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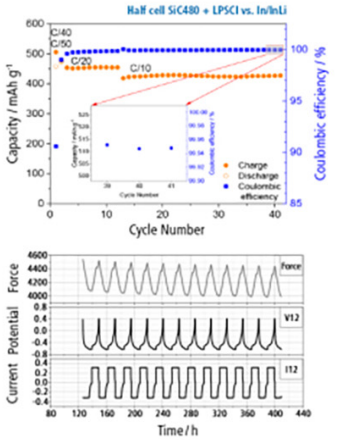
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Synthesis of Polypyrrole-Intercalated Layered Manganese Oxide Nanocomposite by a Delamination/Reassembling Method and Its Electrochemical Capacitance Performance

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A polypyrrole-intercalated layered manganese oxide nanocomposite (PPy–MnO_2) has been synthesized by a delamination/reassembling process. X-ray diffraction analysis shows that the basal spacing of the PPy–MnO_2 nanocomposite is 1.38 nm. The room-temperature conductivity of the PPy–MnO_2 nanocomposite is found to be 1.3×10^{-1} S/cm, which is 4–5 orders of magnitude higher than that of the pristine manganese oxide (6.1×10^{-6} S/cm). The improved specific capacitance of the PPy–MnO_2 nanocomposite (290 F/g) compared with that of the pristine manganese oxide (221 F/g) is attributed to a combination of the conductivity effect and the high specific capacitance of PPy.
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Electrochemical capacitors (or supercapacitors) are charge-storage devices which possess high power density, excellent reversibility, and long cycle life compared with batteries.[1-4] Depending on their charge-storage mechanism, electrochemical capacitors are divided into electric double-layer capacitors (EDLCs) and pseudocapacitors. The energy-storage mechanism of EDLCs relies on the separation of charges at the interface between an electrode and an electrolyte. Various carbonaceous materials ranging from amorphous carbons to carbon nanotubes have been used as electrode materials in EDLCs.[2] In the case of pseudocapacitors, a faradaic process occurs in addition to a simple charge separation. Numerous metal oxides and conducting polymers have demonstrated qualifications as electrode materials for pseudocapacitors. Among these materials, hydrated ruthenium oxide exhibits remarkably high specific capacitance, as high as 1300 F/g, and excellent reversibility.[5,6] However, the high cost and the toxicity to the environment have limited its wide application. Therefore, much research interest has focused on other transition metal oxides. In this respect, manganese oxide is one of the most attractive candidates for electrochemical capacitor electrode materials because of its environmental friendliness and low cost.[7-9] However, manganese oxide exhibits inferior specific capacitance and electrical conductivity to ruthenium oxide. Polypyrrole (PPy), as a kind of conducting polymer, has advantageous properties with respect to low cost, high conductivity, and high doping/dedoping rate during charge/discharge.[10-15] However, it exhibits the disadvantage of a low cycle life because swelling and shrinkage may occur during doping/dedoping processes, thus leading to mechanical degradation of the electrodes and fading of electrochemical performance.[16,17]

A combination of manganese oxide and conducting polymer appears interesting for supercapacitor electrodes. The resulting composite is expected to possess synergic properties from both components, such as enhancement in electrical conductivity or electrochemical cycling stability. Recently, Sivakkumar et al. prepared polypyrrole/hydrous MnO_2 composite by in situ redox reaction of $KMnO_4$ and pyrrole.[18] However, the composite with MnO_2 particles embedded in a polypyrole matrix showed low electrical conductivity and poor electrochemical properties. It is believed that the nanocomposite with molecular-level hybrid and a relatively ordered polymer chain structure should be useful in improving the properties of electrode materials.[19,20] Therefore, it is of great significance, but it is a challenge to prepare the nanocomposite of layered manganese oxide intercalated with conducting polymer.

In this paper we report on a polypyrrole-intercalated layered manganese oxide nanocomposite (PPy–MnO_2) prepared by a delamination/reassembling process with polypyrrole and *n*-octadecyltrimethylammonium-intercalated layered manganese oxide (OCTA–MnO_2) in *N*-methyl-2-pyrrolidone (NMP) solvent. We study the synthesis mechanism of conducting polymer-intercalated layered manganese oxide and the charge-storage properties of the resulting nanocomposite in aqueous KCl solution. The intercalated nanocomposite shows enhanced electrical conductivity and electrochemical capacitance properties.

Experimental

Preparation and characterization.— The OCTA–MnO_2 was prepared referring to the method described in the literature.[21] A 0.25 g sample of OCTA–MnO_2 was put into 40 mL of NMP and sonicated for 3 h, while 0.05 g polypyrrole was added to 20 mL NMP and sonicated for 1 h. The polypyrrole–NMP colloid was added to the OCTA–MnO_2 suspension and then allowed to stir for 24 h at 40°C. The reaction mixture was filtered and washed with acetone and NMP, and then the products were dried at 50°C for 12 h. The product was designated as PPy–MnO_2. For comparison, 0.25 g of OCTA–MnO_2 was added to 40 mL NMP and sonicated for 3 h, and then centrifuged at 5000 rpm for 10 min. The product was washed with acetone several times and dried at 50°C for 12 h. The product was designated MnO_2(R).

X-ray diffraction (XRD) data were collected from a Shimadzu XRD-6000 powder diffractometer using Cu Kα radiation (40 kV and 30 mA) between 3 and 40° with a scanning rate of 2°/min. Electrical conductivity was measured on compacted pellets by a four-probe conductivity method using a four-point probe instrument (Suzhou Telecommunications Instrument Factory, model SX1934). Before measurement, the obtained samples were pressed into cylindrical pellets (13 mm diam and 0.4–0.6 mm high). The field-emission scanning electron microscope (FESEM) images were taken from a Hitachi S4700 scanning electron microscope.

Electrochemical measurements.— The working electrode was prepared by mixing 70 wt % active material, 20 wt % acetylene black, and 10 wt % poly(vinylidene fluoride) in NMP and the slurry was spread onto a nickel sheet with 1 cm^2 geometry area. The electrode was heated at 100°C for 2 h to evaporate solvent. The total mass of electrode material was about 0.5 mg/cm^2. The electrode performance was measured in a beaker-type electrochemical cell equipped with the working electrode, a platinum sheet as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. The electrolyte was 1 M KCl aqueous solution. Cyclic voltammetry (CV) scans were recorded from 0 to 0.9 V (vs SCE)

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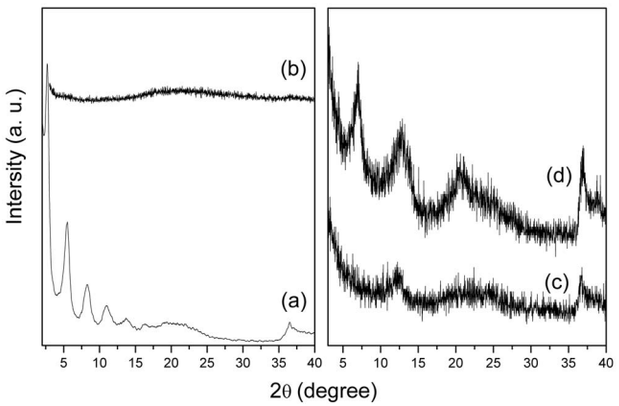


Figure 1. XRD patterns of (a) OCTA–MnO_2, (b) delaminated OCTA–MnO_2 slurry (wet state), (c) MnO_2(R), and (d) PPy–MnO_2.

using a Zahner IM6e electrochemical workstation. Electrochemical impedance spectroscopy (EIS) analyses were conducted using an IM6e over a frequency range of 100 mHz to 100 kHz at an ac amplitude of 10 mV. The galvanostatic charge–discharge cycling properties were evaluated with an Arbin MSTAT4 + multichannel galvanostat/potentiostat.

Results and Discussion

The OCTA–MnO_2 has a layered structure with a basal spacing of 3.24 nm (Fig. 1a). When the OCTA–MnO_2 and NMP mixed solution was treated by ultrasonics, a colloid suspension of manganese oxide was obtained. The delaminated OCTA–MnO_2 slurry was collected by centrifugation and subjected to XRD analysis in the wet state. The wet-state XRD pattern (Fig. 1b) shows no clear peaks but only an amorphous halo in contrast to that of OCTA–MnO_2. The absence of OCTA–MnO_2 reflections indicates that loss of the original crystalline structure and the layered manganese oxides are delaminated to the individual primary layers.[22] The delaminated OCTA–MnO_2 slurry was dried, and a layered structure with a basal spacing of 0.72 nm reappeared [MnO_2(R)], as shown in Fig. 1c. When polypyrrole was treated with delaminated OCTA–MnO_2 suspension in NMP solvent, a new layered structure with a basal spacing of 1.38 nm was obtained (Fig. 1d), which suggests that polypyrrole-intercalated layered manganese oxide nanocomposite is successfully prepared by a delamination/reassembling process. The room-temperature electrical conductivities of MnO_2(R) and PPy–MnO_2 samples are 6.1×10^{-6} and 1.3×10^{-1} S/cm, respectively. The electrical conductivity of PPy–MnO_2 nanocomposite is 4–5 orders of magnitude higher than that of MnO_2(R), which indicates that intercalation of polypyrrole into layered manganese oxide can greatly improve the electrical conductivity of manganese oxide.

Figure 2 shows FESEM images of PPy–MnO_2 and MnO_2(R), respectively. It is apparent that PPy–MnO_2 and MnO_2(R) products are comprised of platelike particles, which are 200–500 nm in lateral dimensions and about 40 nm in thickness. The electrode materials in nano-size should give the opportunity of obtaining enhanced capacitance due to surface effects.

CV and galvanostatic charge/discharge tests were employed to characterize the electrochemical capacitance performance of PPy–MnO_2 nanocomposite. Figure 3a shows the cyclic voltammograms of PPy, MnO_2(R), and PPy–MnO_2 electrodes with a sweep rate of 5 mV/s in a potential range between 0 and 0.9 V (vs SCE). The CV curves of MnO_2(R) and PPy–MnO_2 electrodes show roughly rectangular mirror images with respect to the zero-current line, indicating the capacitive behaviors. However, the pure PPy electrode has poor capacitive behavior in the potential range between 0 and 0.9 V (vs SCE). The potential window is an important

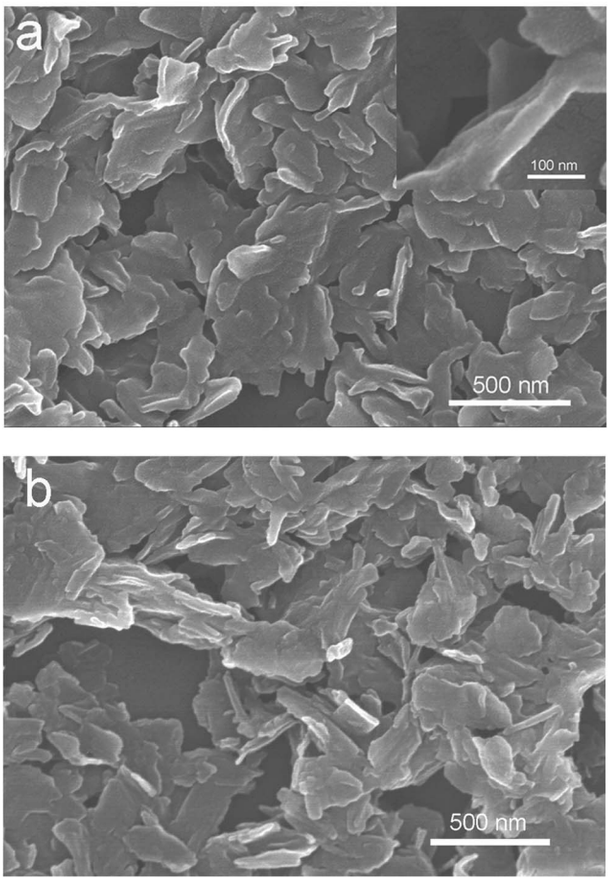


Figure 2. FESEM images of (a) PPy–MnO_2 and (b) MnO_2(R).

effect on the capacitive behavior of PPy. In a previous report, Hu and Lin indicated that a good electrochemical reversibility of PPy in the potential region of −600 and 500 mV (vs Ag/AgCl) was obtained.[13] Generally, manganese oxide electrodes exhibit highly electrochemical reversibility between 0 and 0.9 V (vs SCE or Ag/AgCl) in neutral electrolyte.[7] In our experiments, we thus chose the potential range between 0 and 0.9 V in order to fit the capacitive behaviors of manganese oxide electrodes.

Figure 3b shows EIS plots of PPy, MnO_2(R), and PPy–MnO_2 electrodes at open-circuit potential. The impedances of the above three electrodes consist of a depressed arc in the high-frequency regions and a straight line in the low-frequency regions. Generally, the semicircle reflects the charge-transfer process at the electrode/electrolyte interface, and the straight line represents the diffusion of electroactive species.[23-27] The lowest impedance at the low-frequency end for the PPy electrode among the three spectra indicates that the PPy electrode can provide higher pseudocapacitance than that of PPy–MnO_2 and MnO_2(R) electrodes. PPy–MnO_2 electrode shows a lower charge-transfer resistance and diffusion impedance than those of MnO_2(R) electrode. The result suggests that a better kinetics of PPy–MnO_2 electrode can be obtained by intercalating polypyrrole into manganese oxide, which may be ascribed to the enhanced conductivity and capacitance of PPy–MnO_2 nanocomposite.

Figure 4a shows the charge/discharge curves of MnO_2(R) and PPy–MnO_2 electrodes at current densities of 0.2 and 2.0 A/g (based on the total mass of electrode material) or 0.1 and 1 mA/cm^2, respectively. All the charge curves are very symmetric to their corresponding discharge counterparts in the whole potential region, and

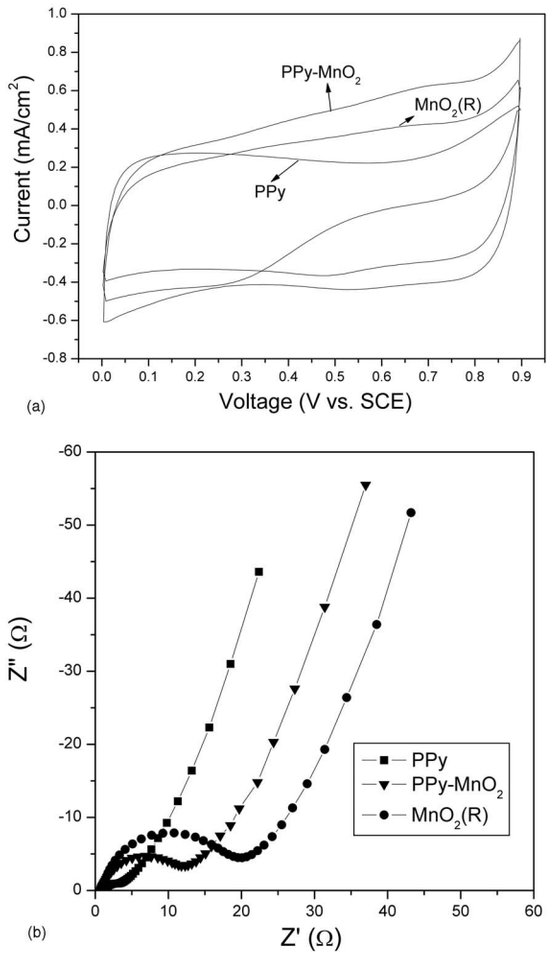


Figure 3. (a) CV images of PPy, MnO_2(R), and PPy–MnO_2 electrodes. Electrodes are scanned in a potential range of 0–0.9 V (vs SCE), and the scan rate is 5 mV/s. (b) EIS plots of PPy, MnO_2(R), and PPy–MnO_2 electrodes.

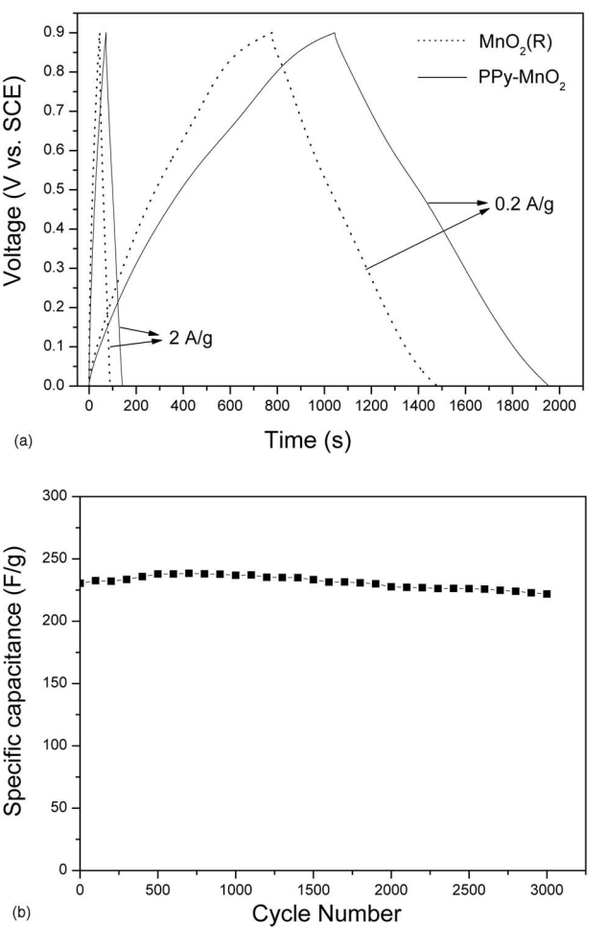


Figure 4. (a) Charge/discharge curves of MnO_2(R) and PPy–MnO_2 electrodes in the potential range of 0–0.9 V (vs SCE) at different current densities. (b) Cyclic performance of PPy–MnO_2 electrode at a current density of 2.0 A/g.

the slope of every curve is potential-independent. The obtained charge/discharge curves are used for the calculation of specific capacitance (SC) from the equation

$$C = \frac{I}{(dV/dt)m} \quad [1]$$

where dV/dt is the slope of the linear discharge curve, I is the current, and m is the mass of active material within the electrode material. The SC value of PPy–MnO_2 at current densities of 0.2 and 2.0 A/g are 290 and 230 F/g, respectively. The capacitance retention is about 79%. In the same process, the SC value of MnO_2(R) decreases from 221 F/g (at a current density of 0.2 A/g) to 159 F/g (at a current density of 2.0 A/g). The capacitance retention is about 72%. The PPy–MnO_2 nanocomposite shows higher capacitance and rate capability than that of MnO_2(R), which is due to the combination of the conductivity effect and the high specific capacitance of PPy.[28]

The values of specific power (SP) and specific energy (SE) are calculated using the following equations

$$SP = C(\Delta E)^2/2t \quad [2]$$

$$SE = C(\Delta E)^2/2 \quad [3]$$

where t is discharge time, and ΔE is the potential window of charge–discharge cycling. The SE values of PPy–MnO_2 electrode are in the range of 26–33 Wh/kg, while the SP values are in the range of 130–1350 W/kg, revealing that there is a decrease in SE of the electrode material with an increase of SP. The SE values of MnO_2(R) electrode are in the range of 18–25 Wh/kg, while the SP values are in the range of 128–1460 W/kg. Thus, the PPy–MnO_2 electrode shows a better specific energy than that of MnO_2(R) electrode.

After 3000 cycles of charge/discharge tests at a current density of 2.0 A/g, the PPy–MnO_2 electrode can maintain ~96% of its initial capacitance (Fig. 4b). This result indicates that the PPy–MnO_2 nanocomposite has a good long-term electrochemical stability at a relatively high current density.

Conclusions

A polypyrrole-intercalated layered manganese oxide nanocomposite is synthesized through a delamination/reassembling process between *n*-octadecyltrimethylammonium-intercalated precursors and polypyrrole in an organic solution. The PPy–MnO_2 nanocomposite shows good electrochemical properties in 1 M KCl solution. The SC for PPy–MnO_2 nanocomposite is about 290 F/g at a charge/discharge current density of 0.2 A/g. The SC of PPy–MnO_2 nanocomposite can maintain 96% of initial SC after 3000 cycles at a

current density of 2.0 A/g. The intercalation of polypyrrole into layered manganese oxide can improve the electrical conductivity and electrochemical capacitance properties of nanocomposite, which is due to the synergic effects from each pristine component.

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References

1. A. Burke, *J. Power Sources*, **91**, 37 (2000).
2. E. Frackowiak and F. Béguin, *Carbon*, **39**, 937 (2001).
3. M. Winter and R. J. Brodd, *Chem. Rev. (Washington, D.C.)*, **104**, 4245 (2004).
4. A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, and W. V. Schalkwijk, *Nature Mater.*, **4**, 366 (2005).
5. C. C. Hu, W. C. Chen, and K. H. Chang, *J. Electrochem. Soc.*, **151**, A281 (2004).
6. C. C. Hu, K. H. Chang, M. C. Lin, and Y. T. Wu, *Nano Lett.*, **6**, 2690 (2006).
7. C.-C. Hu and T.-W. Tsou, *Electrochem. Commun.*, **4**, 105 (2002).
8. M.-S. Wu, *Appl. Phys. Lett.*, **87**, 153102 (2005).
9. Y. Dai, K. Wang, J. Zhao, and J. Xie, *J. Power Sources*, **161**, 737 (2006).
10. M. D. Ingram, A. J. Pappin, F. Delalande, D. Poupard, and G. Terzulli, *Electrochim. Acta*, **43**, 1601 (1998).
11. S. Suematsu, Y. Oura, H. Tsujimoto, H. Kanno, and K. Naoi, *Electrochim. Acta*, **45**, 3813 (2000).
12. S.-H. Song, D.-S. Han, H.-J. Lee, H.-S. Cho, S.-M. Chang, J.-M. Kim, and H. Muramatsu, *Synth. Met.*, **117**, 137 (2001).
13. C. C. Hu and X. X. Lin, *J. Power Sources*, **149**, A1049 (2002).
14. K. A. Noh, D.-W. Kim, C.-S. Jin, K.-H. Shin, J. H. Kim, and J. M. Ko, *J. Power Sources*, **124**, 593 (2003).
15. L.-Z. Fan and J. Maier, *Electrochem. Commun.*, **8**, 937 (2006).
16. R. Kotz and M. Carlen, *Electrochim. Acta*, **45**, 2483 (2000).
17. J.-I. Hong, I.-H. Yeo, and W.-K. Paik, *J. Electrochem. Soc.*, **148**, A156 (2001).
18. S. R. Sivakkumar, J. M. Ko, D. Y. Kim, B. C. Kim, and G. G. Wallace, *Electrochim. Acta*, **52**, 7377 (2007).
19. A. V. Murugan, A. K. Viswanath, G. Campet, C. S. Gopinath, and K. Vijayamohanan, *Appl. Phys. Lett.*, **87**, 243511 (2005).
20. G. Yang, W. Hou, X. Feng, L. Xu, Y. Liu, G. Wang, and W. Ding, *Adv. Funct. Mater.*, **17**, 401 (2007).
21. X. Zhang, L. Ji, S. Zhang, and W. Yang, *J. Power Sources*, **173**, 1017 (2007).
22. Z. Liu, K. Ooi, H. Kanoh, W. Tang, and T. Tomida, *Langmuir*, **16**, 4154 (2000).
23. L. Bai, L. Gao, and B. E. Conway, *J. Chem. Soc., Faraday Trans.*, **89**, 235 (1993).
24. L. Bai, L. Gao, and B. E. Conway, *J. Chem. Soc., Faraday Trans.*, **89**, 243 (1993).
25. C. Gabrielli, M. Keddam, N. Nadi, and H. Perrot, *J. Electroanal. Chem.*, **485**, 101 (2000).
26. C.-C. Hu and C.-H. Chu, *J. Electroanal. Chem.*, **503**, 105 (2001).
27. W.-C. Chen, T.-C. Wen, C.-C. Hu, and A. Gopalan, *Electrochim. Acta*, **47**, 1305 (2002).
28. J. H. Park, J. M. Ko, O. O. Park, and D.-W. Kim, *J. Power Sources*, **105**, 20 (2002).