

Tolerance effect by tuning substrate and catalysts centers entities

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Currently, one of the most important challenges for PEMFCs in terms of facilitating their widespread commercial use is to improve the performance and durability of the electrocatalyst by developing novel catalyst-support materials. In this context, a variety of carbon-based materials such as carbon nanotubes (CNT), graphite (HOPG), and graphene as well as non-carbonaceous based materials, such as oxides (Titania, tungsten oxide, etc.) can be used as catalyst support materials. Among them, graphitic carbon is a considerable choice due to its remarkable stability and electronic properties (1, 2). To understand this complex interplay, a series of Pt/carbon electrocatalysts using original chemical synthesis route, namely the carbonyl and photo-deposition methods, respectively, were used. The method of deposition is responsible for a controlled heterogeneous nucleation of metal nanoparticles onto different domains of the substrate's surface, e.g., carbon. One such an example is summarized and contrasted in figure 1.

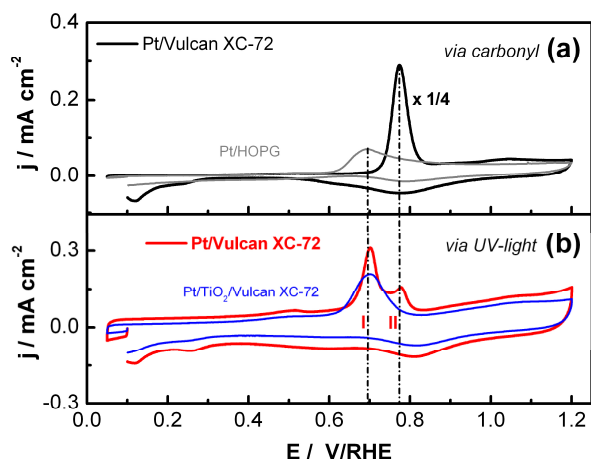


Figure 1. CO-stripping in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C with 5 mV s<sup>-1</sup> for Pt-based electrocatalysts generated via carbonyl (a), and photodeposition (b).

The one-metal center is deposited via carbonyl onto carbon and onto HOPG. The CO stripping in figure 1(a) is different. The coupling of UV-light (photodeposition) to perform a similar process onto carbon and onto a composite made of oxide-carbon results on the carbon Vulcan XC-72 as the sum of the process depicted in figure 1(a). This simple experimental approach reveals that the one-metal center interacts with the substrate differently. This phenomenon is supported by the effect observed of platinum onto the oxide sites of the composite (3, 4). This phenomenon is at the origin of an increase of CO tolerance of the catalyst with positive influence onto the oxygen reduction reaction (ORR). As a result of such interaction, between platinum and well-ordered graphitized domains of carbon-based supports, it is possible that the charge transfer occurs from Pt to C (according to the respective electronegativities of the elements) leading to a decrease in the *d*-orbital back-donation and consequently to a weakening of the Pt-CO bond. X-ray photoelectron spectroscopy (XPS) and in-situ

FTIR point out to a similar phenomenon. We thus arrive at the conclusion that a strong interaction can be observed between graphitic domains of carbonaceous supports and platinum NPs induced by the UV irradiation, as shown in Figure 1(b).

In this work, we will focus on the catalytic oxidation of CO, the selectivity and the tolerance towards small organics during oxygen reduction reaction (ORR). The results will be described in terms of physical-chemical interaction between the metal center and the support for tailoring the catalytic activity and the tolerance of electrocatalysts.

1. F. Hasche, M. Oezaslan and P. Strasser, *Phys. Chem. Chem. Phys.*, **12**, 15251 (2010).
2. J. Ma, A. Habrioux, N. Guignard and N. Alonso-Vante, *J. Phys. Chem. C*, **116**, 21788 (2012).
3. L. Timperman and N. Alonso-Vante, *Electrocatalysis*, **2**, 181 (2011).
4. B. Ruiz Camacho, C. Morais, M. A. Valenzuela and N. Alonso-Vante, *Catal. Today* (2012) <http://dx.doi.org/10.1016/j.cattod.2012.03.033>.