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Notes

The Preparation of Polyaniline Electrode Modified by Copper Phthalocyanine on Supporting Carbon Paper

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Abstract: Cathode materials for the polymer electrolyte membrane fuel cell was prepared by electropolymerization of aniline at carbon paper in the presence of copper tetrasulfonato-phthalocyanine (CuTsPc) and their electrocatalytic behavior was studied. The amount of polyaniline and CuTsPc in the carbon paper was determined by UV spectroscopy of residual solution in electrochemical cell. The redox process of the prepared electrodes was investigated with cyclic voltammetry. The highest reversible current density was observed at the electrode that contains 27.6 wt% of polyaniline and 19.7 wt% of CuTsPc. The morphology of composite electrode from SEM showed the presence of large cluster of polyaniline with CuTsPc, which should be more finely interpenetrated into macropores of carbon for the better electrocatalytic activity.

Introduction

The catalytic properties of metal phthalocyanines have been widely studied for diverse applications. Various techniques were described in the literature for the preparation of the electrodes containing metal phthalocyanines, such as dipping techniques, vacuum sublimation, solvent evaporation, chemical bonding to a substrate, irreversible adsorption onto an electrode surface, and composite with carbon.[1-3] However from the practical point of view, the uses of metal phthalocyanine are still limited because of the instability of the modified electrode, the low charge transfer rate through poor electroconductive electrode, or the too small contact area between the substrate and reagent.

A promising method to overcome the above limitations is to disperse the electrocatalytic material at the molecular level. For the molecular dispersion of metal phthalocyanine, organic conductive polymers are good candidates for the matrix materials.[4-6] Polyaniline, polypyrrole, polythiophene, and their derivatives have been widely studied for organic conductive materials because of their relatively high conductivity, high chemical stability, and easy preparation. Metal phthalocyanine catalyst was reported to be easily incorporated into conductive polymers as a counter-anion during the electrochemical polymerization of monomers in the presence of metal phthalocyanine catalyst.

A possible application of phthalocyanine-modified polymer is electrodes in polymer electrolyte membrane fuel cells (PEMFCs). PEMFCs are characterized by high power density, low operating temperature, and minimal environmental pollution. But for the commercial application of PEMFC, it has to decrease the production cost by decreasing or eliminating the use of platinum catalyst on electrodes.[7,8]

In this study, CuTsPc was incorporated into polyaniline at carbon papers and their electrocatalytic behavior for oxygen reduction was examined for the application in cathode materials in PEMFC.

Experimental

Material and Chemicals. Supporter for electrode material was carbon papers from Toray. The carbon black for supporting catalyst was Vulcan XC-72, that was used for preparing the compara-

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tive electrode. The binding polymer in preparing electrodes was poly(tetrafluoroethylene) (PTFE) suspension from Aldrich. Diluent used for manufacturing electrode was Mic Sol from Aldrich. Aniline and tetrasulfonated copper phthalocyanine (CuTsPc) was purchased from Aldrich.

Equipment and Apparatus. The uniform dispersion of particles in manufacturing electrodes was promoted by the ultrasonic treatment with ultrasonicator (VCX 600, Sonics and Materials). Electrode materials were deposited on carbon supporter by using bar coater (0.3 mm). All the electrochemical experiments was carried out in a three-compartment electrochemical cell with 273A potentiostat of EG & G. A TOPCON SM-500 instruments was used at 25 KV for scanning electron microscope. A UNICAM HELIOS Alpha UV/VIS spectrophotometer was used for quantitative analysis of aniline and CuTsPc.

Preparation of Electrodes.

Carbon Electrode: Carbon papers was treated with immersion in PTFE suspension, dried for 24 hrs at room temperature, and sintered in tubular furnace for 25 minutes at 350°C under nitrogen atmosphere. 1 g Vulcan XC-72 was mixed with 8 mL Mic Sol and sonicated for 15 minutes. The obtained slurry was stirred with 0.5 g PTFE suspension to give carbon paste. The carbon paste was coated on carbon papers with bar coater, dried for 24 hrs at R.T., 24 hrs at 100°C, and sintered for 25 minutes at 350°C.

PAni/C Electrode: Polyaniline was electrochemically polymerized at the prepared carbon electrode in 100 mL 1 N HCl solution of aniline 4.65 g (50 mmole). The solution was deaerated by the nitrogen bubbling for 30 minutes. Cyclovoltammetric method was chosen for the electrochemical polymerization at the scanning range from 0.5 to -0.8 V with various cycle number. The woking electrode was the prepared carbon electrode with SCE reference electrode and counter electrode was glassy carbon.

PAni-CuTsPc/C Electrode: 10 mL aqueous solution of CuTsPc with concentration of 10^{-3} Mol/L was added into the 90 mL 1 N HCl solution containing 4.65 g (50 mmole) of aniline. Other processes for electrochemical polymerization with simultaneous doping of CuTsPc were same as the preparation of above PAni/C electrode.

Voltage-Current Profiles. Voltage-current profiles through electrochemical measurements were obtained with the prepared electrodes as working electrodes, SCE reference electrode, and glassy carbon counter electrodes. The electrochemical measurements were performed with saturated solution of nitrogen or oxygen in 0.5 Mol/L H_2SO_4 solution.

Results and Discussion

To confirm the incorporation CuTsPc during the electrochemical polymerization of aniline, aniline was electrochemically polymerized at the surface of ITO glass, that is then analyzed by UV/VIS spectrophotometer. Figure 1 shows the UV/VIS spectra of pure polyaniline and polyaniline incorporated with CuTsPc, that were prepared by electrochemical polymerization by cyclovoltammetry. Electrochemical polymerization was conducted in acidic solution (1 N HCl) of aniline with scanning velocity 50 mV/sec and 20 cycles at the range of -0.8~0.7 V. The UV/VIS spectrum of polyaniline depends on its oxidation state i.e. leucoemeraldine, emeraldine, and pernigraniline, which is easily transformed to other oxidation state by applying potential. From the spectra in Figure 1, the form of polyaniline in electrode is almost leucoemeraldine, that results from the final reductive scanning in cyclovoltammetry.[9] In comparison with spectrum of pure polyaniline, the spectrum

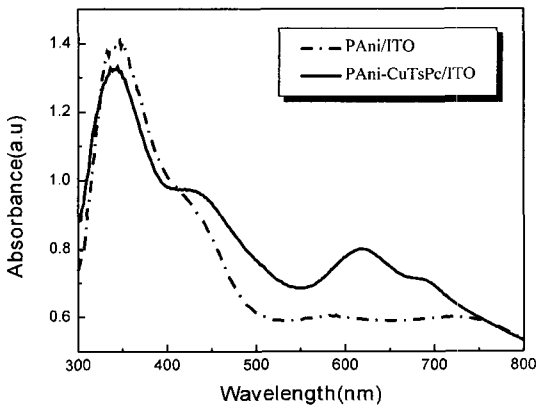

Figure 1. UV/VIS spectra of PAni and PAni-CuTsPc on ITO substrate.

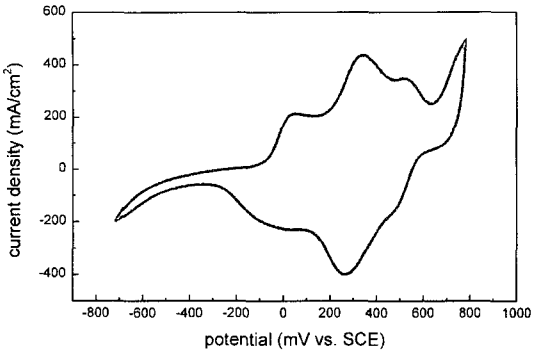

Figure 2. Cyclic voltammogram of carbon electrode during electrochemical polymerization of aniline by cyclic voltammetry at 20th cycle.

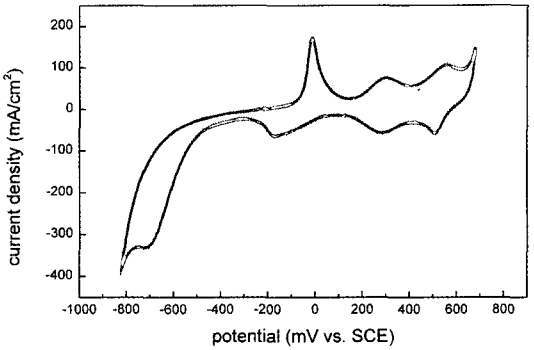

Figure 3. Cyclic voltammogram of carbon electorde during electrochemical polymerization of aniline in the presence of CuTsPc by cyclic voltammetry at 20th cycle.

incorporated with CuTsPc shows characteristic absorption peaks of CuTsPc at 440 and 630 nm.

Electrochemical polymerization of polyaniline at carbon papers were performed under the same electrochemical condition. The formation and its mechanism of polyaniline film at electrode has been intensively reported in literatures.[10] The shape of voltammogram and potential of oxidation and reduction are similar to the literature. Figure 2 and 3 show the cyclic voltammogram of electrochemical polymerization of polyaniline at carbon papers after 20 cycles. The electrochemical polymerization of aniline is generally explained by the coupling of aniline radical cation formed through the loss of electrons. The formation of aniline radical cation was observed near 750 mV. The two redox couples at 50 and 500 mV are reported as the formation of radical cation and radical dication of polyaniline. The middle peak of 350 mV is known as result of degradation of radical cation to give benzaquinone.

Electrochemical polymerization of polyaniline in the presence of CuTsPc shows different shape of cyclic voltammogram as in Figure 3, which is characterized by relative strong current at 50 mV. This tendency supports that CuTsPc can strongly prompt the radical cation formation in polyaniline as well as inhibit the degradation of polyaniline to benzaquinone.

The quantities of polyaniline and CuTsPc that is deposited at carbon papers were analyzed by UV/VIS spectra of residual electrochemical solution. The concentration of aniline and CuTsPc in residual electrochemical solution could be determined by absorbance peak of aniline and CuTsPc, that is compared with calibration curve obtained from prepared solutions of aniline and CuTsPc with known concentrations.

Table I shows the electrodes containing various amount of polyaniline and CuTsPc that were pre-

Table I. The Amount of Polyaniline and CuTsPc Incorporated at Carbon Papers by Electrochemical Polymerization

No. of Cycles	Wt% of PAni	Wt% of CuTsPc	Ani/CuTsPc[a]
10	17.2	12.9	14.4
15	20.0	18.7	11.6
20	26.8	19.2	15.1
25	27.6	19.7	15.1
30	28.8	20.2	15.4
35	30.4	21.7	15.1
40	34.8	29.4	12.8

[a]Mole ratio of repeating aniline unit to CuTsPc.

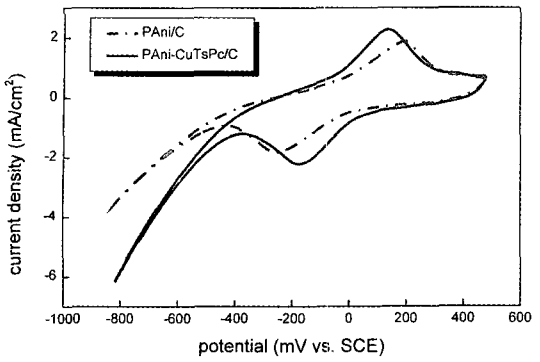

Figure 4. Cyclic voltammogram of PAni/C and PAni-CuTsPc/C electrodes in nitrogen saturated solution of 0.5 M H_2SO_4.

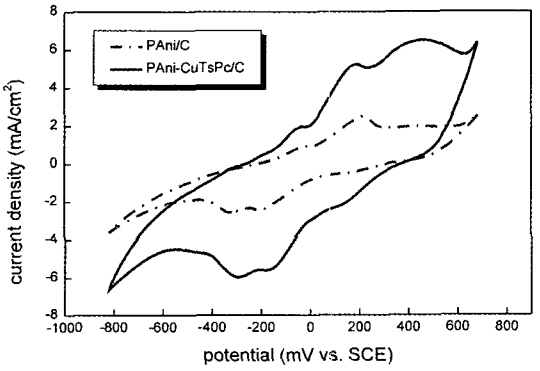

Figure 5. Cyclic voltammogram of PAni/C and PAni-CuTsPc/C electrodes in oxygen saturated solution of 0.5 M H_2SO_4.

pared by increasing number of cycling in cyclic voltammetry during electrochemical polymerization. The mole ratio of aniline to CuTsPc in electrode lies between 11~15, which is less than mole ratio 20 in electrochemical solution.

The cyclic voltammogram of polyaniline or polyaniline incorporated with CuTsPc shows a couple of redox current due to oxidation and reduction of polyaniline as shown in Figure 4. It is also observed that the presence of CuTsPc decreases the oxidation potential of polyaniline. Figure 5 shows the cyclic voltammogram of PAni/C and PAni-CuTsPc/C electrodes in the saturated electrochemical solution with oxygen. As shown in Figure 5, the presence of CuTsPc results in large increase of oxidation and reduction current,

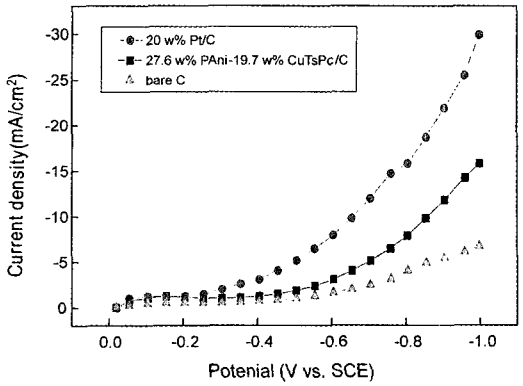

Figure 6. Current-potential curves of Pt, PAni/C, and PAni-CuTsPc/C for oxygen reduction in oxygen saturated solution of 0.5 M H_2SO_4.

which indicates that CuTsPc mediates the oxidation or reduction of polyaniline. The electrocatalytic reduction of oxygen with metal phthalocyanine in organic conductive polymer was widely reported in the literatures.[11] The mechanistic role of oxygen was generally explained as four-electron reduction, that is strongly dependent on metals of phthalocyanine and microenvironmental condition.[2] Although the current correlated to the oxygen reduction was expected in this study, any remarkable asymmetric reduction current could not be observed irrespective of scanning direction. This phenomena is different from the reported similar studies.[12] It is deduced that copper phthalocyanine is much less effective in oxygen reduction than other metal phthalocyanine including iron or cobalt.

Among the electrodes that were prepared in this study, the electrode containing 27.6% polyaniline and 19.7% CuTsPc showed the largest current density. The current density of PAni-CuTsPc/C electrode was compared with the commercial platinum electrode as shown in Figure 6. Although the reduction current of PAni-CuTsPc/C is lower than that of Pt/C electrode, it is assumed that the stronger catalytic power is possible through the systematic modification of electrode with metal phthalocyanine.

Figure 7 shows the SEM images of carbon, PAni/C, and PAni-CuTsPc/C electrodes. The particle size of PAni and PAni-CuTsPc were observed as much larger than that of carbon particles. It is

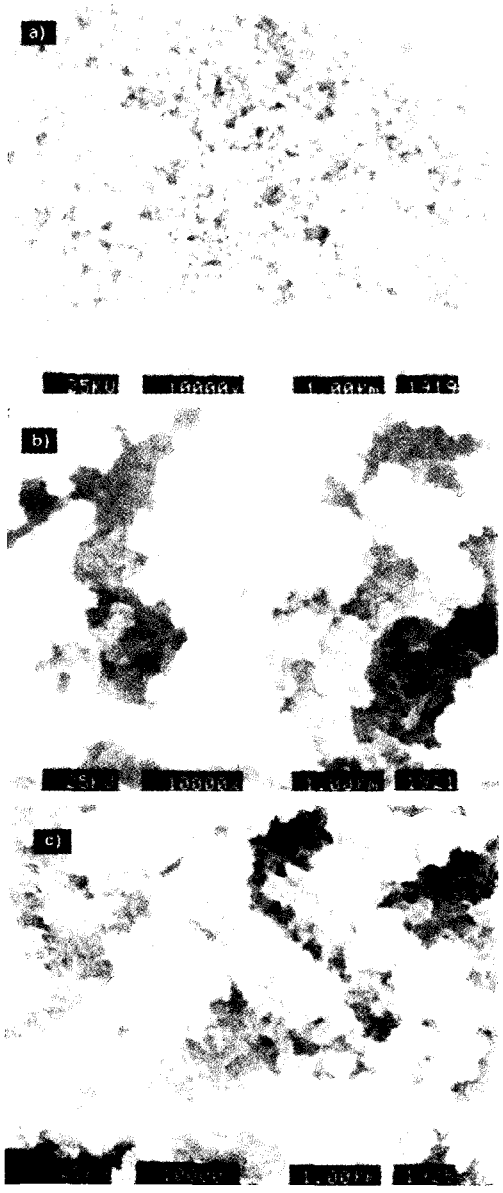

Figure 7. SEM images of (a) bare carbon electrode, (b) PAni/C electrode, and (c) PAni-CuTsPc electrode.

generally accepted that the surface area of catalyst makes the most dominant effect on the efficiency of catalyst. This morphology and paticle size of polyaniline in Figure 7 illustrates that the efficiency of composite electrode in this study can be improved through the finer dispersion by more controlled electrochemical condition, which is under study.

Conclusion

Polyaniline electrode was prepared at carbon papers with incorporation of CuTsPc through the electrochemical polymerization. The composition of electrode was analysed with UV/VIS spectrophotometric method. The reversible current density resulting from the redox process of electrode materials increases with increase of polyaniline and CuTsPc but decreases after a maximum point that contains ca. 28% polyaniline and 20% CuTsPc respectively. For the better characteristics for electrode materials, the method that leads to the finer dispersion CuTsPc as well as polyaniline at carbon papers should be found.

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