

Pt particles supported on conducting polymeric nanocones as electro-catalysts for methanol oxidation

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Abstract

The electrochemical synthesis of conducting nanocones of Pt incorporated poly(3-methyl) thiophene, employing alumina membrane templates and its use as an electrode material for methanol oxidation is reported. The activity (131 mA/cm² at +0.4 V versus Ag/AgCl for a Pt loading of 80 μg/cm²) of nanocone-based electrode was found to be more than one order of magnitude higher compared to the regular poly(3-methyl) thiophene electrode (12.2 mA/cm² at +0.4 V versus Ag/AgCl for a Pt loading of 80 μg/cm²). The chronoamperometric response confirms the better activity and stability of the nanocone-based electrode compared to the commercial 20 wt.% Pt/C (E-TEK) and template-free electrode. The XPS data confirmed the presence of Pt in the metallic state. The nanocone morphology of poly(3-methyl) thiophene, helps in the effective dispersion of Pt particles facilitating the easier access of methanol to the catalytic sites.

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1. Introduction

Nanostructured materials synthesized by the template approach [1] have received considerable importance recently because of its wide applications in electronic [2], optics [3], catalysis [4], and energy systems [5]. They are also employed in biosensors [6] and in self-assembly of supramolecular structures [7].

Nanotubules and nanofibrils composed of conductive polymers, metals, semiconductors, and carbons have been prepared using porous alumina membrane as templates [1]. Tubular and fibrillar nanostructures can be assembled in a variety of architectures, for different applications.

Recently [8], there has been an increasing interest in the development of direct methanol fuel cells (DMFC) [9]. The major problems in the development of viable DMFC are the high loading of Pt and the deactivation of Pt activated anodes

[10] by the strongly adsorbed by-product, CO [11]. Though improvement has been made in the catalytic activity and stability of the electrodes by effectively dispersing Pt particles on the electronically conducting supports [12,13], effort to disperse it further on nanostructured carbon supports [14], which include carbon nanotubules [5,15–18] and nanofibers [19] is still continuing. Numerous attempts have also been made to utilize catalytic microparticles [20,21] dispersed on electronically conducting polymers like polyaniline [22], polypyrrole [23], and poly(3-methyl) thiophene [24]. Yet the utilization of Pt has not reached the level of commercial viability. Template synthesis of nanostructured conducting polymers [25,26] on substrate like Au and Pt have also been reported. These polymers have enhanced conducting and charge transport properties compared to the conventionally synthesized polymers [27]. We recently communicated [28] the synthesis and characterization of conducting poly(3-methyl) nanocone using alumina membrane as a template on carbon cloth. The morphology and the electrochemical properties have been compared with the template-free poly(3-methyl) thiophene synthesized on carbon cloth. We report here, the synthesis of Pt incorporated template

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synthesized poly(3-methyl) thiophene nanocones and its use as an electrode material for methanol oxidation in comparison to Pt incorporated template-free poly(3-methyl) thiophene.

2. Experimental methods

2.1. Substrate preparation

The fuel cell electrodes are generally fabricated by mixing the catalyst with a binder, before coating on to a carbon (typically Vulcan XC 72) coated teflonized carbon cloth. This is then hot pressed over the solid polymer (Nafion) electrolyte [29,30]. In order to configure the electrodes suitably, in our experiments, the electropolymerization was carried out directly on the template (alumina membrane) attached to a carbon cloth [28]. The Pt particles were subsequently electrodeposited, before the dissolution of the template by NaOH. The preparation of template-free Pt incorporated poly(3-methyl) thiophene was carried out in an identical manner, but without the alumina membrane.

A 2.5 cm² rectangular strip of commercially available uncatalyzed 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 cm² and the remaining area

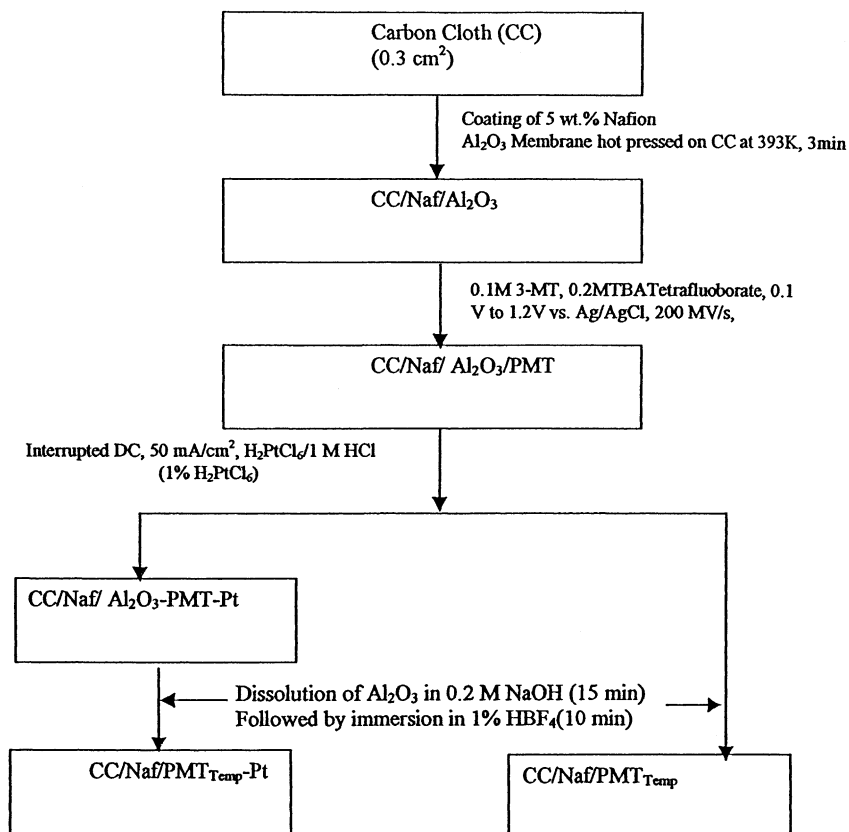
was insulated except for electrical connection. The alumina membrane (0.2 and 60 μm thick and 65% porosity) obtained from Whatman Anapore pore filters was placed on the Nafion-coated carbon cloth (CC) and hot pressed at 393 K for 2 min at a pressure of 50 kg/cm². This configuration of alumina (Al₂O₃) membrane attached Nafion-coated carbon cloth was designated as CC/Naf/Al₂O₃. The area of the working electrode in the case of template attached carbon cloth, taking into account the percentage porosity, was found to be 0.195 cm².

2.2. Electropolymerization of 3-methyl thiophene on CC/Naf/Al₂O₃

The electropolymerization was carried out in acetonitrile, using 0.1 M 3-methyl thiophene and 0.2 M tetrabutyl ammonium tetrafluoroborate, in the potentiodynamic mode by sweeping the potential between 0.1 and +1.6 V versus Ag/AgCl at 200 mV/s. The charge passed between 1.3 and 1.6 V was recorded and denoted as polymerization charge [21]. The charge passed for the polymerization in the present investigation was 600 mC/cm².

2.3. Deposition of Pt particles on CC/Naf/Al₂O₃/PMT_{Temp}

The platinum was electrodeposited by galvanostatic square wave (GSW) method in 1% H₂PtCl₆ and 0.5 M



Scheme 1. Typical procedure for the template synthesis of poly(3-methyl) thiophene nanocones and Pt incorporated poly(3-methyl) thiophene nanocones.

H₂SO₄. A current density of 50 mA/cm² was applied for a total period of 2–8 min in order to vary the loading of Pt on the matrix. The pulse (50 mA/cm²) was applied in start–stop intervals of 10 s each, till the corresponding total period is reached, which is between 2 and 8 min. The whole process of Pt deposition was done before the dissolution of the alumina membrane. The resulting configuration is designated as CC/Naf/Al₂O₃/PMT_{Temp}-Pt.

2.4. Removal of template

The alumina membrane from CC/Naf/Al₂O₃/PMT_{Temp} and CC/Naf/Al₂O₃/PMT_{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. It 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/PMT_{Temp} and CC/Naf/PMT_{Temp}-Pt. A similar experimental condition was adopted to prepare the template-free Pt incorporated poly(3-methyl) thiophene on carbon cloth. The electrode was designated as CC/Naf/PMT-Pt. The details of the synthetic procedure for the preparation of template synthesized poly(3-methyl) thiophene and Pt incorporated template synthesized poly(3-methyl) thiophene are illustrated in Scheme 1.

2.5. Determination of platinum

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.

2.6. Electrochemical and spectroscopic measurements

The electrochemical measurements were performed using a Potentiostat 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 Bio Analytical System, USA was used to prepare electrode using the E-TEK 20 wt.% Pt/C catalyst (purchased from Electrochem Inc., USA). The GSW measurements were performed using EG&G model 283 potentiostat–galvanostat. The X-ray photoelectron spectroscopic studies were performed using a Perkin Elmer PHI 5500 ESCA system using Mg K α as the excitation source.

3. Results and discussion

3.1. Electron microscopic studies

The HR-TEM image of poly(3-methyl) thiophene (without Pt) shown in Fig. 1 clearly reveals the nanocone morphology of poly(3-methyl) thiophene with one cone inserted over the other cone.

Fig. 2a–d shows the electron microscopic images of Pt incorporated template synthesized poly(3-methyl) thiophene nanocones and Pt incorporated template-free poly(3-methyl) thiophene. The bunches of nanocones are distributed throughout the holey carbon grid as revealed from Fig. 2a of Pt-poly(3-methyl) thiophene. In order to demonstrate the presence of Pt on the template synthesized poly(3-methyl) thiophene, electron diffraction image was taken and presented in Fig. 2b. The diffraction pattern of the fine Pt particles is seen as a number of clear concentric rings (these rings can be indexed (from the inside as) 1 1 1, 2 0 0, 2 2 0, 3 1 1 reflectance for fcc Pt) without any spot seen on the ring. This clearly revealed, the presence of fine Pt particles in/on the cones. In the case of Pt deposited on the template-free poly(3-methyl) thiophene, distinct random spots are observed (figure not shown), instead of concentric circles. This suggests that the Pt particles are larger in template-free case, compared to the size of Pt in template-based poly(3-methyl) thiophene. The scanning electron micrograph, shown in Fig. 2c, of poly(3-methyl) thiophene synthesized by template-free method reveals a globular morphology. The Pt deposited on such a matrix (Fig. 2d) is more aggregate in nature and are distributed throughout the polymer. Since, the alumina membrane is removed after the Pt deposition, we presume that, most of the Pt particles will be present inside the nanocone compared to that present on the nanocones.



Fig. 1. HR-TEM image of poly(3-methyl) thiophene nanocones (without Pt).

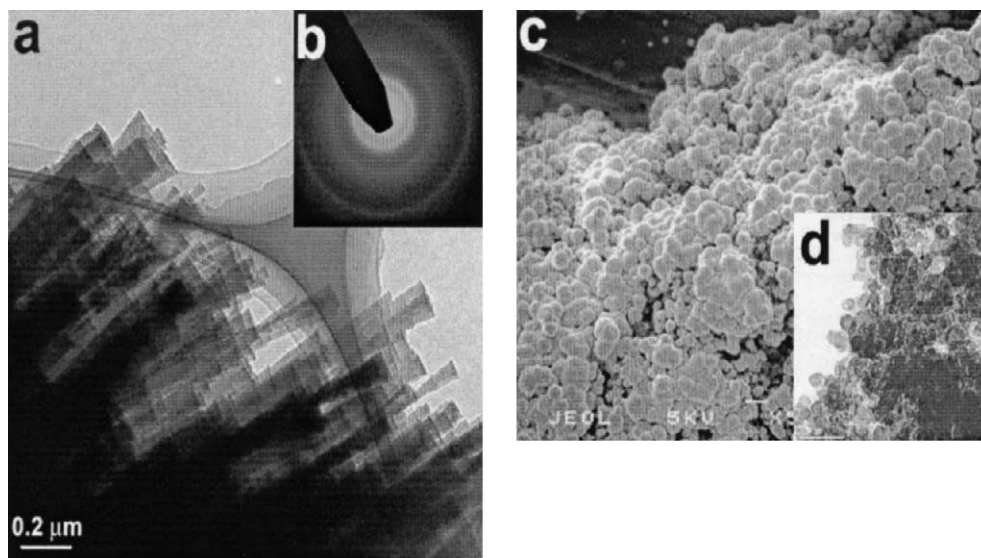


Fig. 2. Electron micrographs of template-based and template-free poly(3-methyl) thiophene. (a) HR-TEM images of template-synthesized Pt incorporated poly(3-methyl) thiophene nanocones. (b) Electron diffraction image of Pt particles in poly(3-methyl) thiophene nanocones. (c) SEM of template-free poly(3-methyl) thiophene. (d) HR-TEM image of Pt incorporated template-free poly(3-methyl) thiophene.

3.2. Characterization of Pt incorporated poly(3-methyl) nanocones by XPS

In order to qualitatively see the presence of Pt as well as to find the oxidation state of the Pt, X-ray photoelectron spectra was taken in the Pt 4f region. The etching experiments were performed at 2 kV and 15 mA and sputtered with Ar at a pressure of 5×10^{-8} mbar for a total period of 360 s with an etching for 120 s, to see the nature of the Pt inside the template-synthesized poly(3-methyl) thiophene. The X-ray photoelectron spectra of the sample before and after 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 and 74.6 eV, which suggest the presence of Pt in the metallic state. The complete etching experiments clearly revealed the uniform distribution of Pt in the metallic state inside the template-synthesized poly(3-methyl) thiophene matrix.

3.3. Evaluation of methanol oxidation activity of CC/Naf/PMT_{Temp}-Pt nanocone and CC/Naf/PMT-Pt electrodes

The CV of Pt-poly(3-methyl) thiophene in the presence of in 1 M H₂SO₄ after the removal of the template is shown in Fig. 3a. A broad peak at -0.0 V in the forward scan was observed, which is due to the ionization of hydrogen on Pt. The CV for the Pt-poly(3-methyl) thiophene in 1 M H₂SO₄/1 M CH₃OH after the dissolution of the template is shown in Fig. 3b. The methanol oxidation was clearly evident from the CV with a maximum current density of 367 mA/cm² at +0.8 V versus Ag/AgCl, with the onset of methanol oxidation starts around 0.01 V itself [21]. Another interesting feature of the CV is that as the applied potential increases, the methanol oxidation current density

also increases without peaking at any particular potential value (in the potential range studied). In the present investigation, the potential was scanned between -0.2 and $+0.8$ V versus Ag/AgCl. Though, there is no peak current observed in the cyclic voltammogram for Pt incorporated template-synthesized poly(3-methyl) thiophene nanocone electrode, the current observed at $+0.8$ V was taken and the values are normalized per unit area (mA/cm²). The difference between the forward and the reverse current was also found to be very low which might suggest the better tolerance of the electrode towards strongly adsorbed intermediates. It was reported [22] that poisoning effect was lower on the Pt dispersed on the polyaniline than the bulk Pt electrodes.

Fig. 3c shows the CV of CC/Naf/PMT-Pt in 1 M H₂SO₄ and 1 M CH₃OH. It is clear from the CV that the onset of methanol oxidation starts around $+0.2$ V in the forward scan and peaks at 0.70 V with a peak current density of 34.3 mA/cm²; the reverse scan shows the oxidation peak at 0.45 V with a peak current density of 25 mA/cm². It is evident from Fig. 3b and c, that oxidation of methanol for Pt incorporated template-synthesized nanocone (Fig. 3b) electrode not only started at a lower potential (190 mV more negative) but also exhibited higher activity in both forward and reverse scans compared to the Pt incorporated template-free poly(3-methyl) thiophene electrode. Since the Pt deposited on the conventionally synthesized poly(3-methyl) thiophene, behaved like a bulk Pt, the curve in Fig. 3c was reminiscent of the Pt electrode [31]. But, though the catalyst is, Pt deposited on the poly(3-methyl) thiophene in both the cases, the curve in Fig. 3b for the templated electrode for methanol oxidation was different compared to the non-templated electrode. The peak potential for methanol oxidation was not observed even up to

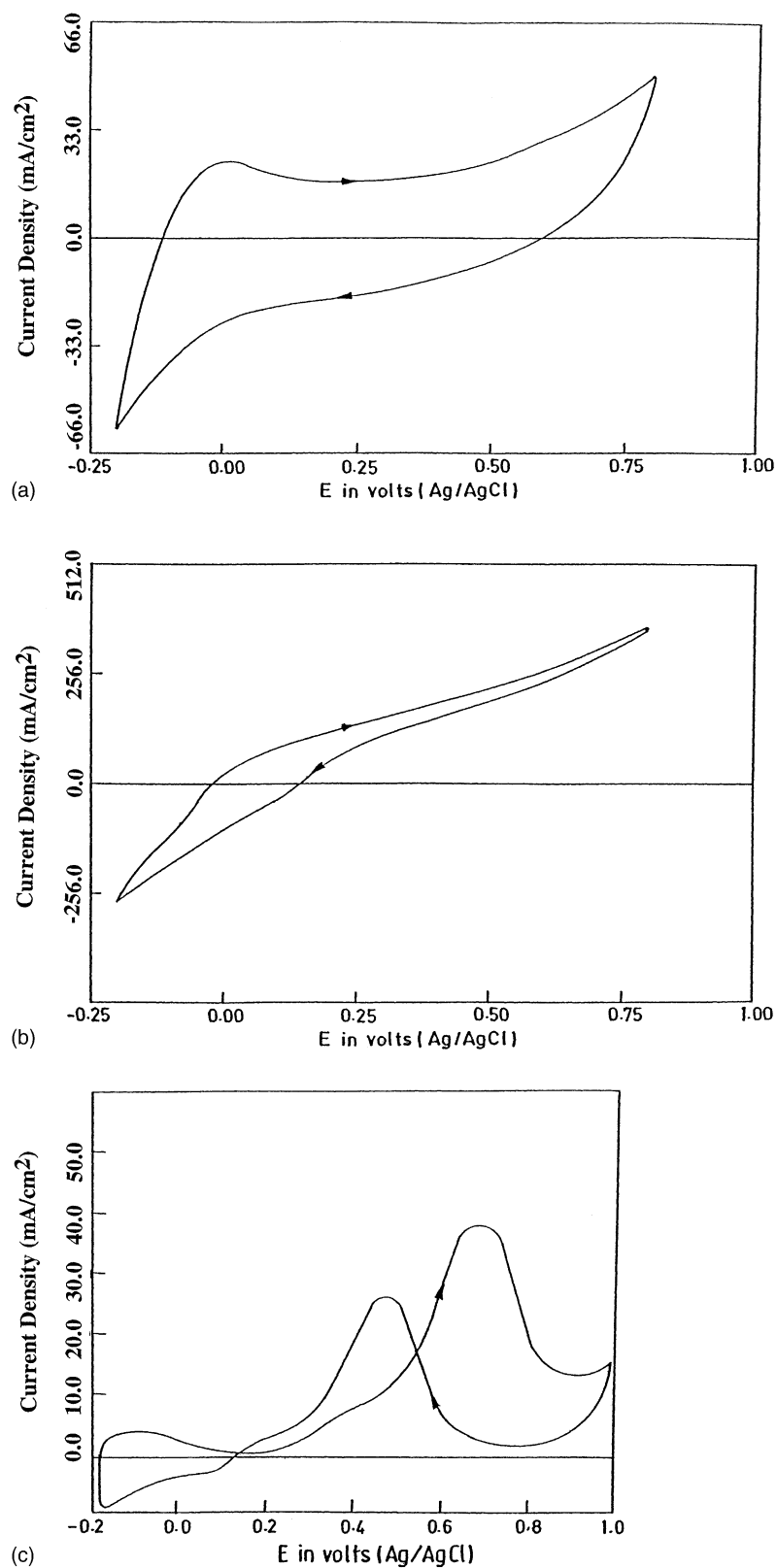


Fig. 3. CVs illustrating the electro-catalytic behavior of the nanocone and non-nanocone based electrodes. Scan rate 50 mV/s. (a) Pt incorporated template-based poly(3-methyl) thiophene (CC/Naf/Al₂O₃/PMT_{Temp}-Pt) electrode (after the removal of template) in 1 M H₂SO₄. (b) Pt incorporated poly(3-methyl) thiophene nanocone (CC/Naf/PMT_{Temp}-Pt, with Pt loading of 60 μg/cm²) electrode (after the removal of template) in 1 M H₂SO₄/1 M CH₃OH. (c) Pt incorporated template-free poly(3-methyl) thiophene (CC/Naf/PMT-Pt electrode, with Pt loading of 80 μg/cm²) in 1 M H₂SO₄/1 M CH₃OH.

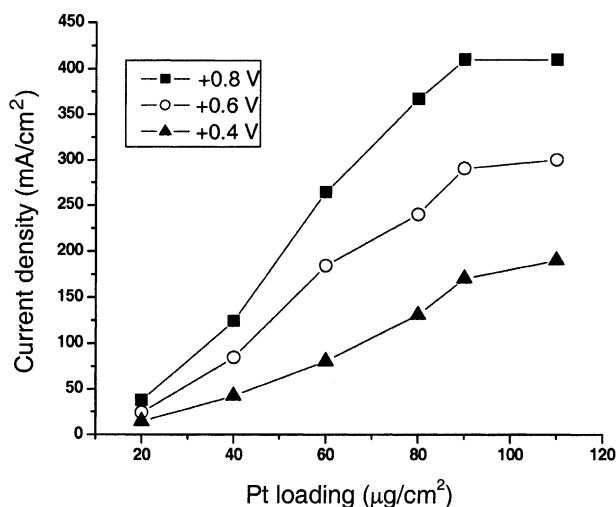


Fig. 4. Variation of current density with Pt loading at +0.4, +0.6, and +0.8 V vs. Ag/AgCl for Pt incorporated templated poly(3-methyl) thiophene nanocone electrodes. Current densities were measured from CV's run in 1 M H₂SO₄/1 M CH₃OH between -0.2 and +0.8 V. Scan rate: 50 mV/s.

+0.8 V versus Ag/AgCl electrode for the templated system. This is the main reason for the differences in the cyclic voltammogram between the two systems. This also probably reflects that the Pt loaded on the templated system was more resistant for oxide formation than the Pt loaded on the conventional poly(3-methyl) thiophene electrode. It is normally observed [32] that a Pt surface at +0.8 V versus Ag/AgCl should be largely oxidized and in the present study with the Pt loaded on the conventionally synthesized poly(3-methyl) thiophene, the same behavior was observed and that was one of the reason for the decrease in activity of methanol oxidation (Fig. 3c) beyond 0.65 V versus Ag/AgCl. In the case of templated system, it appears that the Pt particles in the templated nanocones was comparatively more resistant for the Pt oxide formation and this might be one of the reason for the continuous increase in activity (Fig. 3b) even beyond 0.65 V versus Ag/AgCl electrode. A similar result also has been reported in the literature [33]. Liu et al. [33], observed a maximum activity of 170 mA/cm² at +0.91 V versus saturated calomel electrode (SCE) for Pt-Ru/Vulcan carbon catalyst.

3.4. Variation of methanol oxidation with Pt loading

Fig. 4 shows the variation of activity of methanol oxidation with Pt loading on template-synthesized poly(3-methyl) thiophene at +0.8, +0.6, and +0.4 V versus Ag/AgCl electrodes, respectively. It is evident that as the loading increases, the activity of methanol oxidation at +0.8 V increases almost linearly up to 410 mA/cm² (with a Pt loading of 90 µg/cm²) from 37.7 mA/cm² (with a Pt loading of 20 µg/cm²). Beyond this loading the activity increase is not linear and reaches a saturation value of 410.2 mA/cm² (with

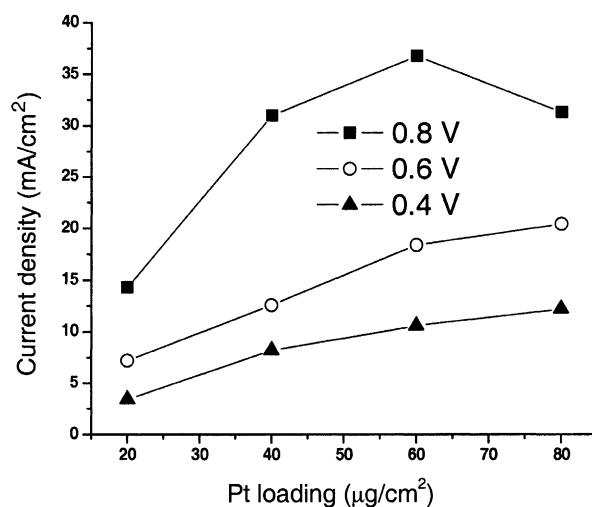


Fig. 5. Variation of current density with Pt loading at +0.4, +0.6, and +0.8 V vs. Ag/AgCl for Pt loaded on template-free poly(3-methyl) thiophene nanocone (conventional) electrodes. Current densities were measured from CV's run in 1 M H₂SO₄/1 M CH₃OH between -0.2 and +0.8 V. Scan rate: 50 mV/s.

the Pt loading between 90 and 110 µg/cm²). In the case of +0.6 V, the activity was increased from 24.2 mA/cm² (Pt loading 20 µg/cm²) to 290.6 mA/cm² (Pt loading 90 µg/cm²). And finally at +0.4 V, the activity was increased from 14.6 mA/cm² (Pt loading 20 µg/cm²) to 190.2 mA/cm² (Pt loading 110 µg/cm²).

Fig. 5 shows the variation of activity of methanol oxidation with Pt loading on conventional poly(3-methyl) thiophene at +0.8, +0.6, and +0.4 V versus Ag/AgCl electrodes, respectively. At +0.8 V, as the Pt loading increases the activity was increased from 14.3 mA/cm² (Pt loading 20 µg/cm²) to 36.8 mA/cm² (Pt loading 60 µg/cm²) but beyond this loading the activity decreases and reached 31.3 mA/cm² (Pt loading 80 µg/cm²). The decrease in activity might be due to the formation of the Pt oxide at +0.8 V, which is not observed for the Pt loaded on the templated nanocone electrode. At +0.6 V, the activity was increased from 7.2 to 20.4 only, for the Pt loading of 20 and 80 µg/cm². And at +0.4 V the activity was increased from 3.4 to 12.2 mA/cm², for the Pt loading of 20 and 80 µg/cm². It is very clear from Figs. 4 and 5 that the activity of methanol oxidation for the templated nanocone electrode at +0.4 V versus Ag/AgCl electrode was nearly 16 times more than the non-templated electrode.

3.5. Chronoamperometric response of CC/Naf/PMT_{Temp}-Pt, GC/20 wt.%Pt/C (E-TEK) and CC/Naf/PMT-Pt electrodes

Fig. 6 shows the activity of CC/Naf/PMT_{Temp}-Pt and CC/Naf/PMT-Pt with respect to time at +0.6 V. The percentage decrease of the catalytic activity of CC/Naf/PMT_{Temp}-Pt was around 14.3% at the end of 2 h

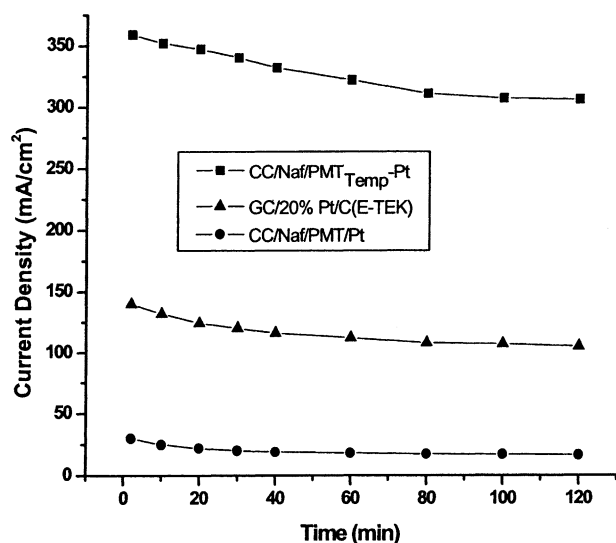


Fig. 6. Variation of current density with time in 1 M H₂SO₄/1 M CH₃OH at +0.6 V vs. Ag/AgCl.

(359–305.7 mA/cm²), whereas the corresponding decrease for GC/20 wt.% Pt/C (E-TEK) was 25% (140–105 mA/cm²) and for CC/Naf/PMT-Pt was 44.6% (30–16.6 mA/cm²). The initial activity of CC/Naf/PMT_{Temp}-Pt is higher by nearly 12 times compared to CC/Naf/PMT-Pt and 2.5 times compared to GC/20 wt.% Pt/C (E-TEK) electrodes. The Pt loading was kept at 80 μg/cm² for all the electrodes.

4. Conclusions

The electrochemical synthesis and characterization of conducting poly(3-methyl) thiophene nanocones and Pt incorporated nanocones by template method have been achieved. The Pt incorporated nanocones have been used as the electrode material for methanol oxidation, a reaction of technological importance for DMFC. The better utilization (by means of high activity at low Pt loading) and stability of the template-synthesized Pt incorporated poly(3-methyl) thiophene electrode have been demonstrated by comparing with Pt incorporated template-free poly(3-methyl) thiophene electrode. One of the major impediments to the commercialization of DMFC is the higher requirement of Pt catalyst. The Pt loading could be considerably lowered by increasing its utilization. The present Pt incorporated template-synthesized polymeric nanocones on the carbon cloth, not only increase the electronic–ionic contact, but also provides an easier electronic pathway between the electrode and the electrolyte, which increases the reactant accessibility to the catalytic sites.

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