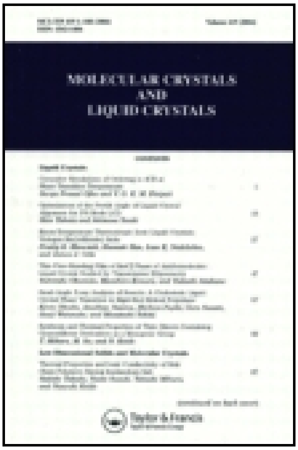

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Metallization of Printed Circuit Boards Using Conducting Polyaniline

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A novel process using polyaniline for plating through hole technology has been developed. Polyaniline was dip-coated onto printed circuit boards and in turn acted as a thin conducting electrode for the electrolytic metallization of Cu on the through holes. This eliminates the necessity for expensive precious metal seeds and toxic electroless copper baths. This process offers simplification, cost reduction, and performance enhancement over current methods used in the industry. Spontaneous deposition of noble metals, e.g. Pd, Ag, occurred on polyaniline coated epoxy substrate by simply immersing the substrate in an aqueous solution containing the corresponding metal salt, e.g., CH_3-C_6H_4-SO_3Ag, $PdCl_2$. The thin metallic layer so plated was then used as an electrode for subsequent electroplating of Cu.

INTRODUCTION

Polyaniline, a classic polymer known for over a century, has been commonly described as a black powder obtained from the oxidation of aniline in acidic aqueous medium.[1] However, the structure and properties of this polymer have only recently been clearly elucidated.[2,3,4,5] It has been found that the material undergoes an insulator to metal transition upon doping with protonic acids. The material has also been found to exist in different oxidation states. The conductivity of these materials is a function of both the degree of oxidation and the degree of protonation. The "emeraldine" oxidation state of polyaniline displays the highest level of conductivity upon protonation reaching a value of ~5 S/cm.

The low cost of polyaniline makes the material very attractive to industry. The potential technological applications of the polymer are also enhanced due to its high electrochemical reversibility, environmental stability and solution processibility.[6] One of the most well known application is energy storage. The possibility of using different forms of polyaniline as the cathodes in rechargeable batteries was investigated by Huang *et al.*[7,8] A battery constructed of a polyaniline cathode and a Li anode was found to display a long cycle life and a high energy density. There are many other applications of polyaniline under investigation. In this paper, an application using conducting polyaniline for metallization of printed circuit boards will be discussed.

This metallization process is operable in a manufacturing environment which is totally different from a previous report using nonprocessible polyacetylene for metal deposition in nonaqueous electrolytes under an inert atmosphere.[9] The polyaniline was processed in air and the electroplating process was carried out in water. This novel process has created a totally new perspective in the Cu plating technology for printed circuit boards, especially the plating through hole technology which is used for electrical interconnection. The traditional plating through hole process uses expensive noble metal seeds. The seed can be activated for electroless plating to form a thin Cu layer on the hole wall, then electrolytic deposition can be applied to the Cu to form a thicker layer. In our process, a thin coating of polyaniline is simply applied onto the hole wall and then followed by electrolytic deposition of Cu on the polyaniline coating.

EXPERIMENTAL

Polyaniline was synthesized as previously reported.[8] Electrochemical studies were carried out using a three electrode cell controlled by a PAR model 273 potentiostat. A potassium chloride saturated calomel electrode (SCE) or sodium chloride saturated calomel electrode (SSCE) was used as the reference electrode. In the cyclic voltammetry studies, both working and counter electrodes are 1 cm^2 Pt foils. The working electrode was coated with polyaniline from an NMP solution. In the plating studies, the counter electrodes are Cu foil with the same dimensions as or slightly larger than the working electrodes. The detailed procedure for the Cu and noble metal deposition is given in the next section.

RESULTS

Electrolytic Cu Plating on Polyaniline

Printed circuit boards (PCBs) can be single or double sided. Plated through holes are usually only required for double sided PCBs in order to facilitate the interconnection between the two surface planes of the boards and the circuitry layers within the two planes. A typical process for Cu electroplating is shown in Figure 1. Copper foil clads are laminated on both sides of an insulating substrate. A pattern of holes is drilled into the laminate and cleaned. A seed or catalyst, usually

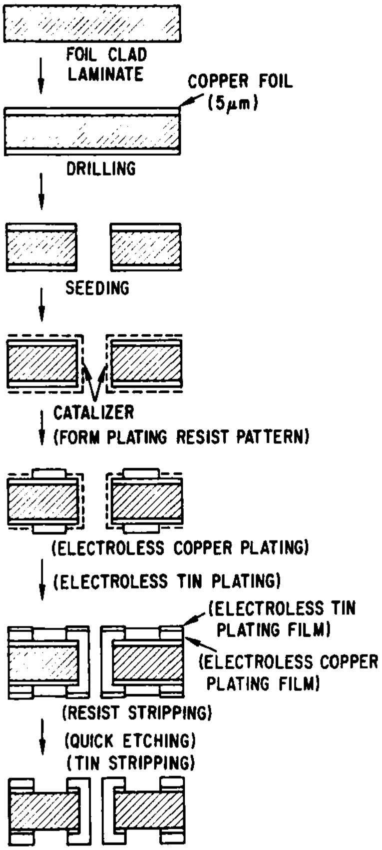

FIGURE 1 A Process for the Fabrication of Printed Circuit Boards and Plating Through Holes.

a noble metal salt, is applied to the circuit board. The seeded circuit board is then immersed in an electroless plating bath, such as a copper sulfate/EDTA/formaldehyde bath, in order to plate a thin layer of copper in the plated through holes. The thin copper layer renders the plated through holes sufficiently conducting so that a thicker copper layer may be added by conventional electrolytic deposition.

While the described process is currently used in the manufacturing of printed circuit boards there are several drawbacks to the process. First, by their very nature, electroless baths are unstable and require close monitoring and control. Electroless copper baths fluctuate between being too stable resulting in plated through hole voids and being too active which results in homogeneous decomposition of the bath. Second, formaldehyde which is probably the most commonly used reducing agent today in electroless copper baths is toxic and poses difficulties in waste treatment and disposal. Third, precious metal seeds are expensive and often have a limited useful lifetime.

An alternative to the current methods is the use of a conducting polymer as a conducting electrode for the electrolytic metallization of Cu. Polyaniline, a solution processible material, was applied to the hole wall by dip coating. The circuit board was immersed in an acetic acid solution of polyaniline for one to two seconds and successively dried in a convection oven. Although the coating appeared to be visually quite thin, the conductivity of the polymer was sufficient to allow Cu deposition. The polyaniline coated circuit board was electrolytically plated by immersion into a copper ion solution. As shown in Figure 2, Cu started to plate on the hole wall from two sides and grew inward until the copper front met at the center of the hole wall. As the plating process was continued, a thicker coating of Cu was obtained (Figure 3). The time needed for the plating process depended on the current density applied to the system. Although higher current density usually gives faster plating speed, the polarization on the circuit board causes the surface of the board to attain a higher Cu thickness than the hole wall.

In the example shown in Figure 2, the Cu was plated with 200 mA current on a 30 mm × 12 mm board having 45 holes with 1 mm diameter. The bath used in this experiment was 0.01 M H_2SO_4/1 M $CuSO_4$ solution. In manufacturing, to improve the throwing power of some bright copper sulfate baths used for plating PCBs, a low copper sulfate concentration such as 60 g/l of $CuSO_4 \cdot 5H_2O$ is combined with 80 g/l of sulfuric acid, 30 mg/l of hydrochloric acid, and appropriate brightners. Analogously, copper fluoroborate solutions containing 56 g/l of Cu $(BF_4)_2$, 160 g/l of fluoroboric acid and brighteners are also regarded as "high-throw" baths for through-hole plating. Air agitation is used for both types of solutions. These acidic baths are not used in this experiment because the polyaniline redox potential increases with decreasing pH (see Figure 4) and thus, the polymer at low pH will

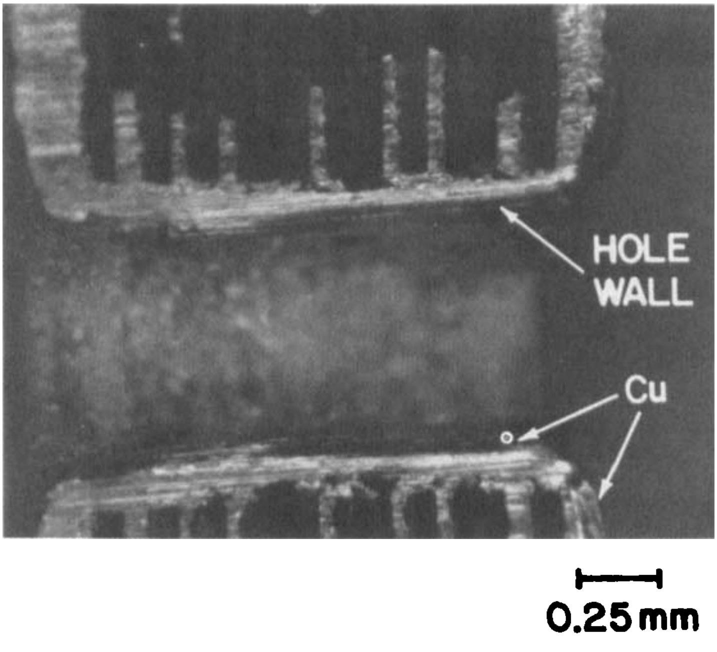

FIGURE 2 A Micrograph of A Through Hole Cross Section Showing that the Copper Plated from Two Sides and Grew Inward on The Polyaniline Coated Hole Wall.

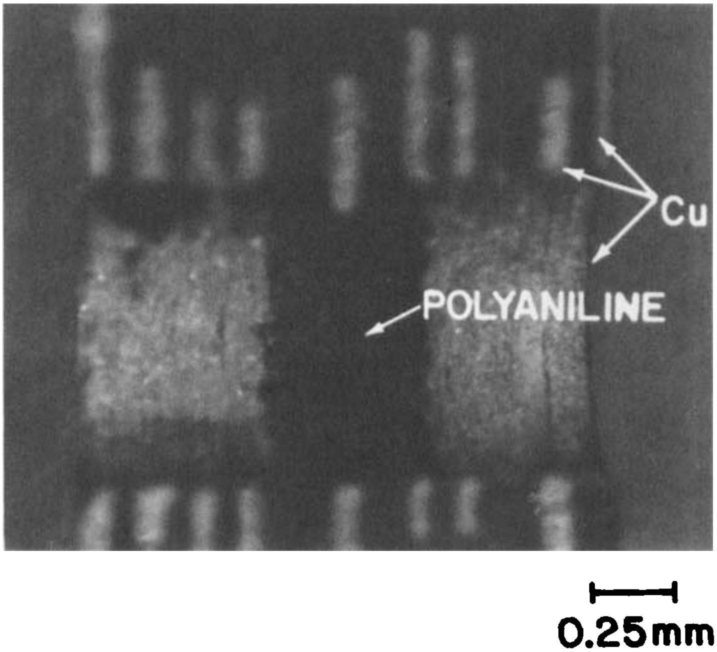

FIGURE 3 A Micrograph of a Cross Section of a Typical Circuit-Board Through-Hole. Cu Deposit Plated on the Polyaniline Surface.

be in a reduced, non-conducting form before the Cu deposition can occur. The dependence of the redox potential of polyaniline on the acidity of electrolytes has been reported before.[3] As shown in Figure 4, polyaniline becomes almost completely reduced at a potential of ~0 V (vs SCE) at a pH of less than 0. Therefore, the polyaniline is not expected to be conducting at the potential where Cu is plated, i.e. E^0 $(Cu/Cu^{2+}) = 0.0982$ V vs. SCE, in high acidic solutions. However, one of the commercial formulations for the fluoroborate bath has a PH of 1.7. This bath still gives good quality Cu film deposition, beyond this pH value the Cu film deposited becomes dull, dark and brittle. Selecting the right bath for the plating, therefore, is quite important. The common pyrophosphate copper bath cannot be used for this polyaniline process, because the pH of this type of bath usually is in the range of 7–9. The polyaniline will not be conducting in this alkaline solution because the material will become undoped, i.e. deprotonated. It seems that the acidic copper baths are the most appropriate for this process. Figure 5 shows that at the potential at which Cu starts to deposit, polyaniline is still sufficiently conducting (i.e. not completely reduced) at pH as low as 0.6 to allow the metallization to occur.

Cu can also be deposited onto a large epoxy substrate coated with polyaniline. An epoxy substrate (approximately 2″ × 2″) was first rinsed for several seconds with acetone then rinsed with distilled water. After the above cleaning procedure, the epoxy substrate was blown dry in a nitrogen stream. Polyaniline (emeraldine base) was dissolved in 80% acetic acid and painted on to the epoxy substrate at a

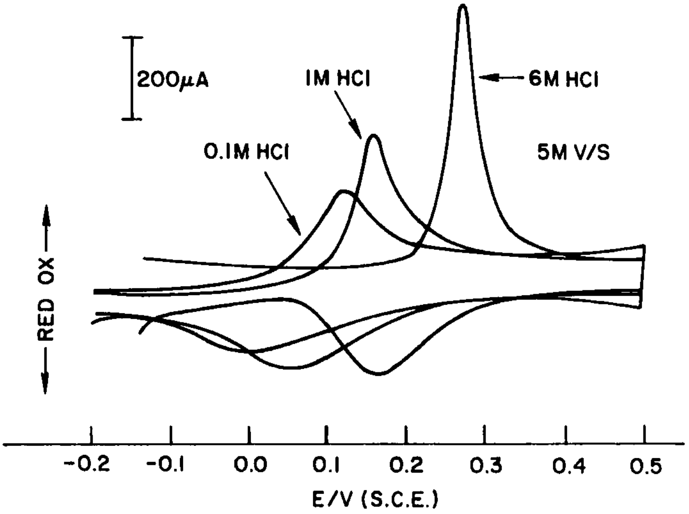

FIGURE 4 Cyclic Voltammogram of An Electrochemically Grown Polyaniline Film on 1 cm^2 of Pt foil Obtained in Different Acid Concentration. The 1 M HCl and 6 M HCl Correspond to The Hammet Acidity Functions (H_o) of -0.2 and -2.12 Respectively.

temperature of approximately 100 to 110 degrees Centigrade to a thickness of approximately 1 to 2 microns. By virtue of the described acetic acid treatment, the emeraldine base is converted to a conducting emeraldine salt in the process. The conductivity of the coating was approximately 0.3 S/cm as measured by the 4-probe method. The epoxy substrate with a polyaniline coating was transferred to a 250 ml electrolyte solution containing saturated copper sulfate (30 g of $CuSO_4$ in 250 ml of water). A piece of copper plate was used as a counter electrode and a 100

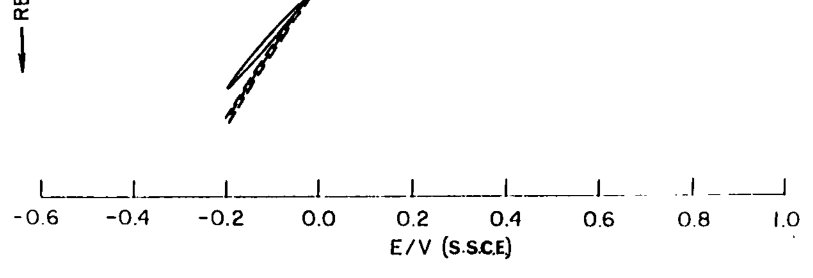

FIGURE 5 Cyclic Voltammograms of a Polyaniline Coated Electrode (1 cm^2 Pt foil) in 1 M Na_2SO_4 + 0.12 M H_2SO_4; in 1 M $CuSO_4$ + 0.1 M H_2SO_4; Bare Pt Foil in 1 M $CuSO_4$ + 0.1 M H_2SO_4.

mA cathodic current was applied to the polyaniline working electrode by a PAR model 273 potentiostat. In the experiment, an alligator clip in slight contact with the solution was coupled to the polyaniline coated epoxy substrate. A bright copper film was deposited at the contact point between the clip and the polyaniline coating immediately upon application of the cathodic current. The area of the copper film continuously grew and spread outward while the cathodic current continued to be applied until the entire polyaniline area was covered with copper. The current was maintained to increase the thickness of the copper film deposit. The pH of this copper bath was around 3 to 4. At high acidic (pH less than 0) copper baths, the plating process was not successful. It was also found that the spreading of copper was faster in the plating process when graphite particles were dispersed in the polyaniline solution and coated on the epoxy substrate. The above finding suggests that the plating of Cu seems to depend on the conductivity of polyaniline. The addition of graphite enhanced the conductivity of the coating therefore making the Cu spreading faster.

Spontaneous Noble Metal Deposition on Polyaniline

The seeds used in the electroless plating usually involve binding of a noble metal salt, e.g., $PdCl_4^{2-}$ to a functional ligand on a polymer surface, e.g. an amine, a quaternary ammonium, or sulphonic acid group, followed by reduction of the noble metal to a zerovalent state, thereby, producing a zerovalent metal polymer *composite.*[10] The zerovalent noble metal particles are the active sites for heterogeneous Cu reduction in the electroless plating process. The metal polymer composites are not conducting and therefore cannot be used directly for electrolytic plating.

We have found that Pd can be spontaneously deposited onto a polyaniline coated epoxy substrate from a palladium chloride solution without the introduction of a reducing agent in the electrolyte. The thin, continuous metallic layer so plated can then be used as an electrode for subsequent electroplating of copper. While this approach does not preclude the use of a precious metal as a base conducting layer it has advantages over existing precious metal seed processes. The precious metal may now be applied from a simple salt solution of the metal and avoids the use of expensive and unstable precious metal colloids. Further, no subsequent activation step is required for the precious metal prior to electrolytic plating of copper or other metals.

Polyaniline (emeraldine base or emeraldine salt) was dissolved in pyrrolidine and then painted onto an epoxy substrate at a temperature of approximately 90 to 100 degrees Centigrade while on a hot plate in an exhaust hood. The pyrrolidine evaporated within a few seconds after painting and all that remained was a thin coating of the polymer. The above described painting process was repeated several additional times until a copper glint color appeared on the surface. The epoxy substrate covered with the polyaniline polymer coating was maintained on the hot plate for an additional 10 to 15 minute period to remove by evaporation any residue pyrrolidine solvent. The entire assembly was then dipped into an aqueous solution containing 0.01 M palladium chloride and 0.012 M hydrochloric acid (or 0.05 M palladium chloride and 0.06 M hydrochloric acid). A shiny metallic Pd film slowly formed on the polyaniline surface. After the entire polyaniline coating was covered with a thin film of palladium, electroplating of copper was performed on the epoxy substrate/polyaniline polymer/Pd assembly under the same conditions as described in the previous experiment. A bright copper film was placed homogeneously on the entire palladium surface immediately upon the application of a cathodic current to the assembly. The thickness of the Cu film increased while the cathodic current continued to be applied. The emeraldine base can also be applied to the epoxy substrate from an NMP solution instead of pyrrolidine for Pd deposition. Other noble metals like Ag can also be spontaneously deposited onto polyaniline-epoxy substrate. The solution used for Ag deposition was a 200 ml aqueous solution containing 1.40 g of silver toluene sulfonate and 0.76 g of toluene sulfonic acid.

Discussion

The inclusion of metal into conducting polymers, e.g. polyacetylene has been known for a decade.[11] The process reported for polyacetylene involved immersion of the polymer film into a toluene solution containing $AgClO_4$. The mechanism simply involves an oxidation of the polyacetylene backbone to form polycarbonium ions and a reduction of Ag^+ to Ag^o. The same mechanism is believed to occur in the reaction of emeraldine base with palladium chloride and also silver toluenesulfonate. Polyaniline is oxidized to a higher oxidation state, while Pd^{2+} or Ag^+ is reduced to Pd^o or Ag^o. The $E_{1/2}$ for Pd/Pd^{2+} is 0.709 V (vs. SCE). This is substantially higher than the open circuit potential of emeraldine salt (Voc = 0.42 V vs. SCE). The $E_{1/2}$ for Pd/Pd^{2+} is expected to be lower than the value given above when one considers the lower concentration of the ions than the unit activity in the experiment and the complex formation of Pd^{2+} to $PdCl_4^{2-}$. However, a sufficient potential gradient is still attained which allows the spontaneous Pd deposition.

The high negative potential of n-doped polyacetylene has been used for all kinds of spontaneous metal *deposition*.[9] It has also been reported that p-doped polyacetylene can be used for metal deposition through electrolytic *plating*.[9] Since polyacetylene is not air stable, all the experiments were carried out in nonaqueous electrolytes under inert atmosphere. Obviously, this process is not practical for the plating application described in this article. The redox potential of p-doped polyacetylene ($E_{1/2}$ = 0.17 V vs. SCE $E_{1/2} = (E_{pa} + E_{pc})/2$)[12] is very similar to polyaniline ($E_{1/2}$ = 0.11 V vs. SCE), however, the processability and air stability characteristic of polyaniline make this polymer a more attractive candidate as compared to polyacetylene for practical plating applications.

Metal inclusion has also been reported in other conducting polymer systems. It has been found that inclusion of the above described noble metals into poly(3-methylthiophene) have very high activity and remarkable stability compared to the polypyrrole *system*.[13] It has also been reported that Cu can be included into poly(3-methyl thiophene) using a large polarization voltage ($-4V$).[14] Since the relatively higher redox potential of poly(3-methyl thiophene) ($E_{1/2}$ = 0.59 V vs. SSCE)[15] makes the polymer completely reduced, i.e. nonconducting before the Cu plating, it appears that polypyrrole ($E^{1/2} = -0.2$ V vs SCE)[16] and its derivatives are better candidates for the electroplating applications, due to their lower redox potentials.

From an industrial point of view, the polyanilines have advantages over these systems including ease of synthesis, processability, air stability, and cost.

CONCLUSION

This paper presents a new process using low cost conducting polyaniline for metallization of printed circuit boards. It has been demonstrated that through holes can be plated with Cu by introducing a thin polyaniline film as an electrode. The plating process was mainly accomplished in the pH range where polyaniline is conducting. The possibility of using conducting polymers for this type of application is mainly an outcome of the development of air stable and solution processible conducting materials. The metallization of printed circuit boards is not limited to Cu deposition, it can be extended to other metals. It is also not limited to the plating through hole technology, it can be extended to all kinds of applications where a conducting substrate is needed. The development of new processible polymers with lower redox potential and higher conductivity is needed for better performance.

The low redox potential of most air stable conducting polymers makes them the electron source for noble metal reduction. It has been demonstrated that Pd and Ag can be spontaneously deposited onto polyaniline coated epoxy substrate from their corresponding metal salts. It is obvious that other noble metals like Au and Pt etc. can be deposited in the same way. The resulting conducting composites may be suitable for applications other than that discussed herein.

References

1. A. G. Green and A. E. Woodhead, *J. Chem. Soc.*, 2388 (1910).
2. W. R. Salaneck, I. Lundstrom, W. S. Huang and A. G. MacDiarmid, *Synth. Met.*, **13**, 291 (1986).
3. W. S. Huang, B. D. Humphrey and A. G. MacDiarmid, *J. Chem. Soc. Faraday Trans.*, **1**, 82, 2385 (1986).
4. A. J. Epstein, J. M. Ginder, F. Zuo, R. W. Bigelow, H.-S. Woo, D. B. Tanner, A. F. Richter, W. S. Huang and A. G. MacDiarmid, *Synth. Met.*, **18**, 303 (1987).
5. W. S. Huang, A. G. MacDiarmid and A. J. Epstein, *J. Chem. Soc. Chem. Commun.*, 1784 (1987).
6. M. Angelopoulos, A. Ray and A. G. MacDiarmid, *Synth. Met.*, **21**, 21 (1987).
7. W. S. Huang, Ph.D. Dissertation, University of Pennsylvania, PA, pp. 205–215, 313–318 (1986).
8. A. G. MacDiarmid, L. S. Yang, W. S. Huang and B. D. Humphrey, *Synth. Met.*, **18**, 393 (1987).
9. W. H. Naarmann, L. V. Munch and F. K. Penzien, U.S. Patent 4,560,593 (1985).
10. A Warshawsky and D. A. Upson, *J. Polym. Sci. Polym. Chem.*, **27**, 2963 (1989); **27**, 2995 (1989).
11. T. C. Clarke, R. H. Geiss, J. F. Kwak and G. B. Street, *J. Chem. Soc. Chem. Comm.*, 489 (1978).
12. J. C. W. Chien and J. B. Schlenoff, *Nature*, **311**, 362 (1984).
13. G. Tourillon and F. Garnier, *J. Phys. Chem.*, **88**(22), 5282 (1984).
14. G. Tourillon, E. Dartyge, A. Fontaine and A. Jucha, *Phys. Rev. Lett.*, 603 (1986).
15. W. S. Huang and J. M. Park, Electrode Materials and Process for Energy Conversion and Storage, The Electrochemical Society Inc. Pennington, NJ, **87-12**, 100 (1987).
16. M. Salmon, A. Diaz and J. Goitia, *ACS Symp. Ser.*, **192**, 65 (1982); A. F. Diaz and J. I. Castillo, *J. C. S. Chem. Comm.*, 397 (1980).