

Polyaniline Matrix Containing Nickel Ferromagnet

Al-Nakib Chowdhury, M. Saiful Islam, M. Shafiul Azam

Department of Chemistry, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

Received 4 September 2005; accepted 24 November 2005

DOI 10.1002/app.23958

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Metallic nickel (Ni) was successfully dispersed onto a polyaniline (PANI) matrix by a simple one-step electrochemical method. Ni particles as deposited onto the polymer seemed to be much smaller compared to those deposited onto bare Pt. The size of the Ni deposits was found to be influenced by the electrolytic bath composition and potential sweep rate. The PANI matrix thus dispersed with Ni particles exhibited ferromagnetic behavior

and a lower electrical conductance. The decrease in conductivity may be attributed to the partial blockage of the conductive path by the Ni particles thus embedded in the polymer matrix. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 321–327, 2007

Key words: conducting polymers; dispersions; microstructure

INTRODUCTION

Polyaniline (PANI) is a conducting polymer that is investigated often because it combines electronic conductivity with the typical features of a plastic. The possible applications^{1–3} of this material, ranging from capacitors, batteries, electronic devices, and anticorrosive coatings to its use in the manufacturing process of printed circuit boards and as a membrane in sensors, largely rely on the conducting polymer being shaped to suit the needs of a specific application.

New polymeric materials with interesting combinations of physical properties can be prepared by the formation of polymer blends, alloys, or composites. Metal particles comprise a fundamentally interesting class of matter in part because of an apparent dichotomy that exists between their sizes and many of their physical and chemical properties. The properties of metal particles, their free electron behaviors, and straightforward surface modification are of potential utility in chemical sensing, linear and nonlinear optics, and a variety of nanoscale electronic device schemes. Metal particles dispersed in conducting polymer films have been described as possible electrocatalysts for various electrode reactions.^{4–9} In fact, composites of conducting polymers containing magnetic particles have many potential applications in electromagnetic interference shielding,¹⁰ electrochromic devices,¹¹ and nonlinear optical systems.¹² Until

now, many studies on composites with electromagnetic properties have been reported. Yoneyama et al.¹³ and Partch et al.,¹⁴ for example, reported the incorporation of metal oxide particles into polypyrrole during electropolymerization. Wan and coworkers^{15,16} also reported a series of PANI composites containing nanomagnets (e.g., Fe₃O₄) prepared by a chemical method. Composites of PANI and polypyrrole containing nanomagnets (e.g., γ -Fe₂O₃ or Fe₃O₄) with highly saturated magnetization and high conductivity were also prepared by a chemical method,^{17–19} and an electrochemical preparation of PANI composite containing nickel (Ni) nanoclusters in a layer-by-layer style has been reported recently.²⁰ In addition, Tang et al.²¹ developed a versatile process employing anionic surfactants to prepare processable free-standing films of PANI containing nanomagnets of γ -Fe₂O₃ in amounts as high as 50%. Because of the current interest in these types of systems, we undertook this study to describe the electrodeposition of Ni magnet onto conventional and nonconventional electrodes. Thus, here we report the electrodeposition of Ni onto Pt and polymer matrices. Voltammetric, microscopic, electrical, magnetic, and other physicochemical analyses of the PANI matrices thus embedded with Ni magnet were also examined.

EXPERIMENTAL

All of the reagents were analytical grade and were purchased either from E. Merck (Darmstadt, Germany) or BDH, Ltd. (Poole, UK). Aniline was distilled twice under a nitrogen (N₂) gas atmosphere. The solutions used throughout the experiment were prepared with doubly distilled water. A standard three-electrode setup with two Pt electrodes as a working elec-

Correspondence to: A.-N. Chowdhury (nakib@chem.buet.ac.bd).

Contract grant sponsor: Bangladesh University of Engineering and Technology.

trode (surface area = 0.50 cm^2), counterelectrode (surface area = 1.0 cm^2), and saturated calomel electrode were used as reference for all of the electrochemical experiments. PANI was prepared from an electrolytic medium comprised of $0.5M$ aniline and $0.8M \text{ H}_2\text{SO}_4$ either by constant potential at 1.0 V or by the sweeping of the potential between -0.2 and 1.0 V . A solution containing $0.1M$ nickel(II) ammonium sulfate $[(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} (\text{Ni complex})]$ was used for Ni deposition both onto Pt and PANI film electrodes. We carried out Ni deposition by either passing a charge of 50 mC at a constant potential of -1.6 V or sweeping the potential between -1.6 and 0.5 V . After several scans (10), the sweeping was terminated as soon as it reached about -1.6 V . The films thus prepared either at constant potential or by the sweeping of the potential were then washed several times with distilled water ($\text{pH} = 5.22$) and peeled off from the substrate, and the pasty mass samples were then dried *in vacuo* before further characterization. All the potentials reported here are given versus the saturated calomel electrode. The solutions used in this study were purged with N_2 gas before use. All cyclic voltammograms (CVs) were recorded with a potentiostat/galvanostat (Hokuto Denko, HABF 501, Tokyo, Japan) equipped with an X-Y recorder (Riken Denshi Co, Ltd., Tokyo, Japan). To maintain a maximum reproducibility better than $\pm 10\%$ in peak current values, Pt electrodes were carefully polished with fine-grained abrasive paper and were then cleaned several times by potential cycling between -0.2 and 1.0 V at 50 mV/s in a $0.8M \text{ H}_2\text{SO}_4$ solution.

Optical microscopic analysis of the samples as deposited onto the Pt substrate was performed with an optical microscope (Swiftmaster II, Swift Instruments, Inc., Tokyo, Japan) coupled with a very high-precision Cannon camera. Density measurements were carried out in a pycnometer (Micromeritics multivolume autopycnometer, model 1305, Norcross, GA) with the conventional standard method. Analysis of Ni samples in the polymer matrix was carried out with an energy disperse X-ray microanalyzer, which was an attachment of a scanning electron microscope (XL-30, Philips, Eindhoven, The Netherlands) that was used for recording scanning electron microscopy (SEM) images of the samples studied. Compressed pellet direct-current conductivity of the solid samples was measured at room temperature by a standard two-point probe method with an autoranging digital multimeter (Keithley 197A, Cleveland, OH). A magnetic balance (Magway MSB Mk1, Sherwood Scientific, Ltd., Cambridge, England) was used to measure the magnetic susceptibility of the samples.

RESULTS AND DISCUSSION

Cyclic voltammetry was used to show and compare the electrodeposition of Ni on bare and PANI-coated

Pt electrodes. A typical CV obtained with the $0.1M$ Ni-complex solution on the bare Pt electrode is shown in Figure 1(a). When the potential was swept from 0.5 to -1.6 V at a scanning rate of 200 mV/s , a sharp rise in cathodic current was seen, although on reverse sweeping anodic current was observed at about -0.3 V . A thin gray deposit was found to adhere on the Pt substrate as soon as the potential reached at or above -1.4 V . As the sweeping was repeated, both the cathodic and anodic current increased further, indicating the formation of more deposit onto the substrate. The cathodic current at about -1.6 V may have arisen due to the reduction of Ni^{+2} to metallic Ni that might have deposited onto the Pt substrate. The anodic current could have been due to the oxidation of the thus deposited metallic Ni to Ni^{+2} . The oxidation and, hence, dissolution of the Ni deposit was further examined by the sweeping of the potential restricted between -0.5 and 0.0 V in $0.1M$ Ni-complex solution at 200 mV/s , as shown in Figure 1(b). The anodic current at about -0.3 V decreased as the sweeping was repeated within the restricted potential range. The decrease in anodic current may have resulted from the dissolution of Ni that adhered previously onto the Pt substrate.

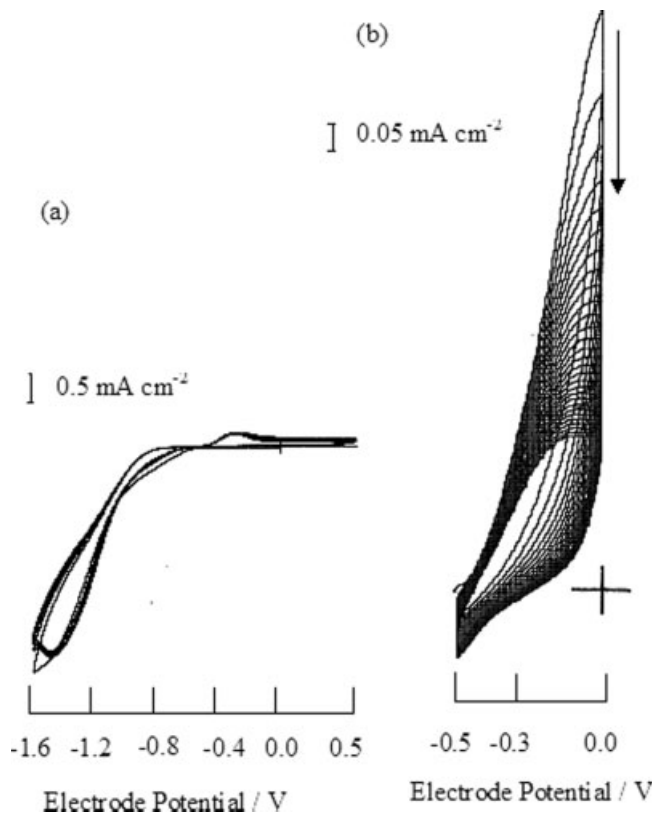


Figure 1 CVs showing the electrochemical (a) deposition of Ni onto the bare Pt electrode and (b) dissolution of thus deposited Ni from the Pt electrode in the $0.1M$ Ni-complex solution at a scanning rate of 200 mV/s .

Figure 2 shows optical microstructures of Ni magnets as electrodeposited onto the Pt substrate under different electrochemical conditions. The micrographs in the rows 1, 2, and 3 result when Ni was deposited from the electrolytic solutions having bath composi-

tions of (1) 0.1M Ni-complex solution (pH = 4.95), 0.1M Ni-complex solution, and 0.1M H₂BO₃ (pH = 4.89); (2) 0.1M Ni-complex solution and 0.1M H₂BO₃, and (3) 1.0 × 10⁻⁴ M H₂SO₄, (pH = 4.58), respectively, by the sweeping of the potential between

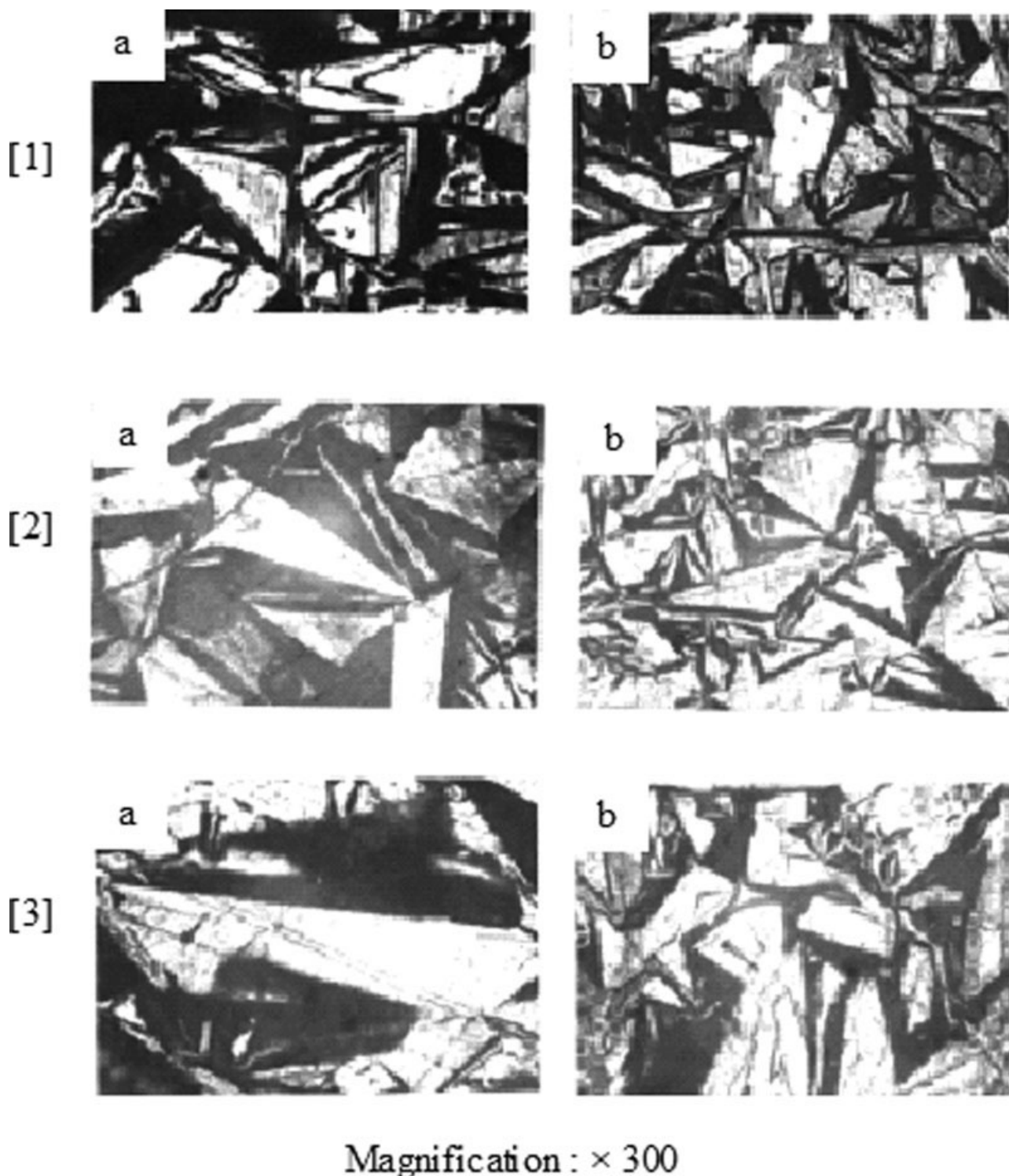


Figure 2 Optical microstructures of Ni deposits onto the Pt substrate (Ni deposition in each case was done by the sweeping of the potential 10 times between -1.6 and 0.5 V). Rows show the influence of the electrolytic bath conditions; columns show the influence of the potential sweep rate on the electrodeposition of Ni.

–1.6 and 0.5 V. As shown in the micrographs, Ni particles as grown onto the Pt had definite shapes with sharp edges and were distributed randomly on the substrate. The result also shows that the particle size of the Ni particles was significantly affected by the variation of the electrolytic solutions as exhibited in the rows. The microstructures as depicted in columns (a) and (b) show the Ni particles as deposited from the same electrolytic solutions as mentioned previously for the rows but with the potential sweep rates maintained at 50 and 200 mV/s, respectively. The Ni particles as deposited at 200 mV/s seemed to be smaller compared to those deposited at 50 mV/s. The result clearly demonstrates that sweep rate used for Ni electrodeposition also significantly affected the particle size of Ni.

An attempt was also made to deposit Ni magnet on the PANI film. For this purpose, PANI film was first grown onto a Pt substrate from an electrolytic solution containing 0.5M aniline and 0.8M H₂SO₄ by the sweeping of the potential between –0.2 and 1.0 V at 100 mV/s. A typical CV during the synthesis of PANI is shown in Figure 3(a). The sharp rise in current at about 0.8 V indicated the oxidation of aniline to PANI.^{22,23} The anodic peak at about 0.2 V and cathodic peak at about 0 V corresponded to the oxidation (doping) and reduction (dedoping) of the PANI film.^{24,25} The film thus grown onto the Pt was then washed several times with distilled water to remove

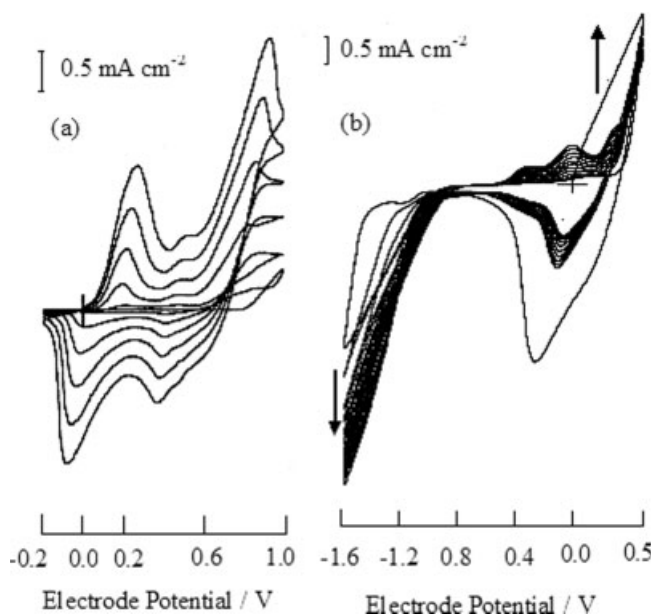


Figure 3 CVs showing the (a) electrochemical synthesis of PANI onto the Pt substrate by the sweeping of the potential five times between –0.2 and 1.0 V in 0.5M aniline and 0.8M H₂SO₄ at 100 mV/s and (b) deposition of Ni onto thus synthesized PANI in the 0.1M Ni-complex solution by the sweeping of the potential several times (for Fig. 4, it is 10 times) between –1.6 and 0.5 at 200 mV/s.

any traces of monomer or byproducts that might have been produced during polymerization. The PANI-coated Pt substrate was then placed in the electrochemical cell containing 0.1M Ni-complex solution, and potential sweeping between –1.6 and 0.5 V was then carried out at 200 mV/s to deposit Ni into the PANI film. A typical CV is shown in Figure 3(b). The sharp rise in cathodic current at about –1.6 V and in the anodic current at about 0.3 V is shown in the voltammogram. The results seem to be identical with those depicted in Figure 1(a) suggesting that Ni²⁺ from the electrolytic solution was reduced to metallic Ni at the PANI substrate (PANI/Ni) at about –1.6 V, and it oxidized back in the reverse scan to the electrolytic solution around –0.3 V. The deposition of Ni onto the PANI substrate was evidenced further from its dissolution process. The result is described in Figure 4. The oxidation and, hence, dissolution of the Ni deposit from the polymer was performed by the sweeping of the potential as restricted between –0.5 and 0.3 V in 0.1M Ni-complex solution at 200 mV/s, as shown in Figure 4(a). The anodic current at about –0.3 V and higher decreased as the sweeping was repeated within the restricted potential range. The decrease in anodic current may have resulted from the dissolution of Ni that incorporated previously into the PANI substrate. This observation was absent, as shown in Figure 4(b), if the PANI substrate without Ni was examined under similar electrolytic and experimental conditions, as shown in Figure 4(a). The results depicted in Figure 4 thus suggest that Ni was successfully incorporated into the PANI matrix under the experimental conditions we used. The charge versus time (*Q*–*t*) plot for the Ni dissolution process was used to get insight into the real charge that indeed was consumed for Ni deposition onto the polymer matrix. For this purpose, Ni was deposited onto the PANI film by the passing of a 50-mC charge at –1.6 V. The film was then held at a constant potential of 0.1 V, and the charge released was recorded with time. The result is shown in Figure 5. The residual charge as observed in the *Q*–*t* plot (Fig. 5) was subtracted from the observed charge passed to obtain the real charge for Ni deposition. The maximum real charge, 0.017 mC, thus predicted (obtained by extrapolation) seemed to be much smaller than the charge originally injected (50 mC) during Ni deposition onto the polymer. With the similar *Q*–*t* plot, the anion and cation doping–dedoping charges of polythiophene films were successfully predicted by other workers.²⁶

The PANI/Ni powder sample was analyzed for its Ni content by an energy disperse X-ray microanalysis method. The average Ni content in the sample was approximately 4.12%. The densities of the PANI and PANI/Ni samples were also measured and were 1.47 and 1.63 g/cm³, respectively. The observed density of PANI seemed to be consistent with results from a pre-

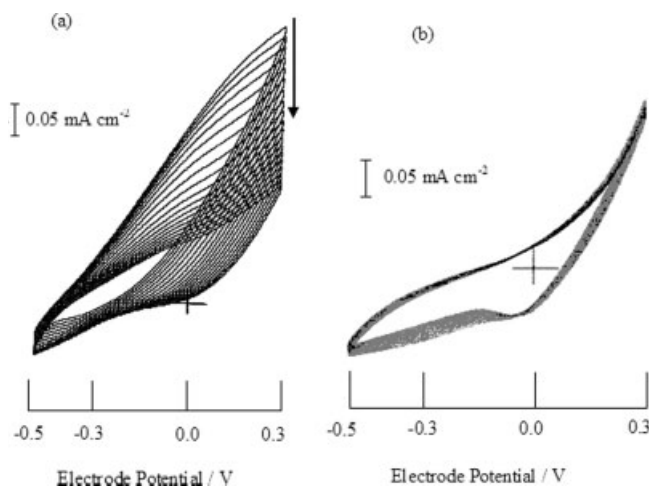


Figure 4 CVs of (a) Ni-deposited PANI and (b) bare PANI matrices (matrices were prepared as in Fig. 3) in the 0.1M Ni-complex solution at 200 mV/s.

vious article.²⁷ The results also show that the observed density of PANI/Ni was higher than that of the bulk PANI. This finding appears to be reasonable if one considers the incorporation of Ni particles into the polymer matrix. The presence of Ni in the PANI/Ni matrix was further evidenced by the number of experiments described next.

Figure 6 shows the optical micrographs of PANI [Fig. 6(a)] and PANI/Ni [Fig. 6(b)] films as electrodeposited on the Pt substrates. A wide distribution of grain particles was seen in the microstructure of PANI/Ni [Fig. 6(b)], whereas such particles were absent in the microstructure of the PANI matrix [Fig. 6(a)]. The grain particles as observed in the microstructure [Fig. 6(b)] could have been the Ni particles that electrodeposited onto the PANI film. Interestingly, the size of Ni grains in the polymer matrix seemed to be much smaller compared to that of those deposited on the bare Pt substrate under identical experimental conditions, as described in Figure 2[1(b)]. Figure 6(c,d) depicts the SEM images for PANI and PANI/Ni films, respectively. In this case, Ni was electrodeposited onto the PANI film from the Ni-complex solution by passing 50-mC charges at a constant potential mode of -1.6 V. The image of PANI surface seemed to be fibril with a rough surface. A similar observation was also reported by Zhang et al.²⁸ for the PANI sample prepared electrochemically. The surface morphology of the PANI/Ni film was quite different from that of PANI. The surface of the PANI/Ni film seemed to have several small hilly zones of triangular shape resembling the shape of Ni deposits onto the Pt substrate, as depicted in Figure 2. This difference in the morphological structure may have resulted from the incorporation of Ni particles into the PANI matrix.

To obtain insight about the magnetic properties, the magnetic susceptibility of the PANI and PANI/Ni

samples was measured with a magnetic balance. The mass susceptibility (χ_g) was predicted with the following relation:

$$\chi_g = \frac{C^{\text{Bal}} \times l(R - R_0)}{10^9 \times m}$$

where l is the sample length (cm), m is the mass of the sample (g), R is the reading for the tube plus sample, R_0 is the empty tube reading, and C^{Bal} is the balance calibration constant. The χ_g values were evaluated to be -3.680×10^{-7} and 9.025×10^{-5} for the PANI and PANI/Ni samples, respectively. The observed higher gram susceptibility obtained for the PANI/Ni sample clearly indicated the ferromagnetic nature of the material.

The compressed pellet direct-current conductivities of the PANI and PANI/Ni samples measured at room temperature by a conventional two-point probe technique were 4.83×10^{-3} and 3.16×10^{-7} S/cm, respectively. The observed conductivity of the PANI sample was consistent with previous work²⁹ reported for a dedoped PANI. The lower conductance for the PANI/Ni sample, presumably due to the interparticle contact resistance arising from the incorporation of Ni particles in the PANI matrix.³⁰ Because the electrical behavior of the sample was so far controlled by the polymer component, the mechanism of conduction was expected to be similar to those of the bulk polymer.

CONCLUSIONS

Free-standing PANI/Ni film with a Ni content as high as 4.12% was prepared by a simple one-step electrochemical method. The control of particle size of Ni

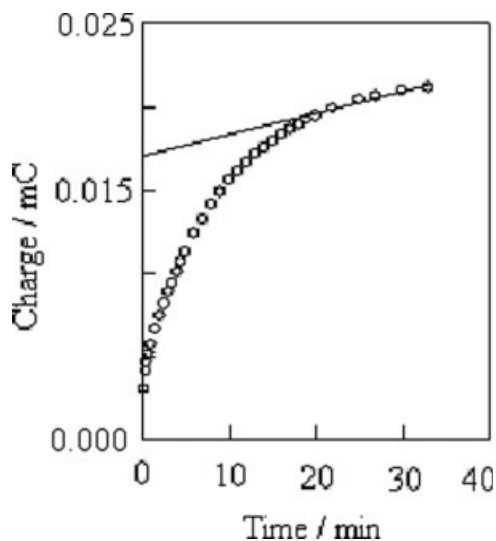


Figure 5 $Q-t$ plot of Ni dissolution from the Ni-deposited PANI matrix in the 0.1M Ni-complex solution. Ni deposition onto the bare PANI was carried out by the passing of a 50-mC charge at -1.6 V.

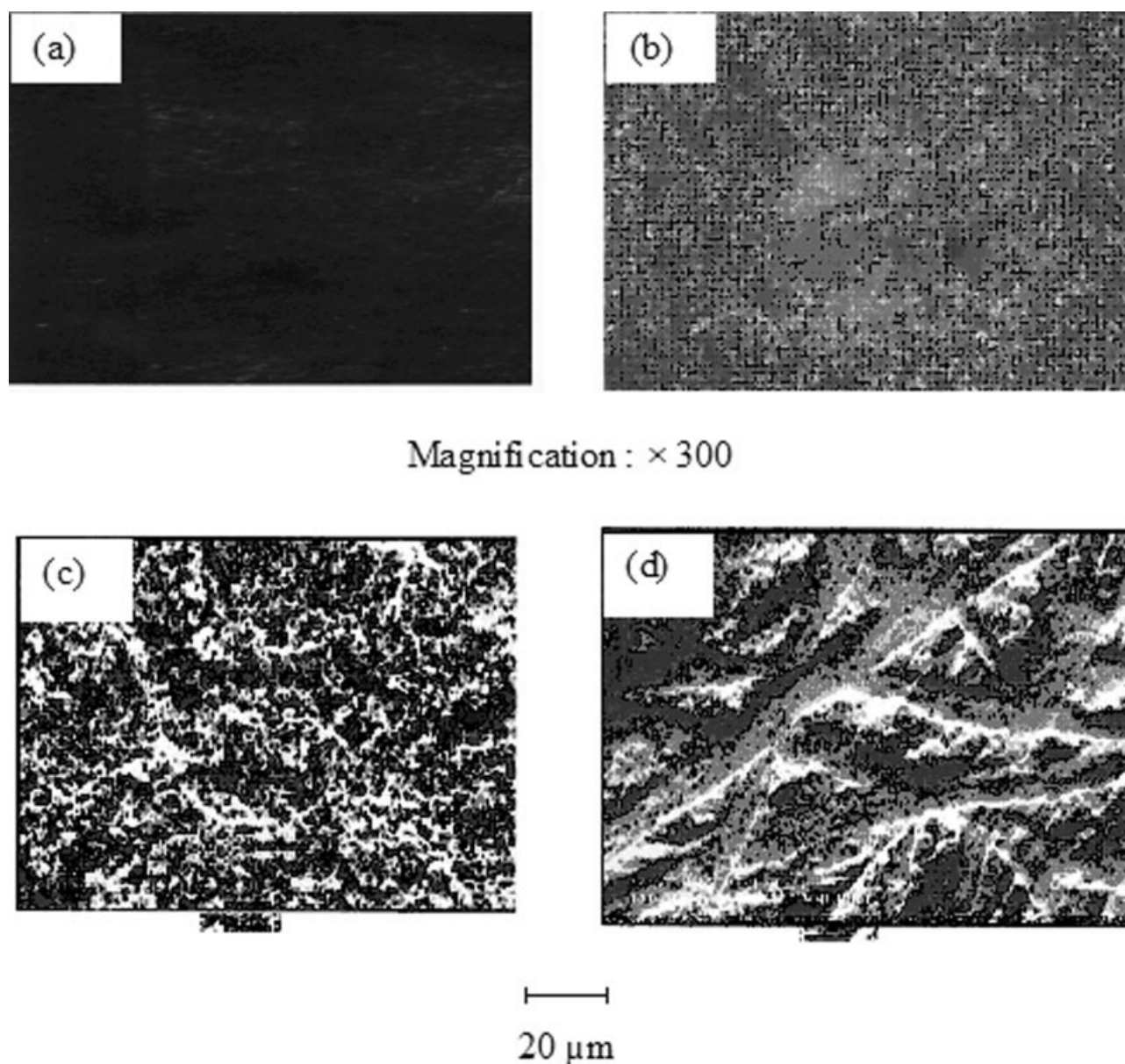


Figure 6 Optical micrographs of (a) bare PANI and (b) Ni-deposited PANI substrates. SEM images of (c) bare PANI and (d) Ni-deposited PANI matrices. Samples (a), (b), and (c) were prepared as in Figure 3, and sample (d) was prepared as in Figure 5.

was achieved by the judicious selection of electrolytic media and potential sweep rate. The size of the Ni particles as deposited onto the PANI matrix appeared to be much smaller compared to that deposited on a bare Pt substrate. The PANI matrix exhibited excellent ferromagnetism on incorporation of Ni in it. The electrical conductance of PANI was also greatly modified by the presence of Ni in the polymer matrix.

The authors thank the Department of Material and Metallurgical Engineering, Bangladesh University of Engineering and Technology, and Department of Chemistry, Dhaka University for assistance with SEM and magnetic susceptibility measurements, respectively.

References

1. Roth, S.; Graupner, W. *Synth Met* 1993, 57, 3623.
2. Jonas, F.; Heywang, G. *Electrochim Acta* 1994, 39, 1345.
3. Alper, J. *Science* 1989, 246, 208.
4. Kost, K. M.; Bartak, D. E.; Kazee, B.; Kuwana, T. *Anal Chem* 1988, 60, 2379.
5. Gholamian, M.; Sundaram, J.; Contractor, A. Q. *Langmuir* 1987, 3, 741.
6. Yassar, A.; Roncali, J.; Garnier, F. J. *Electroanal Chem* 1988, 255, 53.
7. Holdcroft, S.; Font, B. L. *J Electroanal Chem* 1988, 240, 89.
8. Esteban, P. O.; Leger, J. M.; Lamy, C.; Genies, E. *J Appl Electrochem* 1989, 19, 462.
9. Navarro-Flores, E.; Omanovic, S. *J Mol Catal A* 2005, 242, 182.
10. Miyauchi, S.; Aiko, H.; Sorimashi, Y.; Tsubata, I. *J Appl Polym Sci* 1989, 37, 289.

11. Sen, P. K.; Huang, H. T.; Tseung, A. C. C. *J Electrochem Soc* 1992, 139, 1840.
12. Peng, X.; Zhang, Y.; Yang, J.; Zou, B.; Xia, P. L. *J Phys Chem* 1992, 3412.
13. Yoneyama, H.; Shoji, Y.; Kawai, K. *Chem Lett* 1997, 1069.
14. Partch, R.; Gangolli, S. G.; Matijevic, E.; Cai, W. *J Colloid Interface Sci* 1991, 144, 27.
15. Wan, M. X.; Li, W. G. *J Polym Sci Part A: Polym Chem* 1997, 35, 2129.
16. Wan, M. X.; Zhou, W.; Li, J. C. *Synth Met* 1996, 78, 27.
17. Wan, M. X.; Fan, J. H. *J Polym Sci Part A: Polym Chem* 1998, 36, 2749.
18. Wan, M. X.; Li, J. C. *Synth Met* 1999, 101, 844.
19. Liu, J.; Wan, M. X. *J Polym Sci Part A: Polym Chem* 2000, 38, 2734.
20. Trung, T.; Trung, T. H.; Ha, C.-S. *Electrochim Acta* 2005, 51, 984.
21. Tang, B. Z.; Geng, Y. H.; Sun, Q. H.; Zhang, X. X. *Pure Appl Chem* 2000, 72, 157.
22. Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J Phys Chem* 1985, 89, 1441.
23. MacDiarmid, A. G.; Chiang, J.-C.; Haipern, M.; Huang, W.-S.; Mu, S.-L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol Cryst Liq Cryst* 1985, 121, 173.
24. Huang, W.-S.; Humphery, B. D.; MacDiarmid, A. G. *J Chem Soc Faraday Trans 1* 1986, 82, 2385.
25. Focke, W. W.; Wnek, G. E.; Wei, Y. *J Phys Chem* 1987, 91, 5813.
26. Chowdhury, A.-N.; Harima, Y.; Kunugi, Y.; Yamashita, K. *Electrochim Acta* 1996, 41, 1993.
27. Chowdhury, A.-N.; Rahman, J. M. A.; Rahman, M. A. *Indian J Chem A* 2002, 41, 1789.
28. Zhang, A. Q.; Cui, C. Q.; Lee, J. Y. *Synth Met* 1995, 72, 217.
29. McManus, P. M.; Yang, S. C.; Cushman, R. J. *J Chem Soc Chem Commun* 1985, 1556.
30. Zhang, Z.; Wan, M. *Synth Met* 2003, 132, 205.