

Effect of the reductive treatment on the state and electrocatalytic behavior of Pt in catalysts supported on $\text{Ti}_{0.8}\text{Mo}_{0.2}\text{O}_2\text{-C}$ composite

*Cristina Silva**, Zoltán Pászti, Irina Borbáth, Kristóf Zelenka, András Tompos

Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences,
Eötvös Loránd Research Network (ELKH), Budapest, Hungary
*E-mail: flakcriss45@gmail.com

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$\text{Ti}_{(1-x)}\text{Mo}_x\text{O}_2$ -carbon composites are promising new supports for Pt-based electrocatalysis in Polymer Electrolyte Membrane fuel cells offering exciting catalytic properties and enhanced stability against electrocorrosion as a result of the interplay between the dopant, the oxide and the carbon backbone [1]. Pt and the mixed oxide form a couple liable for strong metal-support interaction (SMSI) phenomenon, generally manifesting itself in decoration of the metal particles by ultrathin layers of the support material upon annealing under reductive conditions. The aim of this work is to evaluate the SMSI phenomenon as a potential strategy [2] for tailoring the properties of the electrocatalyst in terms of stability and reactivity.

A 20 wt.% Pt/50 wt.% $\text{Ti}_{0.8}\text{Mo}_{0.2}\text{O}_2$ -50 wt.% C electrocatalyst prepared on Black Pearls 2000 carbon functionalized with HNO_3 and glucose was reduced at 250 °C in H_2 in order to induce SMSI. The electrocatalytic properties and the stability of the reduced and the original catalysts were analyzed by cyclic voltammetry and CO_{ads} stripping voltammetry. X-ray photoelectron spectroscopy (XPS) measurements combined with *in situ* H_2 exposure experiments were performed on the reduced catalyst in order to obtain information about the details of the interaction between the oxide and the Pt particles.

The electrochemical experiments pointed out a small loss of the electrochemically active surface area (ECSA) of Pt with respect to the original catalyst, while XPS suggested only a minimal decrease of the Pt dispersion. At the same time, hydrogen exposure experiments combined with XPS on the reduced catalyst demonstrated the presence of a Mo species very easily reducible to the metallic state, which was interpreted as Mo directly adsorbed on the Pt surface [1]. No such behavior was observed for Ti. Accordingly, even if Mo remains support-bound in the original catalyst [1], the reductive treatment at 250 °C is enough to induce a partial encapsulation of the Pt particles with a Mo-containing overlayer, which explains the decrease of the electrochemically active surface area (ECSA). In addition, enhanced stability of the reduced catalyst was demonstrated by 10,000-cycle stability test.

In conclusion, the results of this preliminary study confirmed that utilization of the SMSI phenomenon can indeed be a valuable approach for improving the stability of the mixed oxide – carbon composite supported electrocatalysts.