

THE EFFECT OF METAL OXIDE-CARBON SUPPORT ON ELECTROCATALYSTS FOR FUEL CELL REACTIONS

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Introduction

Nanocatalysts for fuel cell reactions are supported on Vulcan XC-72 carbon, which is one of the most popular substrates for cathode and anode technical electrodes. There is still great interest in modifying its surface in order to cope with chemical instabilities^{1,2} or finding other substrates that avoid corrosion and agglomeration phenomena. Modification of carbon nanotube (CNT) has also been undertaken.^{3, 4, 5} Another route to stabilize nanoparticles is the development of metal-oxide composite supports, e.g., titania-carbon.^{6, 7} Indeed, Pt deposited on such substrates showed an increase of the activity for the oxygen reduction reaction (ORR) as well as thermal stability as compared to Pt/C.⁶ Summing up, enhancement, and stability are the main key issues.⁸ An improvement of tolerance towards carbon monoxide,^{9, 10, 11} and methanol is desired.^{12, 13, 14} Fuel cell performances were also improved according to the activity increase for ORR of the cathode and tolerance to small organics.

In this communication we discuss the influence of metal cations of high energy-gap oxide semiconductors toward the oxygen reduction reaction. Further, the adsorbed carbon monoxide probes the electronic state of platinum, solely deposited onto the oxide sites of the oxide-carbon composites.

Experimental

Materials

The synthesis of composites M-Oxide/C (M = Ti, Sn) was prepared via the sol-gel route as described in ref.¹⁵ The carbon Vulcan XC-72 (200 mg) was ultrasonically stirred with propan-2-ol ("isopropanol") for 2 h. The desired amount of metal oxide chemical isopropoxide precursor was added to the carbon containing suspension, and stirred for 1 h. Water was finally added, in excess, to hydrolyze the corresponding metal isopropoxide to TiO₂ (anatase), and SnO₂ (cassiterite).

Apparatus and Procedures

The electrochemical measurements were performed at 25°C, using a potentiostat in a thermostated three-electrode cell. A plate of glassy carbon (GC) served as counter electrode, and a reversible hydrogen electrode (RHE) connected to the working electrode compartment through a Luggin capillary, in 0.5M H₂SO₄ aqueous solution electrolyte, as the reference electrode. A GC rotating disk electrode (0.07cm² geometric surface area) was used as a working electrode where the catalytic powders were deposited from inks, which were prepared by mixing 10 mg of catalyst (e.g., 10 wt% Pt/C and 10 wt% Pt/Oxide/C) in 0.25 mL Nafion® (5 wt% in water/

aliphatic alcohol solution (Aldrich)) and 1.25 mL ultra pure water, in an ultrasonic bath for 1 h. 3μL of the catalyst ink were deposited onto the glassy carbon electrode and dried under nitrogen atmosphere.

Results and Discussion

Figure 1 summarizes the results of the CO stripping of Pt-C (curve 1), Pt-SnO₂-C (curve 2) and Pt-TiO₂-C (curve 3) catalysts in sulphuric acid. The loading of Pt for each system is 10wt%, and the content of the oxide is 5wt%. The current intensity and the electrode potential position of the oxidation

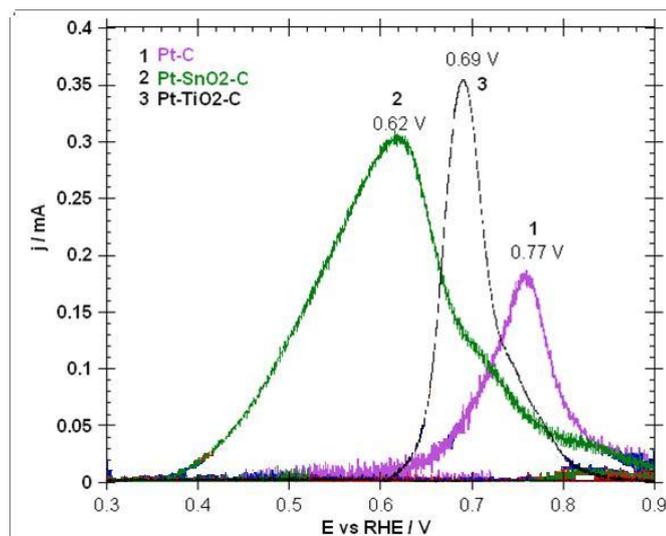


Figure 1. CO oxidation peak on (1) 10 wt% Pt/C, (2) 10 wt% Pt/5 wt% SnO₂/C, and (3) 2) 10 wt% Pt/5 wt% TiO₂/C.

peak put in clear evidence the platinum electronic modification, as well as the number of catalytic sites involved, since the surface of each curve delivers the electrochemical active surface area (EAS). Such electronic modification was recently revealed via XPS measurements.¹⁶ The distinction of the peak potential shifted to negative values is due to the fact that platinum nanoparticles are selectively deposited onto the oxide of the oxide-carbon composites. This process, as described in previous works, is induced by the photo-generated electron-hole (e-h) pairs on the oxide with an energy $E > E_g$.¹⁵

These catalyst materials were evaluated for the oxygen reduction reaction (ORR) in sulphuric acid. Figure 2 shows the resulting RDE current-potential curves for (1) 10 wt% Pt/C, (2) 10 wt% Pt/5 wt% SnO₂/C, and (3) 10 wt% Pt/5 wt% TiO₂/C. One observes clearly, in the activation region, the shift toward a positive electrode potential, and therefore the kinetic enhancement of Pt sites onto oxide-carbon composites.

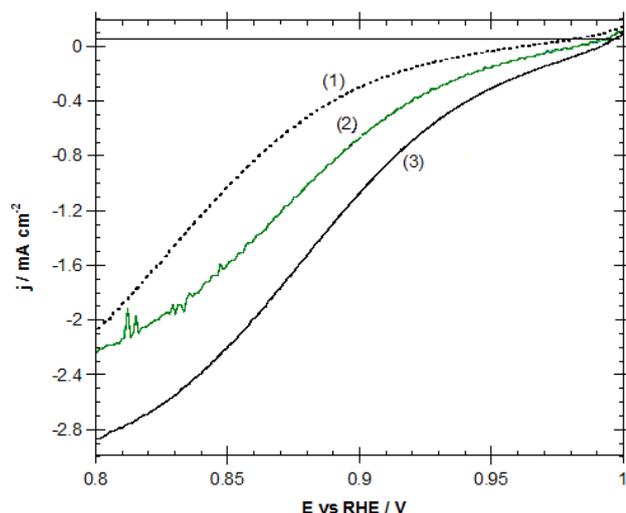


Figure 2. RDE current-potential curves for ORR in oxygen saturated electrolyte H₂SO₄ 0.5M at 900 rpm on (1) 10 wt% Pt/C, (2) 10 wt% Pt/5 wt% SnO₂/C, and (3) 10 wt% Pt/5 wt% TiO₂/C.

Taking into account the EAS determined via CO stripping, one can evaluate the specific activity of platinum enhancement at, e.g., 0.9V. We note that an enhancement of the kinetic current, which is 143 $\mu\text{A cm}^{-2}_{\text{Pt}}$ for 10 wt% Pt/5 wt% SnO₂/C, and 95 $\mu\text{A cm}^{-2}_{\text{Pt}}$ for 10 wt% Pt/5 wt% TiO₂/C, whereas Pt/C is ca. 31 $\mu\text{A cm}^{-2}_{\text{Pt}}$. Therefore, the ORR activity for oxide-carbon supported Pt is higher by a factor of 3 – 4.5 than the home-made Pt/C.

Conclusion

The present work strongly suggests that the deposited platinum, selectively via a photo-process, modifies the electronic structure and probably the nature of the platinum in intimate contact with the metal of the oxide leading to the so-called SMSI-strong metal substrate interaction. This is positive, since it paves the way to improve the electrocatalytic activity as well as the chemical stability of the active sites.

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