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## COMMUNICATION

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

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A. Pavlišič,<sup>a</sup> P. Jovanovič,<sup>a</sup> V. S. Šelih,<sup>b</sup> M. Šala,<sup>b</sup> N. Hodnik,<sup>c\*</sup> S. Hočevar<sup>b</sup> and M. Gaberšček<sup>a\*</sup>

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**Potentiodynamic Pt/C fuel cell catalyst corrosion has been studied as a function of chloride concentration with an electrochemical flow cell (EFC) coupled with highly sensitive ICP-MS. The Pt corrosion mechanism changes significantly: the anodic corrosion is much enhanced compared to the cathodic corrosion that prevails in electrolytes without Cl<sup>-</sup>.**

Despite great efforts in 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.<sup>1,2</sup> On the other hand, this “instability” can be seen as an opportunity in the process of refining (recycling) of platinum from the used catalysts.<sup>3</sup>

The recent introduction of a new advanced characterization technique – the electrochemical flow cell (EFC) directly coupled to an inductively coupled plasma mass spectrometer (ICP-MS)<sup>4</sup> – has enabled completely new insights into Pt dissolution mechanism. For example, Topalov et. al.<sup>2,5</sup> showed that at potentiostatic conditions (as high as 1.8 V) platinum dissolution is minimal due to extensive surface oxide formation (passivation). By contrast, under potentiodynamic conditions the corrosion of platinum is severe. However, quite surprisingly, platinum is predominantly dissolving through the process of cathodic corrosion (when going from positive to negative potentials)<sup>2,5</sup> and not *via* an anodic dissolution mechanism as normally expected in corroding systems. In our recent report,<sup>6</sup> we have found that this unusual mechanism does

not only hold for bulk Pt, but is clearly dominating in nanoparticulate Pt as well. Even more, a particle size dependence of Pt dissolution has been found whereby larger particles tend to dissolve significantly slower.<sup>6</sup>

Chloride is an important fuel cell contaminant that enters the cell through airborne salts or *via* catalyst precursors (hexachloroplatinate) during the synthesis processes.<sup>7</sup> Chlorides have been found to block the platinum surface thus affecting the electrocatalytic adsorption characteristics and, consequently, the activity of Pt based electrocatalysts.<sup>8-11</sup> On the other hand, chloride promotes platinum corrosion,<sup>12</sup> especially under potential cycling conditions.<sup>7,13</sup> The platinum that is dissolved during corrosion can then redeposit inside the PEMFC membrane<sup>14</sup> or on the top of catalyst film, as demonstrated in ex-situ RDE experiments.<sup>15</sup>

In this work we show, for the first time, that chloride not only enhances the corrosion rate but essentially changes the corrosion mechanism if compared to non-chloride environment. It has been shown that chloride affects the cathodic and anodic type of corrosion in a substantially different way. It should be noted that already ppb levels of chloride have a noticeable effect on the overall corrosion rate.

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 Technologie Elettrochimiche S.p.A. (DNTE) (IT)) shown in Figure S1 in supporting information. This is one of the most studied electrocatalysts and also serves as a benchmark for most PEMFC measurements. Thus our results are directly comparable with many reports. In continuation all electrode potentials are given relative to the reversible hydrogen

electrode (RHE). The main objective was to study the effect of the presence of  $\text{Cl}^-$  anions in different concentrations on the corrosion of nanoparticulate Pt under potentiodynamic conditions. Using the present special setup EFC-ICP-MS (more experimental details in supporting info) the corrosion could be followed with a resolution on ppb scale (Figs. 1, 2 and 3).

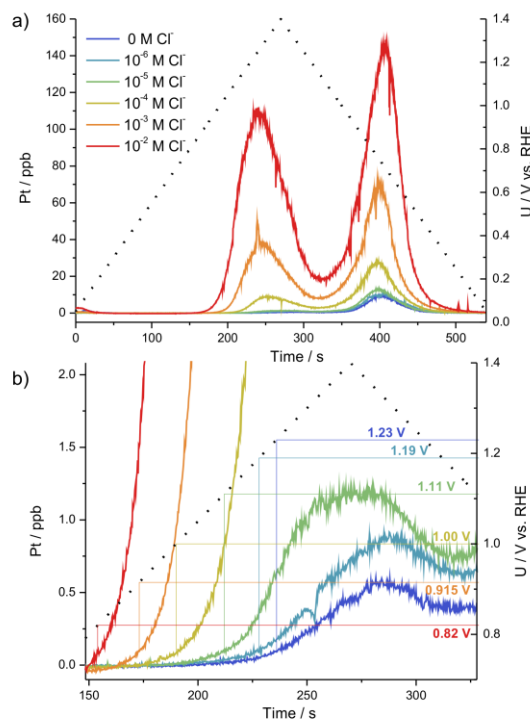


Figure 1: a) Time-resolved potentiodynamic Pt ICP-MS response (cycling between 0.05 V and 1.4 V vs. RHE with 5 mV/s in 0.1 M  $\text{HClO}_4$ ) Pt dissolution profile at different  $\text{Cl}^-$  concentrations (from 0 to  $10^{-2}$  M). b) Close-up of start potentials of Pt dissolution.

From Figs. 1a, 2 and 3 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. 2). The pronounced effect of chloride is not surprising since it is known that platinum dissolves in highly oxidative environments in the presence of chlorides. For example, in aqua regia ( $\text{HNO}_3/\text{HCl}$ ) the nitric acid oxidizes platinum to  $\text{Pt}^{4+}$  whereas  $\text{Cl}^-$  forms a stable platinum complex – hexachloro-platinate ( $[\text{PtCl}_6]^{2-}$ ).

Increasing the chloride concentration also markedly lowers the dissolution potential of platinum in 0.1 M  $\text{HClO}_4$ , as seen from the progressive shift of the curves in Figure 1b to the left. From such curves it is difficult to establish the precise value of corrosion potential. In our case we chose to read the “corrosion potential values” from the constant value of signal of 0.1 ppb, which is just above the detection limit. Using such an approach, 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. The values for these and other concentrations are displayed in Fig. 1b.

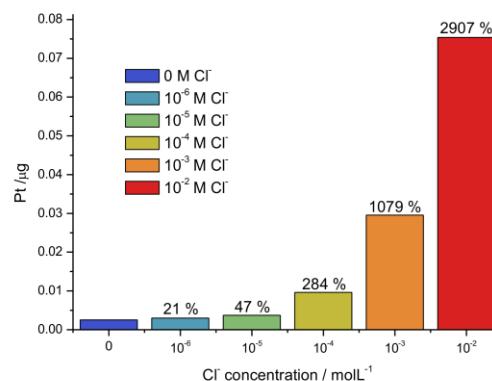


Figure 2: Mass of dissolved Pt per cycle (with the potential upper limit of 1.4 V) plotted against the  $\text{Cl}^-$  concentrations. The percentages on top of the columns are how much more platinum dissolves relative to  $\text{Cl}^-$ -free electrolyte.

In Figure 3 platinum dissolution profiles are shown in conjunction with the corresponding cyclic voltammetry responses. The retardation of the platinum oxide formation and the corresponding shift of reduction peak with increasing chloride concentration are marked with black arrows. Both are a consequence of a strong passivation of Pt surface with  $\text{Cl}^-$  which affects the oxide formation.<sup>8,9</sup> In this sense it might seem surprising that the presence of chloride increases the Pt dissolution. Namely, it has recently been shown that the rate of cathodic corrosion is directly proportional to the amount of surface oxide formed (i.e., the more Pt oxide is formed the more platinum gets dissolved – “oxide assisted corrosion”).<sup>2,5,6</sup> However, the chloride interacts strongly with Pt surface and Pt ions. On the surface it presumably blocks and therefore reduces the amount of available platinum sites for Pt redispersion,<sup>16</sup> whereas in the solution it stabilizes the Pt ions and increases Pt solubility. Therefore there is less Pt “oxide-assisted” and much more “chloride-assisted” corrosion.

A closer inspection of Figure 1a reveals that the rate of anodic corrosion (the left peak) increases much faster with addition of  $\text{Cl}^-$  than cathodic corrosion - the right peak (a quantitative analysis is given in Fig. S2 in Supp. Info). One might say that whereas the presence of chlorides suppresses to some extent the cathodic corrosion (see also Fig. 3), 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 absence of chlorides. For example, in a  $\text{Cl}^-$ -free electrolyte the cathodic corrosion is dominant<sup>2,5</sup>; Fig. S2 reveals that the platinum released in the anodic way only represents 5 % of the amount released in the cathodic direction. By contrast, at highest chloride

concentration ( $10^{-2}$  M) both anodic and cathodic corrosions become comparable. Enhancement of anodic corrosion has been reported for other systems, such as polycrystalline gold dissolution in  $\text{Cl}^-$ -free electrolyte where at high potentials ( $>1.8$  V) the anodic dissolution becomes dominant.<sup>17</sup>

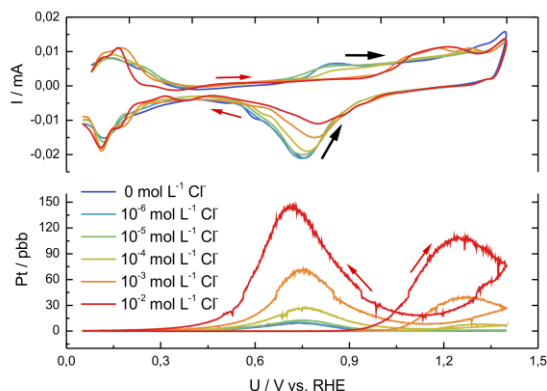


Figure 3: Potential-resolved potentiodynamic Pt ICP-MS response (cycling between 0.05 V and 1.4 V vs. RHE with 5 mV/s in 0.1 M  $\text{HClO}_4$ ) plotted against Pt cyclic voltammetry response on Pt/C (3 nm) at different chloride concentrations (from 0 to  $10^{-2}$  M).

In the anodic direction there are two factors that have important influence on the corrosion enhancement. First, in the presence of  $\text{Cl}^-$  platinum starts to dissolve already at 0.8 V in  $10^{-2}$  M  $\text{Cl}^-$  (see Fig. 1b), much sooner than in the chloride-free solutions (1.23 V). Second, at potentials above 1.1 V chloride retards the formation of Pt oxide, so Pt continues to dissolve at a significant rate. In the cathodic scan there is less oxide, which also means less “oxide-assisted” cathodic type of corrosion and more “chloride-assisted” cathodic type of corrosion (Pt ions stabilized together with blocked Pt surface and less Pt redeposition). Thus, the overall mechanism in the presence of chloride is quite different than in the  $\text{Cl}^-$ -free solution where more or less only “oxide-assisted cathodic corrosion mechanism” is responsible for the Pt removal.<sup>2, 5, 17</sup>

Interestingly, in the potentiostatic experiment the final corrosion behaviour seems to be similar, regardless of the absence or presence of chloride. This can be seen in Figure S3 where during progressive potentiostatic pulses the concentration of Pt in solution is slowly reaching a certain low, steady state number which is more or less the same regardless of the presence or absence of  $\text{Cl}^-$ . Additionally, Figure S3 a and b reveals that the potentiostatic stress test is much less damaging (less Pt gets removed) than the potentiodynamic test - with or without the presence of  $\text{Cl}^-$ , which is consistent with the literature.<sup>2, 5, 13</sup>

In conclusion, a combination of cyclic voltammetry, flow system and on-line ICP-MS platinum concentration measurements (EFC-ICP-MS) used to study the potentiodynamic corrosion of commercial Pt/C electrocatalyst

in perchloric acid in the presence of  $\text{Cl}^-$ . 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  $\text{Cl}^-$ -free electrolyte.

## Notes and references

<sup>a</sup> Laboratory for Materials Chemistry, National Institute of Chemistry Hajdrihova 19, 1000 Ljubljana, Slovenia.

<sup>b</sup> Analytical Chemistry Laboratory, National Institute of Chemistry Hajdrihova 19, 1000 Ljubljana, Slovenia.

<sup>c</sup> Laboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry Hajdrihova 19, 1000 Ljubljana, Slovenia.

Electronic Supplementary Information (ESI) available: [Experimental description, TEM picture of Pt/C, quantitative analysis of anodic and cathodic Pt pack concentrations at different  $\text{Cl}^-$  concentrations and potentiostatic experiment]. See DOI: 10.1039/c000000x/

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