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Conducting polymeric nanotubules as high performance methanol oxidation catalyst support

Bashyam Rajesh,[a] K. Ravindranathan Thampi,*[b] Jean-Marc Bonard,[c] Hans Jorg Mathieu,[d] Nicolas Xanthopoulos[d] and Balasubramaniam Viswanathan*[a]

[a] *Department of Chemistry, Indian Institute of Technology, Madras, Chennai-600036, India. E-mail: bvnathan@iitm.ac.in*

[b] *Laboratory of Photonics and Interfaces, ICMB-LPI, Swiss Federal Institute of Technology (EPFL), Lausanne, CH-1015, Switzerland. E-mail: Ravindranathan.Thampi@epfl.ch*

[c] *Institut de Physique des Nanostructures, Swiss Federal Institute of Technology (EPFL), Lausanne, CH-1015, Switzerland*

[d] *Laboratoire de Métallurgie Chimique, Swiss Federal Institute of Technology (EPFL), Lausanne, CH-1015, Switzerland*

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Pt nanoparticle-supported conducting nanotubules of polypyrrole prepared by a template method exhibited excellent catalytic activity and stability for the electrooxidation of methanol in comparison to Pt supported on conventionally synthesised conducting polypyrrole.

Supported metal catalysts play an important role in many chemical reactions.[1] The support enables the metal particles to be well dispersed for their better utilisation and efficiency. This is particularly important with expensive metal catalysts such as platinum. The most widely used supports are carbon, SiO_2, Al_2O_3, TiO_2 and zeolites. Though carbon is the only electronically conducting support that has been widely used for this purpose, polymers[2] like polyaniline, polypyrrole (PPY), poly(3-methyl)thiophene, poly(3-ethylenedioxy)thiophene and composites[3,4] based on these polymers have also been studied for such applications. In recent years, nanostructured conducting materials like carbon nanotubules, nanofibers and mesoporous carbon have been used as supports for Pt catalysts in a variety of chemical and electrochemical applications.[5–8] Nanotubules and nanofibrils of conductive polymers[9] have also been prepared using porous alumina membranes as templates. It is reported that these polymers have enhanced electronic conductivity and charge transport properties, compared to the conventionally synthesised polymer.

Here we report, for the first time, the synthesis of a Pt supported well aligned array of conducting nanotubules of PPY grown on a Nafion coated carbon cloth backbone by using an alumina membrane template. Though the nanotubules of PPY can be employed in a variety of applications[2] like sensors, electrochromic devices, antistatic coatings, electromagnetic shieldings *etc.*, our primary interest in using the PPY nanotubules as a catalyst support arises from their potential applications in fuel cells.[10] To our knowledge, there have been no reports concerning methanol oxidation,[11] a reaction of importance for the development of direct methanol fuel cells (DMFC), utilising nanosized Pt supported on conducting nanotubules of polypyrrole.

In a typical synthesis, a 2.5 cm^2 rectangular strip of commercially available uncatalysed carbon coated carbon cloth (E-TEK) was coated with 30 µl of 5 wt% Nafion as a thin layer. The Nafion coated area was 0.3 cm^2 and the remaining area was insulated. The alumina membrane (60 µm thick, 200 nm pore diameter and 65% porosity) obtained from Whatman Anapore pore filters was placed on the Nafion coated carbon cloth (CC) and hot pressed at 393 K for 2 min at a pressure of 50 kg cm^{-2}. This configuration was designated as CC/Naf/Al_2O_3. The area of the working electrode, after taking into account the porosity of the template, was found to be 0.195 cm^2. The electropolymerisation of pyrrole was carried out in acetonitrile medium using 0.05 M pyrrole and 0.1 M tetrabutylammonium tetrafluoroborate in galvanostatic mode, by applying a current density of 75 mA cm^{-2}. The thickness of the free PPY was estimated from the total charge passed for the polymerisation. It was reported that the charge of 100 mC cm^{-2} corresponds to a film thickness of 0.3 µm. In the present investigation, the charge used for the polymerisation was 200 mC cm^{-2}.

The platinum was electrodeposited by the Galvanostatic Square Wave (GSW) method in 1% H_2PtCl_6 and 0.5 M H_2SO_4. A current density of 50 mA cm^{-2} was applied for a total period of 2 to 8 min in order to vary the loading of Pt on the matrix. The pulse was applied in start–stop intervals of 10 s each, for the required total duration. The whole process of Pt deposition was done before the dissolution of the alumina membrane. The resulting configuration is designated as CC/Naf/Al_2O_3/PPY-$_{Temp}$-Pt. The alumina membrane was completely removed by immersing the composite in 0.1 M NaOH for 15 min. It was then repeatedly washed with deionised water to remove the residual NaOH. It was subsequently immersed in 1% HBF_4 for 10 min and again washed with deionised water to retrieve the original PPY characteristics. The composites after the dissolution of the template were designated as CC/Naf/PPY_{Temp} and CC/Naf/PPY_{Temp}-Pt. The template free Pt incorporated polypyrrole on carbon cloth (CC/Naf/PPY/Pt) was prepared by an identical electrochemical step mentioned above. Electrochemical (cyclic voltammetry (CV) and chronoamperometry) measurements for methanol oxidation were performed in a conventional three electrode cell with Ag/AgCl as the reference electrode.

The electron microscopic (EM) images of the template and conventionally synthesised conducting polypyrrole (with and without Pt) projected from the carbon cloth are shown in Fig. 1. It is evident from Fig. 1a that the uniform, cylindrical, monodisperse nanotubules of PPY after the removal of the template are projecting perpendicularly to the carbon cloth. These tubes are uniformly distributed in a regular array on the carbon cloth with an outer diameter (200 nm) that almost matches the pore diameter of the template. Fig. 1b shows the picture of the conducting polymeric tubules taken at a tilted angle, in a different region. It is evident from the image that the density of the nanotubules is quite high, in all the regions. The open ends of the uniform nanotubules are clearly seen in this image. Fig. 1c shows the high-resolution transmission electron micrograph (HR-TEM) of Pt incorporated template synthesised polypyrrole. Though the nanotubules are clearly seen, the Pt particles are not visible due to the thickness of the wall of the tubules. In order to demonstrate the presence of embedded Pt,[12] electron diffraction was recorded and is presented as an inset in Fig. 1c. The diffraction patterns of the Pt embedded particles are seen as number of concentric rings (these rings can be indexed from the inside as 111, 200, 220, 311 reflectance for fcc Pt) which demonstrated that the Pt particles are finely dispersed inside the nanotubules. The SEM image of the conventionally

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synthesised polypyrrole on Nafion coated, uncatalysed carbon cloth is shown in Fig. 1d. The morphology of the PPY as it is reflected from Fig. 1d shows the non-uniform agglomerates of polypyrrole on the carbon cloth. The inset of Fig. 1d shows the Pt deposited conventionally synthesized polypyrrole on carbon cloth. Large numbers of spherical and dense agglomerates of Pt crystallites are seen from the image. The electron diffraction image of the Pt deposited on the template free polypyrrole (not shown) revealed that the diffraction pattern of the Pt is seen as spots and not as concentric rings as observed with Pt particles in template synthesised polypyrrole. The EM study also demonstrated that the conducting polymeric tubules are strongly adhering to the carbon cloth.

The XPS spectra of the Pt 4f region in the CC/Naf/PPY$_{\mathrm{Temp}}$-Pt before and after Ar ion etching exhibited a well defined doublet for the Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ with peak binding energies centered at 71.1 eV and 74.0 eV, suggesting the presence of Pt in the metallic state. The ohmic and the charge transfer resistances by impedance analysis were found to be 0.25 and 0.27 Ω cm^2 and 7.5 and 45 Ω cm^2 for CC/Naf/PPY$_{\mathrm{Temp}}$ and CC/Naf/PPY electrodes respectively in 1 M H_2SO_4 at 0.6 V *vs.* Ag/AgCl. This suggests that there is no diffusion limitation in nanotubule electrodes.

Fig. 2 shows the variation in performance of methanol oxidation current densities with Pt loading on CC/Naf/PPY$_{\mathrm{Temp}}$-Pt and CC/Naf/PPY/Pt electrodes. It is evident that for the template based nanotubule electrodes, as the Pt loading increases, there is a continuous increase in activity from 25.6 mA cm^{-2} (Pt = 10 μg cm^{-2}) to 302.5 mA cm^{-2} (Pt = 140 μg cm^{-2}). In the case of the template free polypyrrole electrode the activity was increased from 9 mA cm^{-2} (Pt = 10 μg cm^{-2}) to only 119.4 mA cm^{-2} (Pt = 80 μg cm^{-2}). Beyond this loading the activity saturates at 120.4 mA cm^{-2}. This reflects that the array of well aligned tubular morphology of the polymeric nanotubules helps to achieve a fine dispersion of Pt particles inside the PPY matrix. The template based electrode not only showed higher activity but also accommodated more Pt than the template free PPY electrode. The results were reproducible.

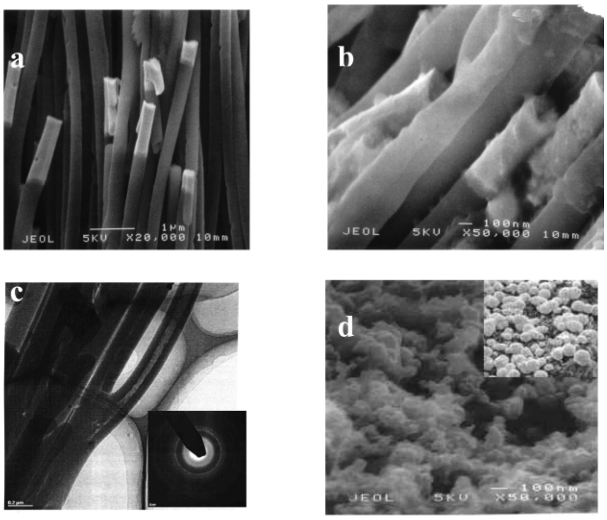

Fig. 1 (a–b) SEM images of Pt free CC/NAf/PPY$_{\mathrm{Temp}}$. (c) HR-TEM image of CC/Naf/PPY$_{\mathrm{Temp}}$-Pt and *inset* shows the electron diffraction pattern of Pt nanoparticles. (d) SEM image of CC/Naf/PPY and *inset* shows SEM image of CC/Naf/PPY/Pt.

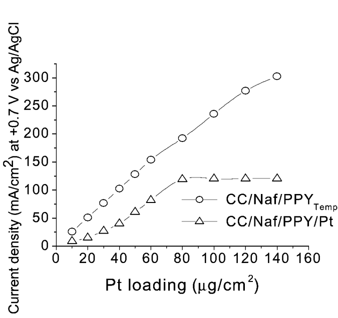

Fig. 2 Variation of current density at +0.7 V *vs.* Ag/AgCl with Pt loading. Current densities were measured at +0.7 V for CV's run in 1 M H_2SO_4/1 M CH_3OH between −0.2 and +0.8 V. Scan rate: 50 mV s^{-1}.

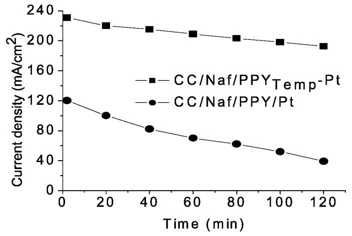

Fig. 3 Variation of current density with time in 1 M H_2SO_4/1 M CH_3OH at +0.6 V *vs.* Ag/AgCl.

Fig. 3 shows the activity of CC/Naf/PPY$_{\mathrm{Temp}}$-Pt and CC/Naf/PPY/Pt electrodes with respect to time at a constant potential of +0.6 V in 1 M H_2SO_4 and 1 M CH_3OH. The decrease in catalytic activity was found to be around 14.3% for the template based electrode at the end of 2 h and the corresponding decrease for CC/Naf/PPY/Pt was found to be 67.5%. This demonstrates that the activity and the stability of the Pt incorporated template synthesised PPY nanotubule electrode was higher than the Pt deposited on the template free polypyrrole. Another interesting observation is that though the initial activity of CC/Naf/PPY$_{\mathrm{Temp}}$-Pt was only 2 times higher than the template free electrode, the activity at the end of 2 h. was found to be nearly 5 times higher. This demonstrates the better utilisation and the stability of the template based polypyrrole electrode compared to template free PPY electrode.

To the best of our knowledge, there have been no reports either on the synthesis of Pt incorporated conducting polymeric nanotubules or its use in the electrocatalytic oxidation of methanol. Our results show that an electrocatalyst for methanol oxidation with high performance and stability can be prepared using a low level of Pt loading on a conducting PPY nanotubule support. These catalysts can also be employed for hydrogen oxidation in proton exchange membrane (PEM) fuel cells. Such conducting nanotubules of polypyrrole have good potential to find a variety of applications in various electronic and electrochemical devices. The effect of polymerisation conditions on the morphology of the tubules and catalytic activity is currently under investigation.

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Notes and references

1 *Heterogeneous catalysis: Principles and Applications*, ed. G.C. Bond, Clarendon Press, Oxford, 2nd edn., 1987.
2 A. Malinauskas, *Synth. Met.*, 1999, **107**, 75.
3 Z. Qi and P. G. Pickup, *Chem. Commun.*, 1998, 15.
4 B. Rajesh, K. Ravindranathan Thampi, J. M. Bonord, N. Xanthopoulos, H. J. Mathieu and B. Viswanathan, *Electrochem. Solid-State Lett.*, 2002, **5**, E71.
5 G. Che, B. B. Lakshmi, E. R. Fischer and C. R. Martin, *Nature*, 1998, **393**, 346.
6 B. Rajesh, K. Ravindranathan Thampi, J. M. Bonard and B. Viswanathan, *J. Mater. Chem.*, 2000, **10**, 1757.
7 B. Rajesh, K. Ravindranathan Thampi, J. M. Bonard, N. Xanthopoulos, H. J. Mathieu and B. Viswanathan, *J. Phys. Chem. B*, 2003, **107**, 2701.
8 S. H. Joo, S. J. Chel, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, *Nature*, 2001, **412**, 169.
9 L. S. V. Dyke and C. R. Martin, *Langmuir*, 1990, **6**, 1118.
10 L. Carrette, K. Andreas Friedrich and V. Stimming, *ChemPhysChem*, 2000, **1**, 162.
11 C. K. Witham, W. Chun, T. L. Valdez and S. R. Narayanan, *Electrochem. Solid-State Lett.*, 2000, **3**, 497.
12 T. Kyotani, L.-F. Tsai and A. Tomita, *Chem. Commun.*, 1997, 701.