Novel supported catalysts: platinum and platinum oxide nanoparticles dispersed on polypyrrole/polystyrenesulfonate particles

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Platinum and platinum oxide nanoparticles are deposited on electronically and ionically conducting polypyrrole/polystyrenesulfonate particles by the reduction of $Pt(NH_3)_4Cl_2$ with formaldehyde and the oxidation of $Na_6Pt(SO_3)_4$ with H_2O_2, respectively.

Supported metal catalysts play a crucial role in many industrially important chemical reactions.[1] The support enables the metal particles to be highly dispersed and thermostable to retard sintering so that they can be used with high efficiency. This is particularly important with expensive noble metal catalysts such as platinum. The most widely used supports are carbon, SiO_2, Al_2O_3, TiO_2 and zeolites. Carbon is the only electronically conducting support in widespread use.

We introduce here a new type of support, polypyrrole/polystyrenesulfonate, which is both electronically and ionically conductive. The polypyrrole (PPy) provides electronic conductivity that can be controlled either chemically or electrochemically.[2] The polystyrenesulfonate (PSS) counter-ion, incorporated into the PPy during preparation, provides cation exchange sites. When the oxidation state of the polypyrrole is decreased, mobile cations are drawn into the particles to compensate the loss of cationic polymer sites. This causes an increase in the ionic conductivity that can be chemically or electrochemically controlled.[3]

Our primary interest in using PPy/PSS particles as a catalyst support arises from their potential application in proton exchange membrane fuel cells. The ideal catalyst support in such fuel cells would be gas and water permeable, and conduct both protons and electrons.[4] None of the conventional catalyst supports possess all these properties, but PPy/PSS does.

Although using conducting polymers as catalyst supports has been attracting research interest for more than 10 years, the deposition of metal particles has been restricted to the use of electrochemical methods and polymer films.[5] In one case, chemically prepared colloidal Pt particles were dispersed in a polypyrrole film during its electrochemical synthesis,[6] but there are no reports on the deposition of metal particles on conducting polymer particles. We have developed simple methodology that enables the fabrication of size-controllable PPy/PSS particles with dimensions ranging from *ca.* 30 to 1000 nm, and the chemical deposition of highly dispersed Pt on these particles.

The sizes of chemically synthesized PPy/PSS particles were controlled by varying the concentrations of pyrrole and the iron(III) oxidant.[7] The higher the concentration, the smaller the resulting polymer particles. The presence of PSS is essential in the size-control process. In a typical procedure (*i.e.* the preparation of the PPy/PSS particles shown in Fig. 1), a mixture consisting of 7.0 ml of 0.1 M NaPSS(aq) (0.70×10^{-3} mol, Aldrich; *M ca.* 70 000), 150 μl of neat pyrrole (2.1×10^{-3} mol), and 61 ml of water was shaken for 10 min before addition of 12 ml of 0.5 M $FeCl_3$ (6.0×10^{-3} mol) in 0.1 M HCl(aq). Following stirring for 15 min and centrifuging, the PPy/PSS particles were washed five times with water. The average diameter of the PPy/PSS particles produced under these conditions was *ca.* 500 nm, and their electronic conductivity was *ca.* 10^{-2} S cm^{-1}. Based on a model of spherical particles with a density[8] of *ca.* 1.5 g cm^{-3}, the estimated surface area is *ca.* 8 m^2 g^{-1}. The sample shown in Fig. 2 has an estimated surface area of *ca.* 100 m^2 g^{-1}.

The deposition of Pt nanoparticles on PPy/PSS particles was accomplished by the reduction of $Pt(NH_3)_4Cl_2$ with formaldehyde. PPy/PSS was heated at reflux in 60 ml of formaldehyde for 1 h to ensure full dispersion, followed by the addition of 72 mg of $Pt(NH_3)_4Cl_2$ and stirring for 30 min. The mixture was then heated at reflux for 30, 60, 90, 120 or 150 min.

Transmission electron microscopy (TEM) revealed that little Pt deposition occurred during the first 1.5 h, while large quantities of Pt nanoparticles with diameters of *ca.* 4 nm were produced after *ca.* 2 h. The reaction time had little influence on the Pt particle size. Fig. 1 shows a TEM of a Pt/PPy/PSS sample following 2.5 h of reflux. The distribution of Pt nanoparticles is quite homogeneous. Electronic conductivity measurements following Pt deposition revealed a *ca.* three order of magnitude decrease to *ca.* 10^{-5} S cm^{-1}. A similar decrease in conductivity was observed when PPy/PSS particles were treated with formaldehyde alone, suggesting that it is due to irreversible reduction of the polypyrrole.

Deposition of Pt oxide nanoparticles on PPy/PSS particles was also performed.[9] In this case, the PPy/PSS was produced from a mixture consisting of 0.14 M pyrrole, 0.70 M $Fe(NO_3)_3$ and 0.04 M PSS with a 90 min reaction time. The resulting PPy/PSS particles were of an irregular shape, with an average dimension of *ca.* 40 nm. After 0.2000 g of dried PPy/PSS and 0.1695 g of $Na_6Pt(SO_3)_4$[9] were stirred in 80 ml of water for 5

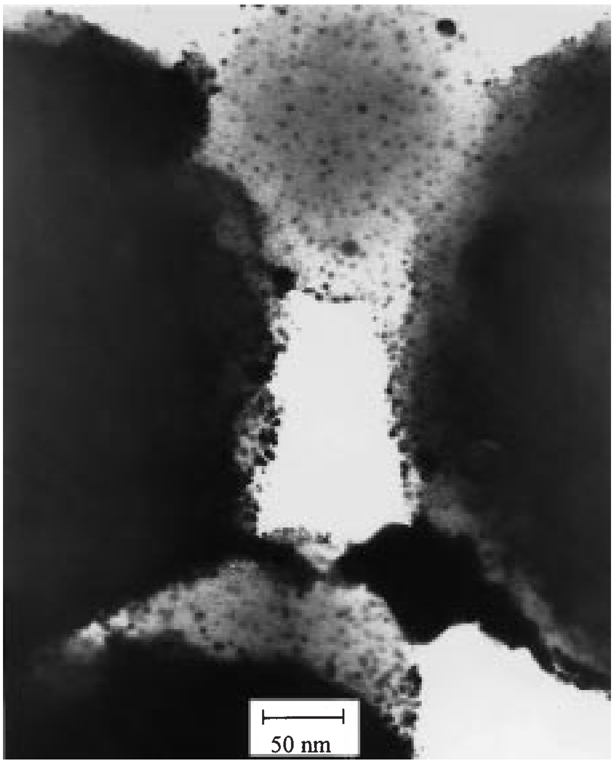

Fig. 1 TEM of Pt nanoparticles dispersed on PPy/PSS particles

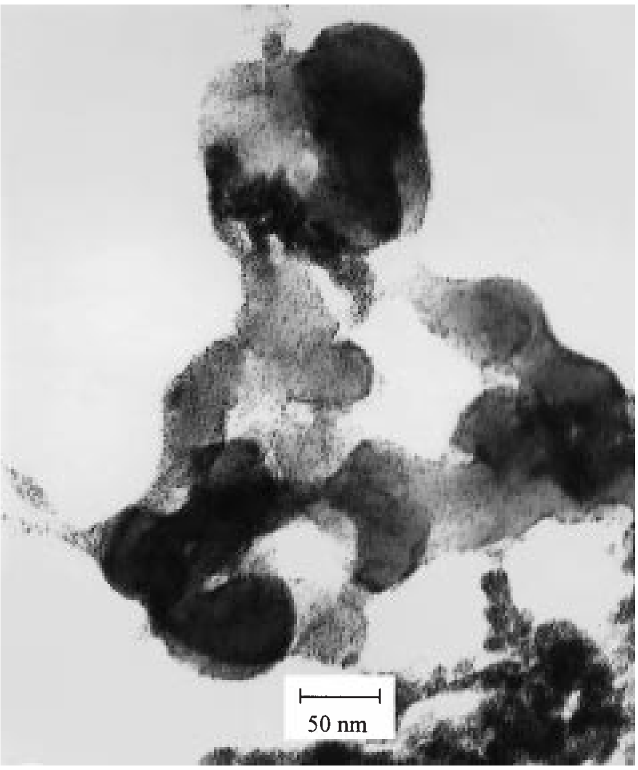

Fig. 2 TEM of Pt oxide nanoparticles dispersed on PPy/PSS particles

min, 1 M H_2SO_4 was added dropwise to adjust the pH from *ca.* 4 to 2.0, followed by the dropwise addition of 0.5 M NaOH to adjust the pH to 3.0. Then 1.00 ml of 30% H_2O_2 was added and the mixture was stirred for 1 h and then boiled. The Pt oxide/PPy/PSS particles were separated from the reaction medium by centrifuging, washed three times with water, and dried under vacuum overnight at room temperature.

Fig. 2 shows a TEM of the resulting Pt oxide/PPy/PSS particles. Pt oxide nanoparticles were *ca.* 2 nm in diameter and evenly distributed on the PPy/PSS particles. Although the exact chemical nature of the Pt oxide particles is unknown, they can be converted to highly catalytic Pt particles simply by heating.[9] This sample exhibited electronic conductivities of *ca.* 3 and 10^{-5} S cm^{-1} before and after Pt oxide deposition, respectively. The decrease in conductivity is presumably due to over-oxidation[10] of the polypyrrole by the H_2O_2.

Preliminary results (Fig. 3) have indicated that the supported catalysts described here are effective for oxygen reduction in

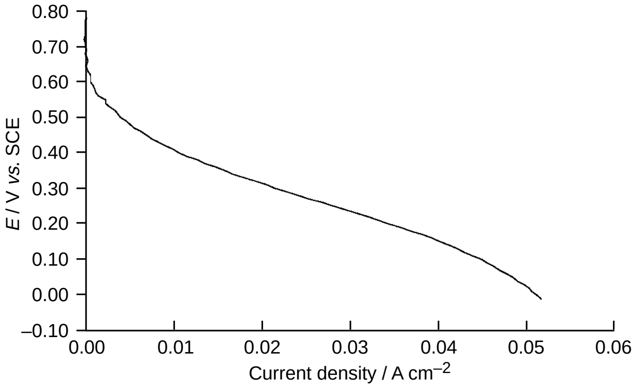

Fig. 3 Polarization curve for oxygen reduction in a C | O_2 (1 atm), PPy/PSS/Pt oxide (0.15 mg Pt cm^{-2}) | Nafion | 1 M H_2SO_4(aq), SCE | Pt cell at ambient temperature. Experimental details are reported elsewhere.[11]

proton exchange membrane fuel cells, despite their low electronic conductivities. However, significantly high conductivities are required to compete with the carbon supported catalysts currently in use.

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Footnotes and References

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