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Nanostructured Conducting Polyaniline Tubules as Catalyst Support for Pt Particles for Possible Fuel Cell Applications

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Nanotubules of polyaniline synthesized by template method on commercial carbon cloth have been used as the catalyst support for Pt particles for electro-oxidation of methanol. The ohmic and the charge transfer resistances of the nanotube-based electrode were considerably lower than the polyaniline electrode synthesized by the conventional route. The Pt incorporated polyaniline nanotube electrode exhibited excellent catalytic activity and stability compared to the 20 wt % Pt supported on the VulcanXC 72R carbon and Pt supported on the conventional polyaniline electrode. The electrode fabrication used in the present investigation is particularly attractive to adopt in the solid polymer electrolyte-based fuel cells, which is usually operated under methanol or hydrogen. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1799955] All rights reserved.

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Over several years, considerable effort¹ has been devoted to the electrochemical preparation of conducting polymers and microparticles dispersed on conducting polymers such as polyaniline, polypyrrole, and polythiophene for various applications which include mainly electronic and electrocatalytic applications.² Polyaniline, which is easy to synthesize in aqueous medium, is an interesting material, it is generally homogeneous, strongly adherent to the support, and chemically stable in acid medium.

The possibility of dispersing metallic particles inside these polymers gives rise to electrocatalytically active electrodes. Promising results have been reported for many reactions,³ including the electro-oxidation of methanol (a reaction of importance for the development of direct methanol fuel cells (DMFCs) for portable and vehicular applications) on Pt, Pt-Ru, and Pt-Sn microparticles dispersed on conducting polymers.⁴⁻⁷ Research over the past two or three decades⁸⁻¹³ identified the best catalyst as Pt and Pt-Ru supported on carbon for methanol oxidation. The poor utilization of Pt particles and the poor stability for methanol oxidation due to strongly adsorbed CO, requires the modification of the existing electrode materials. In the literature,² conducting polymer also has been used as the electronically conducting support apart from most widely used carbon to disperse catalytic nanoparticles. These materials are usually fabricated as thin films deposited through electropolymerization on an inert conductive support (C, Pt, and Au) to form a three-dimensional conductive microstructure or chemically modified electrodes.¹ The synthesized material shows the conductivity in the range of 5-50 S/cm depending on the conditions employed for polymerization and the dopant ions. The catalytic particles will then be deposited electrochemically on the conducting matrix for electrocatalytic applications. The tubular and fibrillar polymeric materials have been synthesized using polycarbonate and aluminum oxide as templates on Au and Pt substrates.¹⁴⁻¹⁷ It has been shown that the tubular and fibrillar morphology of the polyaniline plays an important role for the enhanced charge transport across the electrode/ electrolyte interface and conductivity, compared to the conventionally synthesized polyaniline.¹⁸ The present study represents the first example of nanotubules of polyaniline as catalyst support for Pt nanoparticles for methanol oxidation for possible application in DMFCs. The activity of Pt incorporated template synthesized polyaniline is compared with the Pt deposited on the conventionally synnthesiszed polyaniline and Pt loaded Vulcan XC72 R carbon synthesized by the method reported in the literature.¹⁹

Experimental

Substrate preparation.—In the fabrication of gas diffusion electrodes for fuel cells, the catalyst (either supported or unsupported) mixed with proper binder will be coated on the teflonized, uncatalyzed carbon coated carbon cloth, before it is hot pressed on the solid polymer (Nafion) electrolyte.²⁰ To configure the electrodes suitably, for use in the fuel cell mode, in the present investigation, for the first time the electropolymerization was carried out on the template (alumina membrane) attached carbon cloth and, subsequently, Pt particles were electrodeposited before the dissolution of the template by NaOH.

A known area (2.5 cm² rectangular strip) of commercially available uncatalyzed carbon coated carbon cloth (E-TEK) was coated with 30 μ L of 5 wt % Nafion as a thin layer. The Nafion coated area was 0.3 cm² and the remaining area was insulated. The alumina membrane (Whatman Anodisc 47, pore diam *ca.* 200 nm, 60 μ m, and 65% porosity) was placed on the Nafion coated carbon cloth and hot pressed at 393 K for 2 min at a pressure of 50 kg/cm². This configuration of alumina (Al₂O₃) membrane attached Nafion coated carbon cloth (CC) was designated as CC/Naf/Al₂O₃.

All the chemicals used were of analytical grade and purchased from Fluka and freshly distilled aniline was used for the polymerization.

*Electropolymerization of aniline on CC/Naf/Al*₂ O_3 .—The electropolymerization was carried out by potentiodynamic method in 0.1 M aniline and 1 M H₂SO₄. The potential was swept between -0.2 and +1.0 V at a scan rate of 50 mV/s. The resulting composite electrode was designated as CC/Naf/Al₂O₃/PANI_{Temp} (before the dissolution of alumina membrane).

Deposition of Pt particles of $CC/Naf/Al_2O_3/PANI_{Temp}$.—The platinum was electrodeposited by interrupted dc (galvanostatic square wave) method in 1% H₂PtCl₆ and 0.5 M H₂SO₄. The current density of 50 mA/cm² was applied for a total period of 2 to 8 min to vary the loading of Pt on the matrix. The pulse (50 mA/cm²) was applied initially for 10 s and stopped for 10 s until the total period was reached. The whole process of Pt deposition was done before the dissolution of the alumina membrane. The resulting configuration is designated as CC/Naf/Al₂O₃/PANI_{Temp}-Pt.

Removal of template.—The host (alumina membrane) from $CC/Naf/Al_2O_3/PANI_{Temp}$ and $CC/Naf/Al_2O_3/PANI_{Temp}$ -Pt was removed by immersing the composite in 0.1 M NaOH for 15 min. The composite after the dissolution of the template was repeatedly washed with deionized water to remove the residual NaOH. The



Figure 1. (a) Electropolymerization of 0.1 M aniline in 1 M H_2SO_4 on CC/Naf/Al₂O₃ electrode. Scan rate 50 mV/s. First 4 cycles. (b) CV of CC/Naf/PANI_{Temp} (after immersion of the template in 0.1 M NaOH followed by immersion 1% HBF₄) in 1 M H₂SO₄. Scan rate 50 mV/s.

composite was subsequently immersed in 1% HBF₄ for 10 min and then washed with deionized water again. The composite after the dissolution of the template was designated as CC/Naf/PANI_{Temp} and CC/Naf/PANI_{Temp}-Pt. The preparation of conventional polyaniline and Pt deposited polyaniline was carried in the similar way as it has been done for the template synthesis method. In the conventional synthetic procedure, the polymerization and the subsequent Pt deposition on carbon cloth was done without the host alumina membrane.

Determination of Pt.—The platinum content on the electrode surface was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, model 3410 ARL), after calibrating with a standard solution of Pt. The Pt was extracted from the electrode by boiling in aqua regia.

Electrochemical, microscopic, and spectroscopic measurement.-The electrochemical measurements were performed using a Potentioscan Wenking (POS 73) with Philips digital X-Y recorder (PM 8033). The Pt foil (1 cm²) and Ag/AgCl were used as the counter and reference electrodes, respectively. The working electrode was varied according to the requirement. The glassy carbon (0.07 cm²) purchased from BioAnalytical Systems, USA was used as working electrode when using Pt loaded Vulcan XC72 R carbon as electrocatalyst. The galvanostatic square wave (GSW) measurements were performed using EG&G model 283 potentiostatgalvanostat. The microscopic features of the sample were observed with a JEOL 1599 scanning electron microscope (SEM) and a highresolution transmission electron microscope (TEM, Philips EM430ST operated at 300 kV). The X-ray photoelectron spectroscopic studies were performed using a Perkin Elmer PHI 5500 ESCA system using Mg K α , as the excitation source.





Figure 2. (a) HR-TEM image of Pt incorporated polyaniline nanotubules projecting perpendicularly from the carbon cloth. (b) Electron diffraction image of the Pt particles, which appear as concentric rings in the template synthesized Pt incorporated polyaniline nanotubules.

Results and Discussion

The cyclic voltammogram (CV) (first four cycles) shown in Fig. 1a illustrates the growth of polyaniline on the CC/Naf/Al₂O₃ electrode. The first cycle shows the monomer oxidation at approximately +0.87 V in the forward scan, though the oxidation of aniline is not clearly seen in the forward scan of the first cycle, the reverse scan shows a small shoulder at +0.43 and +0.01 V, which is due to the reduction of polyaniline formed on the electrode. The growth of the polyaniline upon cycling is reflected from the increase in current response as well as due to the well-defined peaks at +0.25 and +0.48 V, which are due to the oxidation of polyaniline formed on the electrode surface. The electrode CC/Naf/PANI_{Temp} (after the dissolution of the template in 0.1 M NaOH) is immersed in 1 M H₂SO₄



Figure 3. (a) SEM of conventionally synthesized polyaniline. (b) SEM of the Pt particles on the conventionally synthesized polyaniline.

and the CV was recorded (not shown) by scanning between -0.2 and +0.8 V. No characteristic redox wave due to polyaniline was observed, probably due to the NaOH used to dissolve the template. It has been reported, ¹⁸ the base exposed polypyrrole has deleterious effect on their redox electrochemistry.

The CV of CC/Naf/PANI_{Temp} after the immersion in 1% HBF₄ is shown in Fig. 1b. Before recording the voltammogram, the electrode was kept at -0.5 V for 30 s. The electrode was then scanned between -0.2 and +0.8 V in 1 M H₂SO₄. The characteristic peak due to oxidation of polyaniline is observed at +0.28 V and reduction of PANI at +0.01 V. By holding the potential at -0.5 V, the reduction of the oxidized polyaniline is effected, which on cycling exhibited the peak at +0.28 V in the forward scan and +0.01 V in the reverse scan. The immersion in HBF₄, followed by the reduction at -0.5 V causes probably expulsion of OH⁻ ions, which resulted in retrieving the characteristic polyaniline redox waves.

The nature of the CV for the growth of polymerization of aniline on CC/Naf in 1 M H_2SO_4 synthesized through the conventional route (without template) and the redox characteristics of the polyaniline in the monomer free electrolyte matches with that reported in literature.² The same quantity of charge was passed for the deposition of polymer in both cases. (template and conventional). For conventionally synthesized polyaniline, the thickness of the polyaniline was evaluated from the charge under the curve at +0.1 V in the forward scan. It was reported that 80 mC/cm² resulted in 1 μ m thick



Figure 4. Variation of electrocatalytic activity of methanol oxidation with Pt loading on nanotubule and conventional electrodes. (Electrocatalytic activity were evaluated from CV run in 1 M $H_2SO_4/1$ M CH₃OH at 50 mV/s. The activity at +0.6 V vs. Ag/AgCl was taken for the measurement.)

film.⁵ The charge used in the present study was 100 mC/cm².

The HR-TEM image (Fig. 2a) shows oriented, monodisperse nanotubules of template synthesized polyaniline projecting perpendicularly from the carbon cloth. The o.d. of the tube almost matches with the template diameter of 200 nm. Though the dispersion of Pt particles could not be seen from the electron diffraction pattern of the Pt in the template synthesized polyaniline tubules (Fig. 2b). The number of concentric rings observed in the electron diffraction image suggests that the Pt particles are finely dispersed in the nanotubules. These rings are indexed from the inside as 111, 200, 220, 311 reflectance for face-centered cubic (fcc) Pt.

Figure 3a shows the SEM image of conventionally synthesized polyaniline on nafion coated carbon cloth. The image reveals the fibrillar and globular morphology of the conventionally synthesized polyaniline. The fibrils are randomly distributed without any orientation or alignment. Figure 3b shows the SEM image of the Pt deposited on conventionally synthesized polyaniline. It is evident from the figure that large clusters of Pt particles of size around 100-150 nm are distributed throughout the polymer. Though, a similar deposition condition as that of the Pt deposited on the template synthesized polyaniline is adopted, the clusters of Pt atoms formed on the conventionally synthesized polyaniline were large. This suggests that the deposition of the Pt particles with the porous template (which is an insulator) provide a crucial role in controlling the growth of the particle. Because between any two adjacent pores alumina membrane will be acting as an insulating spacer, the growth of the particle can be easily controlled. The electron diffraction image of the Pt deposited on the template free polyaniline (not shown) revealed that the diffraction pattern of the Pt are seen as spots and not as concentric rings as observed with Pt particles in template synthesized polyaniline.

The ohnic and the charge transfer resistances by impedance analysis were 0.52 and 0.78 Ω cm² and 3.8 and 15 Ω cm² for CC/Naf/PANI_{Temp} and CC/Naf/PANI_{Conv} electrodes, respectively, in 1 M H₂SO₄ at 0.6 V vs. Ag/AgCl. This suggests that the diffusion limitation is minimum in nanotubule electrodes. The XPS spectra of Pt 4f region in the CC/Naf/PANI_{Temp}-Pt exhibited a well defined doublet for the Pt 4f_{7/2} and Pt 4f_{5/2} with peak binding energies centered at 71.1 and 74.0 eV, suggesting the presence of Pt in metallic state.

Figure 4 shows the variation of performance of methanol oxida-



Figure 5. Variation of current density with time in 1 M H₂SO₄/1 M CH₃OH at +0.6 V vs. Ag/AgCl. The Pt loading was kept at 80 μ g/cm².

tion current densities with Pt loading on CC/Naf/PANITemp-Pt and CC/Naf/PANI/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 10.0 mA/cm² (Pt = $10 \mu g/cm^2$) to 80.0 mA/cm² (Pt = $80 \mu g/cm^2$). In the template, free polyaniline electrode the activity was increased from 5.0 mA/cm² (Pt = $10 \,\mu g/cm^2$) to only 26.0 mA/cm² (Pt = $80 \,\mu g/cm^2$). 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 PANI matrix. The methanol oxidation activity of the template-based electrode was more than three times that of the template-free electrode for identical loading of 80 μ g/cm². The template-based electrode not only showed higher activity but also accommodated more amount of Pt than the template free PANI electrode.

Figure 5 shows the activity of CC/Naf/PANI_{Temp}-Pt and CC/Naf/ PANI/Pt electrodes with respect to time at a constant potential of +0.6 V in 1 M H₂SO₄ and 1 M CH₃OH. The decrease in catalytic activity was $\sim 19.0\%$ for template-based electrode at the end of 2 h and the corresponding decrease for 20 wt % Pt/Vulcan XC72R Carbon and CC/Naf/PANI/Pt was 50 and 75%, respectively. This demonstrates that the activity and the stability of the Pt incorporated template synthesized PANI nanotubule electrode was higher than the Pt deposited on the template free polyaniline. Note also that though the initial activity of CC/Naf/PANI_{Temp}-Pt was only 1.6 times higher than 20 wt % Pt/Vulcan XC72R Carbon and 3.7 times higher than the CC/Naf/PANI/Pt electrodes, the activity at the end of 2 h was nearly three times higher than 20 wt % Pt/Vulcan XC72R Carbon and 12 times higher than CC/Naf/PANI/Pt electrode. This demonstrates the better utilization and the stability of the template based polyaniline electrode compared to 20 wt % Pt/Vulcan XC72R Carbon and template free PANI electrode.

Conclusions

In summary, we report here preliminary results on the usage of electronically conducting polyaniline nanotubules as catalyst support for Pt particles for methanol oxidation. The activity of methanol oxidation for nanotube-based electrode was more than three times than conventional (template free) polyaniline electrode. It also accommodated a larger amount of accessible Pt compared to the conventional electrode. The stability of the nanotube-based electrode was also considerably higher than the conventional electrode. Though the use of conducting polymer nanotubules as catalyst support has been demonstrated, much work must be done to correlate the impedance behavior of the nanotube electrode observed experimentally with the theoretical model. We are currently investigating the effect of varying the polymerization condition, Pt/Pt-Ru deposition on electrocatalytic activity of methanol oxidation and finally to prototype fuel cells.

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