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Pt/SnO$_x$-C composite material for electrocatalysis

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The Pt/SnO$_x$-C composite material was obtained by an electrochemical dispersion method, and a good catalytic activity of this material in the electrochemical oxidation of CO has been demonstrated.

Nanosized carbon-supported platinum (Pt/C) catalysts are good catalytic materials for proton exchange membrane fuel cells (PEMFCs). The efficiency of a PEMFC is determined by the system parameters: polymer membrane stability under fuel cell operation conditions, good water and heat management, high catalytic activity and stability of Pt/C catalysts. Meantime, these catalysts can be poisoned with CO, which always occurs in hydrogen generated by the steam reforming of light hydrocarbons. The presence of CO traces in hydrogen leads to an increase in the anode overvoltage and a decrease in the PEMFC power density. Thus, enhancing the resistance of platinum catalysts to carbon monoxide is a challenge of considerable current interest for PEMFC technology.

The chemisorption of carbon monoxide on platinum irreversibly occurs in a wide range of potentials, and CO can be removed from the platinum surface only by oxidation which proceeds *via* the Langmuir–Hinshelwood mechanism.[1] However, the adsorption of oxygen-containing species on platinum starts at relatively high potentials $E \geqslant 0.6$ V (RHE).[2] Therefore, if the adsorption potential of the oxygen-containing species is lower, the oxidation potential of adsorbed CO$_{\text{ad}}$ can decrease. For this purpose, metals that adsorb oxygen better than platinum are introduced into the catalyst.[3–5]

Tin has a good oxygen adsorption capacity, and it can be introduced into the catalyst system as adatoms,[6] platinum–tin alloy[7] or tin oxide which serves as a support for platinum nanoparticles.[8] We used this approach for the preparation of a Pt/SnO$_x$-C catalyst.

Nanocrystalline tin oxides are currently produced by hydrothermal and sol-gel methods.[9] Then, tin oxide is introduced into a carbon support with the subsequent deposition of platinum nanoparticles onto the SnO$_x$-C support to obtain the Pt/SnO$_x$-C catalyst.

In this work, we used the electrochemical oxidation and dispersion of the metal.[10,11] Earlier, Pt/C catalysts with a Pt particle size of 6–8 nm and a uniform distribution of Pt particles over the carbon support surface were obtained.[11]

We found that, in neutral and alkaline solutions, tin electrodes are oxidized and dispersed under the action of an alternating current. The structure of the products depends on current density used in the synthesis, as found by XRD analysis [Figure 1(*a*)] and SEM [Figure 1(*b*),(*c*)]. At a low current density, agglomerates with a lamellar structure and a crystallite size of 15–120 nm were obtained [Figure 1(*b*)]. Tin oxide particles with a narrow size distribution of 15–20 nm were prepared at a current density higher by a factor of 10 [Figure 1(*c*)]. These particles consisted of SnO$_2$ doped with SnO and Sn.

The Pt/SnO$_x$-C catalysts were produced in two stages:[†] (i) the preparation of tin oxide nanoparticles and the simultaneous deposition of the particles on a carbon support and (ii) the deposition of platinum nanoparticles onto the SnO$_x$-C support in accordance with a previously published procedure.[11]

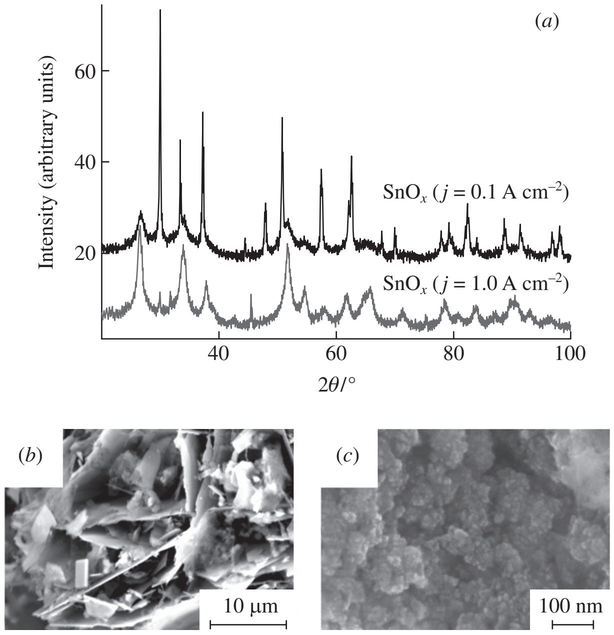

Figure 1 (*a*) X-ray diffraction patterns and (*b*), (*c*) SEM images of SnO$_x$ powders prepared at current densities of (*b*) 0.1 and (*c*) 1.0 A cm^{-2}.

For the electrochemical studies of Pt/SnO$_x$-C catalysts, catalyst ink[‡] was prepared. The electrochemical oxidation of CO on Pt/C

[†] At the first stage of Pt/SnO$_x$-C catalyst preparation, two tin electrodes with the equal surface areas were immersed in a suspension of a Vulcan XC-72 carbon support (CabotCorp., 240 m^2 g^{-1}) in a 2 M aqueous solution of NaCl. In a non-diaphragm electrolytic cell, the electrodes were connected to an ac source operating at 50 Hz (pulse duration, 2.5 ms; current density, 1 A cm^{-2}) at 50–55 °C. After the synthesis, the suspension was filtered, and the SnO$_x$-C composite was washed with distilled water and dried at 80 °C to constant weight. At the second stage, platinum nanoparticles were deposited onto the SnO$_x$-C support. Two platinum electrodes with equal areas were immersed in the suspension of the SnO$_x$-C composite in a 2 M aqueous solution of NaOH. The electrodes were connected to the ac source operating as described above. Then, the suspension was filtered; the prepared catalyst was rinsed with H$_2$O to a neutral pH and dried at 80 °C to constant weight. Platinum loading for all catalysts was 25%.

[‡] Catalyst ink and working electrodes for electrochemical measurements were prepared by mixing 0.0140 g of the synthesized catalyst with 1 ml of isopropanol and a 10% aqueous solution of Nafion DE-1020 (25% on a catalyst weight basis). After stirring with a magnetic stirrer (30 min), the ink was dropped onto a glassy carbon electrode and dried at 80 °C in air for 40–50 min.

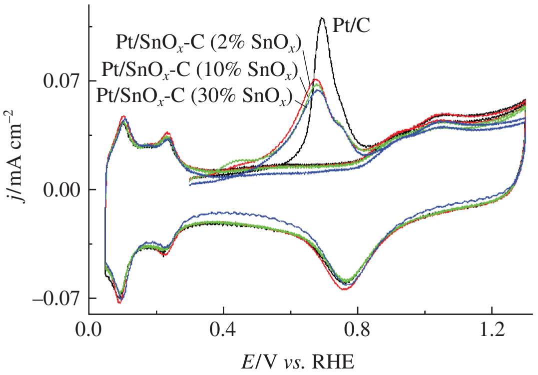

Figure 2 CV curves of the oxidation of CO_{ad} on Pt/C and Pt/SnO_x-C catalysts in 0.5 M H_2SO_4 at $E = 0.3$ V; scan rate, 20 mV s^{-1}.

and Pt/SnO_x-C catalysts was studied[§] after CO pre-adsorption. A small amount of tin oxide in the catalyst shifted the start of the CO oxidation potential by 200 mV and the CO stripping peak potential by 60 mV to the cathode side, as compared with the Pt/C catalyst obtained by the same method (Figure 2). Thus, the greatest effect was observed in a SnO_x concentration range of 2–10% in the Pt/SnO_x-C catalyst: the rate of CO oxidation at $E = 0.6$ V (RHE) increased by a factor of 2 (Figure 3). Moreover, in the course of the long-term investigations of Pt/SnO_x-C, the CO stripping peak potential remained almost unchanged (Figure 4).

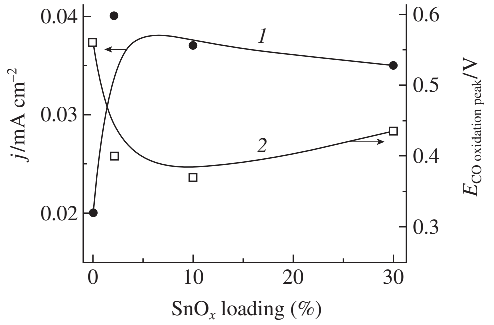

Figure 3 Effect of SnO_x loading on (*1*) the catalytic activity of Pt/SnO_x-C at 0.6 V and (*2*) the initial oxidation potential of CO.

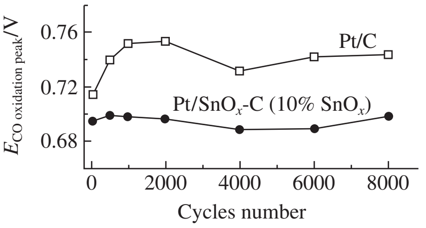

Figure 4 Changes of CO oxidation peak potentials during long-term studies.

Thus, the mechanism of electrocatalysis was implemented on the Pt/SnO_x-C bifunctional catalysts.[12] CO_{ad} species adsorbed on platinum nanoparticles were oxidized by oxygen-containing species (OH_{ad} or O_{ad}) adsorbed on tin oxide *via* the Langmuir–Hinshelwood mechanism at lower potentials than those of pure platinum.

In conclusion, the method proposed for obtaining Pt/SnO_x-C by electrochemical dispersion is technologically simple and environmentally safe. The presence of a small amount of tin oxide in platinum-based catalysts increases the stability of carbon-supported platinum catalysts.

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[§] All electrochemical measurements were performed in a three-electrode cell with separated compartments using a P-150 potentiostat/galvanostat (Elins). Platinum wire and saturated Ag/AgCl were used as counter and reference electrodes, respectively. All potentials are referred to a reversible hydrogen electrode (RHE). For the CO oxidation kinetics, at first Ar was bubbled into a 0.5 M H_2SO_4 electrolyte solution for 60 min. Then, CO was adsorbed on the surface of the working electrode by bubbling CO into a 0.5 M H_2SO_4 electrolyte solution for 15 min, while the electrode was kept at a constant potential of 0.3 V *vs.* RHE. After CO bubbling, the electrolyte was purged with Ar (30 min) to remove dissolved CO, and the CV curves were measured (potential was scanned from 0.05 to 1.3 V at a scan rate of 20 mV s^{-1}).