution · Stability · Platinum · Inductively coupled plasma mass spectrometry · Scanning flow cell · Fuel cell

1 On-Line Inductively Coupled Plasma Mass Spectrometry in Electrochemistry

The degradation of electrocatalysts as a consequence of their dissolution in the operating conditions of fuel cells and electrolyzers remains one of the main challenges in electrochemical energy conversion. In order to investigate and predict the kinetics of dissolution of electrocatalysts in real conditions, the electrochemical on-line inductively coupled mass spectrometry (ICP-MS) technique was developed [1]. This approach is employed in electrocatalysis research as a tool for enabling the detection of dissolved elements in the electrolyte going down to the parts-per-trillion (ppt) range and providing at the same time multielement analysis and a wide linear dynamic range of quantification. In this way, on-line ICP-MS has been successfully applied for fundamental studies of noble metal dissolution [2, 3] and for the investigation of several electrocatalytic reactions such as oxygen and hydrogen evolution reactions (OER and

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HER) [4, 5], hydrogen oxidation reaction (HOR) [6], and oxygen reduction reaction (ORR) [7]. Among the different ways for connecting the ICP-MS to an electrochemical cell, the scanning flow cell coupled to the ICP-MS (SFC-ICP-MS), in which the outlet of a V-shaped SFC is directly hyphenated to the sample introduction system of ICP-MS, stands out for its ability to screen stability and high-throughput activity of gradient composition libraries [8].

2 On-Line ICP-MS in Platinum Stability Studies

Fuel cell cars use polymer electrolyte membrane fuel cells (PEMFCs) with Pt nanoparticles for ORR at the cathode, primarily because of their better long-term stability in comparison to other electrocatalysts. However, even pure Pt catalysts degrade under real-life conditions, and this degradation is mainly linked to electro-oxidation and dissolution processes. Polycrystalline platinum dissolution was studied in both acidic and alkaline media by SFC-ICP-MS, and it was observed that the oxidation and subsequent reduction of the surface lead to transient dissolution, which is higher by a factor of two in base [9]. In addition, the results suggested that varying the pH does not modify the mechanism of the OER on Pt, since its dissolution rate is the same in acidic and alkaline solutions. More recently, investigations with Pt single-crystal electrodes have been carried out, which offer the possibility of a more detailed understanding of these processes at the atomic level [10]. These studies have shown clear trends in the onset potential for dissolution and the amounts of dissolved Pt that can be correlated to the differences in the surface structure energies and coordination of the different well-defined surfaces. In this way, Pt(111) resulted to have a more positive onset potential for dissolution, and the generalized observed trend in dissolution rates and dissolved amounts was Pt(110) > Pt(100) > Pt(111).

The dissolution results for Pt single-crystal electrodes from on-line ICP-MS can be combined with in situ surface X-ray diffraction (SXRD) measurements, and by following this approach, it was proposed that the differences in the onset potential for anodic dissolution on Pt(100) and Pt(111) have their origin in the different atomic structures of the initial oxide [11]. On Pt(111), the extracted Pt atom lies directly above its original site, and therefore the reversibility observed at low coverage is explained in terms of its facile return to that site. However, on Pt(100), the extracted Pt atom moves laterally away from its initial site and provokes the immediate extraction of a second atom, leading to the formation of a stripe structure. According to Density Functional Theory (DFT) studies, this mechanism would produce unstable surface atoms at strip ends that could dissolve both during the oxidation itself and during the subsequent oxide reduction, making the process irreversible from its onset. More recently, potentiostatic hold experiments for Pt(100) and Pt(111) have been carried out. This program allows separating the anodic and cathodic dissolution peaks and studying oxidation and dissolution kinetics versus time. The fundamental knowledge obtained from model bulk electrodes will contribute to delve into the understanding of restructuring and dissolution processes of Pt, which ultimately will provide guidelines for minimizing Pt catalyst degradation, both in half-cell aqueous electrolyte and fuel cell environment.

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