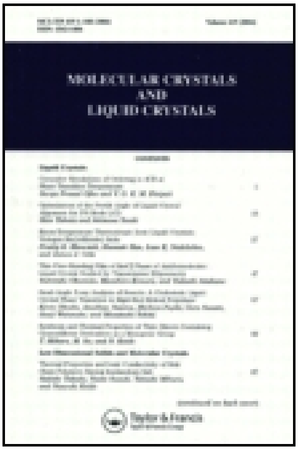

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Fabrication of PAN/Pt Composite Electrode for Direct Methanol Oxidation in Aqueous Media

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Version of record first published: 22 Sep 2010

To cite this article: Miaomiao He, Jungsik Choi, Yongkeun Son, Youngkwan Lee, Dae-Ho Yoon & Su-Jeong Suh (2007): Fabrication of PAN/Pt Composite Electrode for Direct Methanol Oxidation in Aqueous Media, Molecular Crystals and Liquid Crystals, 464:1, 23/[605]-30/[612]

To link to this article: http://dx.doi.org/10.1080/15421400601028468

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 23/[605]–30/[612], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601028468

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This study was focused on the preparation and characterization of conducting polymer and metal composite, PAN/Pt, electrodes showing catalytic activity in acidic aqueous media. Electropolymerization deposited PAN thin film on ITO and this film was used as a Pt matrix. The polyaniline (PAN) matrix could adopt Pt particles catalysts into polymer itself visa either way of spontaneous reaction between PAN and $PtCl_6^{2-}$ *or electrochemical reduction of the Pt (IV). Both procedures ended up with the formation of PAN/Pt composites. In-situ spectroelectrochemistry was used to investigate the composite formation processes. These composite electrodes were identified with SEM and EDAX. Catalytic decomposition of methanol on these electrodes was observed by using cyclic voltammetry method.*

Keywords: composite electrode; electrocatalytic; methanol oxidation; platinum; polyaniline

The authors are grateful to acknowledge the financial support from The ministry of Commerce, Industry, and Energy (RRC No 20020322-100) and The ministry of Education and Human resources Developement (Brain Korea 21 program).

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INTRODUCTION

Inherently conducting polymers are very important materials because they have many of distinctive optoelectronic properties and potential applications [1–3]. Among them polyaniline (PAN) have been known one of the most widely studied conducting polymers [4–8]. It shows good stability in air and controllable conductivity depending on its redox states. It also shows nice electrochromic property based on proton doping.

Platinum and Pt-alloy catalysts induce various electrochemical reactions; oxygen reduction, hydrogen oxidation and oxidation of small organic molecules, such as HCOOH, HCHO, CH_3OH, and so on. Methanol is a unique organic fuel can be used directly in generator a cell (DMFC), which is one of the most promising fuel cells in the future [9,10]. Making the particle size of catalysts smaller for this purpose, the electrocatalytic activities, in most cases, are enhanced. However for practical applications, supporting materials are needed to hold these catalysts safely and to collect current properly in acidic media.

It is polyaniline that could meet those two requirements. Especially electrosynthesis offers highly porous PAN which can be used as a matrix for holding the electrocatalysts inside. This product is known to be stable in the potential window in which methanol oxidation occurs and highly conductive in that potential window, therefore we can minimize any impediment for electron transport between platinum and substrate electrode. These conducting polymer/metal composite electrodes could be easily obtained by the chemical or electrochemical reduction of metal ions. These composite electrodes have relatively large metal surface area and are expected to be of use in electrocatalytic system for fuel cell.

This study is focused on the preparation and characterization of PAN/Pt composite electrodes that show better catalytic activity compared to other composite electrode *i.e.*, PEDOT/Pt, because PANi is the only active material in acidic electrolyte. In previous work it was shown that the soluble PEDOT can provide easy way of matrix fabrication but the matrix itself is not very active electrochemically in aqueous conditions. PAN as a thin film was directly prepared onto ITO glass electrode by electropolymerization. Pt particles were dispersed into polymer film by two methods; the electrochemical formation by applying constant potential or potential cycle and the spontaneous redox reaction between reduced PAN and $PtCl_6^{2-}$. *In-situ* spectroelectrochemistry was used to investigate the composite formation processes. The composite electrodes were inspected with SEM and EDAX. Catalytic decomposition of methanol on these composite electrodes was observed with cyclic voltammetry method.

EXPERIMENTAL

Chemicals and Apparatus

ACS grade chemicals were obtained from Sigma-Aldrich Ltd. and used without further purification except aniline. Monomer aniline was purified by using an Al_2O_3 column and stored in a refrigerator before use. Three-electrode system adopting indium tin oxide (ITO, Samsung Corning, Korea) glass working, Pt plate counter and Ag/AgCl (sat'd KCl) reference electrodes was connected with potentiostat (BAS 100B, Bioanalytical Systems Inc., USA) for electrochemistry. *In-situ* UV/Vis spectra were measured by using UV/Vis spectrophotometer (HP 8453, HP, USA). The final PAN/Pt composite electrodes were observed with SEM (JSM 6700F, JEOL, Japan) and EDAX (JEM 2100 F (JEOL, Japan) with EDS unit (Oxford INCA Energy)). All electrochemical experiments were performed after N_2 purging for 10 min. All potentials in this work referred to the Ag/AgCl (sat'd KCl) electrode.

Preparation and Characterization of Composite Electrodes

PAN was synthesized as thin films on ITO electrodes by applying cycling or constant potential. The electropolymerization was completed with a solution of 0.1 M aniline in 0.5 M H_2SO_4. Polymer characterization was carried out in a monomer-free electrolyte using cyclic voltametry(CV) and *in-situ* UV/Vis spectrophotometry. The PAN films were fully reduced with constant potential before making the composite electrodes and this reduced PAN was dipped in 0.01 M K_2PtCl_6 aqueous solution for 10, 20, 30 and 60 min, respectively. The composite electrodes were also prepared by electrochemical reduction 0.01 M K_2PtCl_6 in 0.5 M H_2SO_4 solution. Methanol oxidations were performed in 0.5 M methanol in 0.2 M H_2SO_4 solution.

RESULTS AND DISCUSSION

PAN thin films were prepared by electropolymerization of aniline in acidic media by using both ways of potential cycling (PC) of $-0.30 \sim 1.00$ V and applying constant potential (CP) of 0.9, 1.0, and 1.1 V for 60 sec. spectroelectrochemistry provided typical spectral changes and current responses against the redox of this polymer product and these (not shown) are well matched with reported results of PANi [4,11–12]. The only different thing exist between PC polymer and CP polymer was morphology. As shown in Figure 1(a), PAN thin film synthesized by PC has porous and three-dimensional network structure which is homogeneously distributed all over the ITO

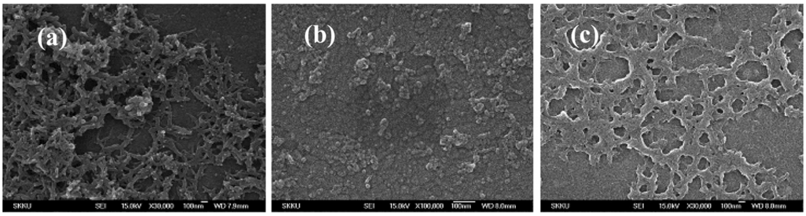

FIGURE 1 SEM images of PAN thin films synthesized by (a) PC method (− 0.30 ~ 1.00 V for 15 cycles), (b) CP method (1.00 V for 60 sec.) and (c) CP method (1.10 V for 60 sec.). These are in similar time scale for polymerization.

electrode. On the other hand, Figure 1(b) show that polymer synthesized by CP method during the similar time scale was patchily distributed the ITO. Applying higher potential, they grew two-dimensionally and fill up the electrode surface as shown in Figure 1(c). These results suggest that polymer thin films by PC method are more suitable form to be a catalyst matrix.

The most porous PAN prepared by PC method was selected be used as a matrix and fully reduced electrochemically. The reduction of polymer was done by applying constant potential. There is almost no current change after 300 sec with the application of −0.30 V and also no definite spectral change was observed. The reduced PAN electrode was dipped into 0.01 M K_2PtCl_6 solution. Polymer films were oxidized by K_2PtCl_6 and part of Pt (IV) was simultaneously reduced to Pt (0). The Pt particles can grow and dispersed within the polymer matrix. The absorption spectral change of the PAN due to this redox reaction was monitored *in-situ*. The spectral changes are in Figure 2(a). As the reaction proceeds, absorption at longer wavelength increases. Representative spectral changes at 550 nm and 900 nm are appeared in (b) of the same Figure. The reduced PAN is changed to oxidized state rapidly at the beginning of the reaction, that is why we can not observe a spectrum which has flat structure above 600 nm. This spectral change in tells how fast the reaction completed in this process.

Figure 2(c) shows the chronoamperogram for Pt(IV) reduction. The formal reduction potential of $PtCl_6^{2-}$ is *ca.* 0.5 V, however, it was reported that the reduction peak current of platinum deposition appears at more negative potentials than 0.5 V because of a kinetic hindrance of $PtCl_6^{2-}$ in polymer film [13]. Therefore in this study, we applied more negative potential to form platinum particles. Platinum was formed into PAN electrodes from 0.01 M K_2PtCl_6 in 0.5 M H_2SO_4 solution by applying −0.25 V for 900 sec. As soon as applying external potential, the current increases and decreases swiftly at very

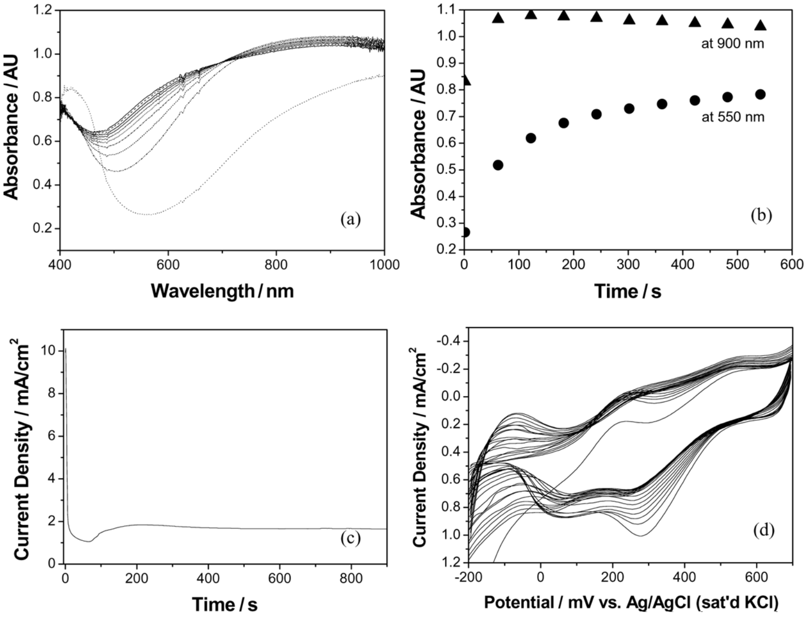

FIGURE 2 Changes during various Pt particle formation processes: (a) UV/Vis spectra changes during spontaneous redox reaction (for 10 min), (b) absorbance changes measured at 550 and 900 nm from (a), (c) current change after applying constant potential (at -0.25 V) and (d) cyclic voltammogram earned by PC method (for 20 cycles).

the first moment due to the charging process. After a short induction time the current is increased to form wide peak and reached to a plateau region. Potential cycling method ($-0.20 \sim 0.70$ V for 5 and 20 cycles) for Pt formation was also done on the PAN electrode and the cyclic voltammogram is shown in Figure 2(d). It can be noticed that the shape of cyclic voltammogram is similar to that of PAN polymer. But the reduction current appeared at the most negative potential region is unmistakable in this CV. At this potential region PAN is in reduced form and nonconductive, but the reduction of Pt (IV) makes the polymer oxidized and conductive. In this way PAN can collect both reduction current due to oxidized PAN and Pt (IV).

SEM images of these composite electrodes were carefully investigated and EDAX spectrum was also obtained. Figure 3(a) shows SEM image of composite electrode prepared by spontaneous redox reaction for 1 hour. Even longer reaction time allowed, there was no big difference in quantity of catalyst in this experiment condition

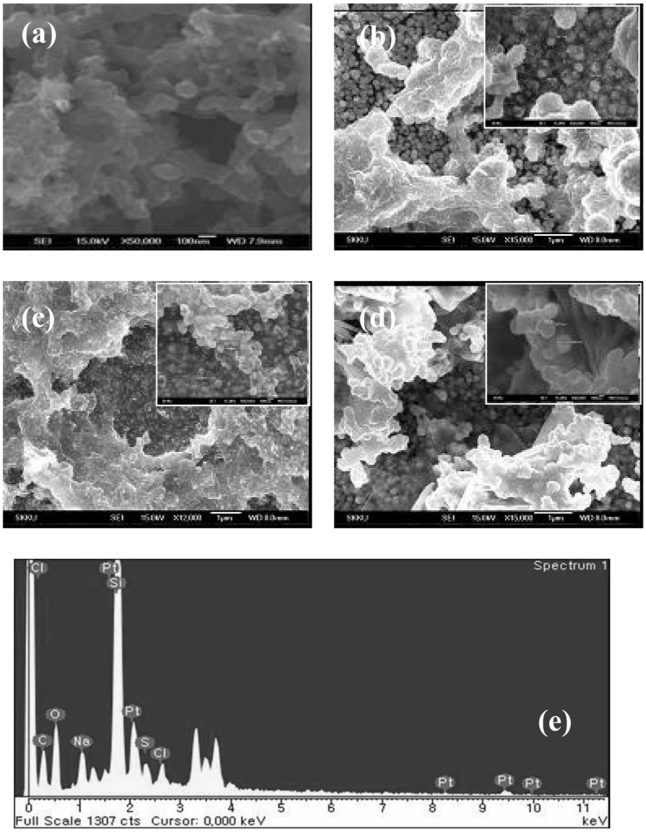

FIGURE 3 SEM images and EDAX spectrum of composite electrodes prepared by (a) spontaneous redox reaction for 1 hour, (b) CP method at $-0.25\,\mathrm{V}$ for 900 s, (c) PC method for 5 cycles, (d) PC method for 20 cycles and (e) EDAX spectrum of composite electrode.

(image not shown). That is, even if they have longer reaction time, not much more platinum particles were formed because the amount of reduced form PAN is limited on the electrode. For electrochemical methods, platinum particles were evenly well distributed inside and out of the matrix. EDAX spectrum taken from the composite proved the presence and distributed Pt particles. The particles were in $100 \sim 200\,\mathrm{nm}$ size and also in spherical shape with spikes on it.

We lastly checked the electrocatalytic characteristics of composite electrodes for methanol oxidation using CV method. Figure 4(a) shows there was no significant response related to methanol oxidation. Because enough catalysts were not created on polymers and the

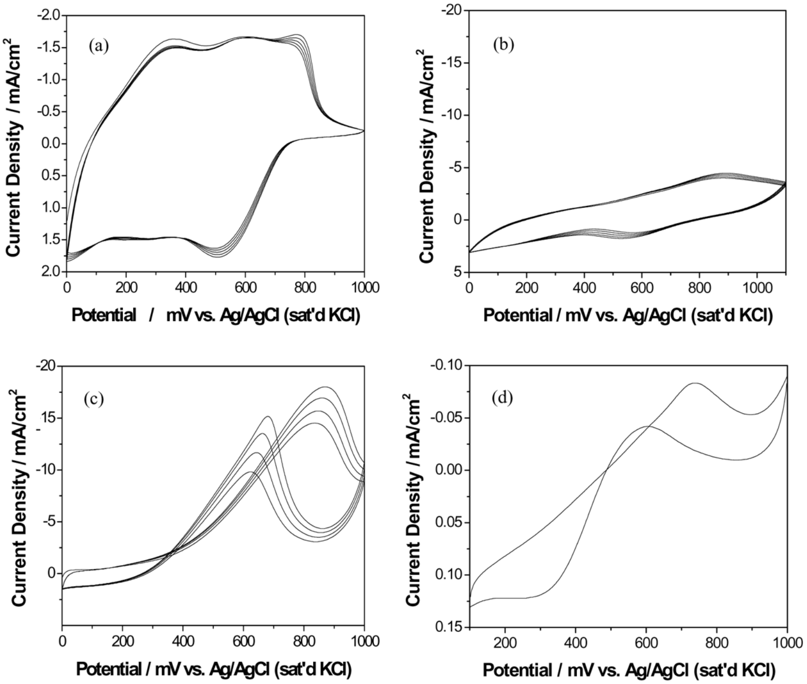

FIGURE 4 CVs of methanol oxidation on (a) composite electrode by spontaneous redox reaction for 1 hour, (b) composite electrode by CP method (at $-0.25\,V$ for 900 sec), (c) composite electrode by PC method (for 20 cycles) and (d) pure Pt electrode.

mostly exposed was the polymer to the methanol solution, therefore the only PAN-like property of was appearing. This fact agrees with results of SEM images of Figure 3(a) in which little platinum found. When electrosynthesized PAN/Pt composite electrodes were used, however, cyclic voltammogram displayed two remarkable catalytic oxidation peaks as in Figure 4(b) and (c) [9–10]. But Figure 4(b) indicated relatively small current density for the oxidation. It was very difficult to distinguish their difference in the catalytic activity by SEM pictures, but judging from results of methanol oxidation, composite electrode by PC method perhaps provided more active surface area for the oxidation.

There is one important thing that should be pointed in this result. The peak current density of composite electrode for methanol oxidation is two hundred times bigger than that of pure platinum electrode and this result is better than other reported results [14–16].

This implies that the composite electrode could provide the better catalytic activity for methanol oxidation.

CONCLUDING REMARKS

Fine catalysts of platinum particles induce the profitable electrochemical reactions such as the oxidation of methanol which is one of the most promising fuels for the generator cells in future. However for practical applications, supporting materials (or matrixes) are needed to hold these catalysts and to keep electrical contact between metals and electrode. Conducting polymers, especially polyaniline have many advantages for this purpose.

Among two electropolymerization methods, potential cycling provided PAN matrix of three-dimensional network structure. Introducing platinum particles into the polymer matrix, preparation of PAN/Pt composite electrodes could be completed. K_2PtCl_6 was used to introduce platinum particles. Platinum particles were dispersed into polymer films by two methods of CP and PC. There found to be $100 \sim 150$ nm Pt particles with spikes on them. Composite electrodes were characterized by *in-situ* spectroelectrochemistry, SEM and EDAX. These composite electrodes showed the better catalytic behavior for methanol oxidation compared to PEDOT/Pt composite electrode. We drew only qualitative result in this study, so quantitative analysis is progressing present for more delicate analysis.

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