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Suppression of corrosion study on polypyrrole /zinc oxide nanoparticle composites for rechargeable battery electrode materials

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Abstract. polypyrrole/zinc oxide nanoparticle (PPy/ZnO) composites are successfully synthesized via *in-situ* polymerization by aiding of ultrasonic irradiation. The different ratio of PPy to ammonium persulfate (APS) at 1:0.5, 1:1 and 1:1.5 is used to control the amounts of PPy in composites. Scanning Electron Microscopy indicates the development of nano/microstructure of PPy with increasing the amount of APS. The surface electrochemical activity of ZnO/PPy anodic electrode is characterized by linear polarization and cyclic voltammetry (CV). The introduce of PPy onto ZnO surface with the appropriate content and structure can improve the anti-corrosion and charge performance of electrode composites. The synthesized ZnO/PPy electrode at PPy/APS ratio of 1:1 can yield the highest values of corrosion inhibition efficiency of 73.50 % in 7 M KOH aqueous solution.

1. Introduction

Currently, several metals such as lithium, sodium and zinc are exploited as materials for battery electrodes. Among of them, zinc and its alloys are the most utilized materials as the anodic electrode for rechargeable aqueous batteries due to their high specific capacity, less expensive and safer for aqueous electrolyte [1, 2]. In addition, ZnO has been gained attraction for many researches owing to the modulating of its energy capacity with the different cathode materials such as manganese, nickel, vanadium and so on. Despite the its advantage, the zinc corrosion in alkaline electrolyte and the dendrite formation are crucial issues which directly affect to performance of zinc oxide electrode. Principally, the corrosion of ZnO electrode and the dendrite formation are occurred via the charge and discharge process. Zinc oxide is dissolved into the alkaline electrolyte and re-locates in non-uniform deposition on the electrode, inducing the dendrite growth on surface. Consequently, these issues lead to limit in the usages of rechargeable battery cycles and diminishing electrochemical properties.

To suppress the dendrite formation and the corrosion of zinc oxide anode, the surface modification of zinc oxide is necessary to reduce reaction rate of the dissolve/deposition. Several reports demonstrated the use of metallic oxides or carbon materials which can also improve the electrochemical performance of zinc oxide anode. However, those of metallic materials are low conductivity and the



cover coating on zinc oxide surface is difficult to control. Thus, the *coverable* materials with high electrochemical activity is need for surface modification. Recently, the conducting polymers (CP) such as polyaniline and polypyrrole are considered as conductive materials which can form tightly on nanoparticle surface [3, 4]. Yong et al. reported the using polyaniline coated onto zinc to inhibit corrosion reactions which can also decrease a self-discharge behavior and the hydrogen evolution reaction in batteries. Polypyrrole is one of interesting material together with high redox reaction. But, the use of PPy still has not been widely addressed for these issues [3].

Therefore, the aims of our study are to investigate the optimum condition for the synthesis PPy/ZnO composite and to compare the electrochemical performance with different amount of PPy coating at different amount of APS using, expecting that the appropriate PPy coated ZnO electrode will reduce the solubility of discharge process, prevent the dendrite formation of anode electrode and provide a good electrochemical behaviours.

2. Experimental

2.1. Preparation of polypyrrole coated ZnO nanoparticles

Polypyrrole coated zinc oxide nanoparticle was synthesized with ultrasonic polymerization. Briefly, 3 g of zinc oxide was dispersed in 20 ml of distilled water by 0.0966 g ammonium persulfate aqueous solution for 5 minutes. Then 0.1 mole of pyrrole in 12 M HCl was gradually added into the mixtures. The polymerization of pyrrole monomer was carried out under the ultrasonic irradiation at frequency of 280 W for 5 minutes, followed by filtration and washed with ethanol several times. The as-prepared PPy coated ZnO samples were obtained after drying at 60 °C overnight. In this present work, the different amount of PPy coated ZnO nanoparticles were prepared by modulating the mole ratio of PPy to APS at 1 to 0.5, 1 to 1 and 1 to 1.5 which were denoted as ZnO/PPy1, ZnO/PPy2 and ZnO/PPy3, respectively.

2.2. Fabrication of polypyrrole coated ZnO nanoparticle electrode

The sample electrodes were prepared by mixing of 80% wt of PPy coated ZnO, 15% wt of conductive carbon and 5 wt% polytetrafluoroethylene in water/ethanol solution. The mixture slurry was pasted on Ni foam and placed in oven at 60 °C for 3 h. The as-prepared electrode was cut in size 0.5 cm x 2 cm.

2.3. Characterizations

The characteristic functional groups of the samples were examined by Fourier transform infrared spectroscopy (FT-IR) with a Thermo scientific Nicolet 6700 (Tokyo, Japan). Polypyrrole coated zinc oxide nanoparticles were dried and coated with 10 nm of gold before being observed the surfaces using scanning electron microscopy (SEM: JSM-6480LV) at an acceleration voltage of 15 keV.

2.4. Electrochemical measurements

To evaluate evaluate the corrosion of the as-prepared ZnO coated PPy, linear polarization technique was applied to conventional three-electrode configuration with the as-prepared ZnO/PPy samples as working electrode, platinum plate as the counter electrode and Hg/HgO as the counter electrode by scanning between -0.75 and 0.35 V with its open circuit voltage (OCV) at the scan rate of 0.166 mV s⁻¹. The electrochemical performance was also determined by using cyclic voltammetry, employing in 7 M NaOH containing saturated ZnO between -0.1 to 0.6 V (*versus* Hg/HgO) at 1 mV sec⁻¹. To determine the corrosion inhibition efficiencies, the corrosion current density of anodic electrode (I_{corr}) was used to calculate the corrosion inhibition efficiency by equation 1.

$$\eta (\%) = \frac{I_{corr} - I_{corr}}{I_{corr}} \times 100 \quad (1)$$

3. Results and discussion

In this work, PPy/ZnO composites is *in-situ* polymerized under ultrasonic irradiation at various PPy/APS ratios. Representative surface morphologies of bare ZnO nanoparticles and PPy coated ZnO nanoparticles at different PPy/APS ratio are illustrated in fig. 1. SEM evidences in fig. 1(a) reveals the typical structure ZnO with hexagonal prism-like nanostructure at average size of 50 nm. Fig. 1(b) exhibits the smooth morphology of PPy coated ZnO nanoparticles at PPy/APS ratio of 1 to 0.5. This morphology of PPy coated ZnO exhibits the similar morphology to bare ZnO, confirming that PPy can homogeneously coat onto ZnO nanoparticles surface. The more adding of APS directly affect to the efficiency of PPy coated onto ZnO surface. At high APS content, the presence of plate-like structure of PPy is found, as seen in Fig. 1c and d, indicating the rapid chain growth of PPy outside ZnO nanoparticles surface at high APS content.

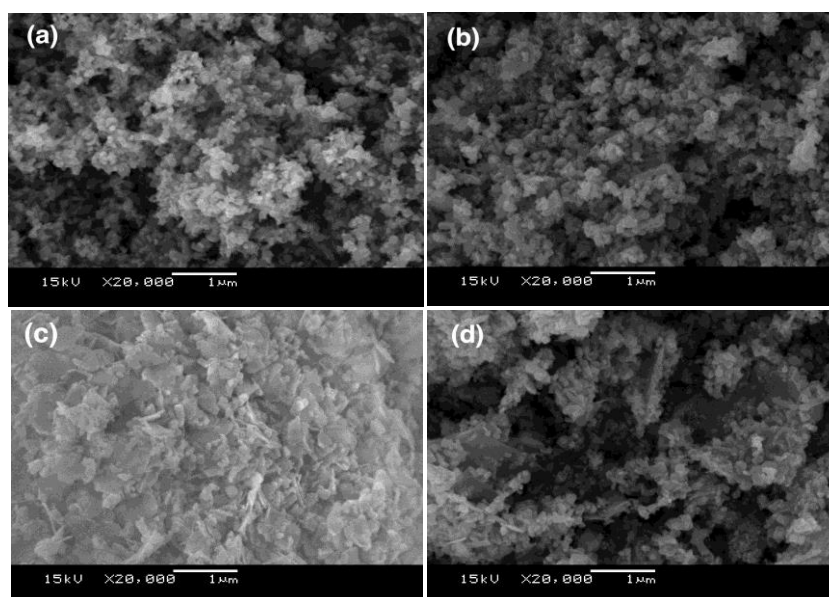


Figure 1. SEM images of bare zinc oxide and PPy coated zinc oxide at three different amounts of APS: (a) ZnO (b) ZnO/PPy1, (c) ZnO/PPy2 and ZnO/PPy3

Fig. 2 illustrates the FTIR spectra of the PPy coated zinc oxide samples at different PPy to APS ratio of 1.0 to 0.5, 1.0 to 1.0 and 1.0 to 1.5, respectively. All of PPy coated zinc oxide samples clearly reveal the evident characteristic of PPy signals. The broad peak at $3500\text{--}3300\text{ cm}^{-1}$ attributes to N-H stretching vibration. The peak at 1637 cm^{-1} is assigned to the characteristic peak for C=C stretching. The minor peak at 1270 cm^{-1} attributes to the C-N stretching of the pyrrole ring. The peak at 1165 and 1040 cm^{-1} corresponds to the C-H stretching of the pyrrole ring and the in-plane deformation vibration of N-H, respectively. The remarkable difference of the signal intensity of transmittance in each sample can be easily recognized, demonstrating that the more adding of APS in polymerization system leads to increase in PPy characteristic signals confirming the PPy chain growth is developed with increase APS content.

The linear polarization curves of the bare ZnO and PPy coated ZnO are illustrated in fig. 3. The calculated potential and current corrosion by Tafel fit are tabulated in table 1. Obviously, the bare ZnO electrode possesses the highest corrosion currents at $52.412\text{ }\mu\text{A}/\text{cm}^2$, while all PPy coated ZnO electrode reveal lower corrosion currents than that of ZnO, implying that the anti-corrosion performance of PPy coated ZnO is superior to ZnO. It can conclude that PPy coating on ZnO surface can suppress the corrosion of ZnO. The direct contact surface of ZnO with electrolyte is decreased by shielding effect of PPy coat, leading to slow down the ZnO corrosion process. ZnO/PPy2 reveals the lowest corrosion currents at $13.888\text{ }\mu\text{A}/\text{cm}^2$, confirming the best anti-corrosion performance. The

slight increase in current corrosion at high APS content (ZnO/PPy3) is observed. This effect might be ascribed to the presence of the excess PPy coated ZnO and the inappropriate PPy structure, participating in the corrosion of PPy, the limitation of the ion mobility and the reaction channels. Consequently, the accumulation of charge on its surface is intensified resulting in increasing in the polarization [5].

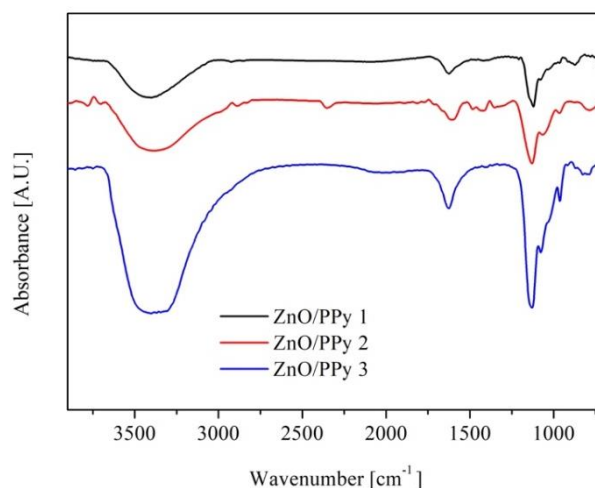


Figure 2. FTIR spectra of as-prepared PPy coated ZnO at different amounts of APS

Table 1. Corrosion parameters for ZnO and PPy coated ZnO electrodes

Materials	E _{corr} (V)	I _{corr} (μ A/cm ²)	η (%)
ZnO uncoated	-0.50967	52.412	-
ZnO/PPy1	-0.49904	20.138	61.58
ZnO/PPy2	-0.50483	13.888	73.50
ZnO/PPy3	-0.45277	15.207	70.98

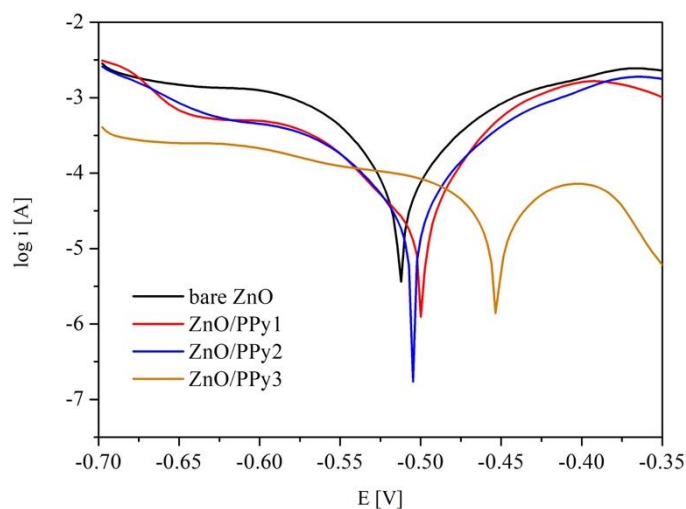


Figure 3. The polarization curves for bare ZnO and PPy coated ZnO electrodes

The electrochemical performance of ZnO and PPy coated ZnO electrode is investigated by cyclic voltammetry as seen in fig. 4. Undoubtedly, PPy coated ZnO affects the CV area by enhancing the electrical capacitive characteristic with increasing the PPy content. This result is due to the synergistic effect of PPy coated on ZnO nanostructure, inducing the electrical double layer and pseudo-capacitance behaviour of ZnO. However, at high PPy content, the dramatic decrease in electrical capacitive characteristics is observed for ZnO/PPy3. As evident support by SEM, the excess PPy chains reveal the inappropriate PPy microstructure. The ion mobility and the charge storage process are restricted, leading to increase electrode resistance and decrease electrical capacitive characteristic.

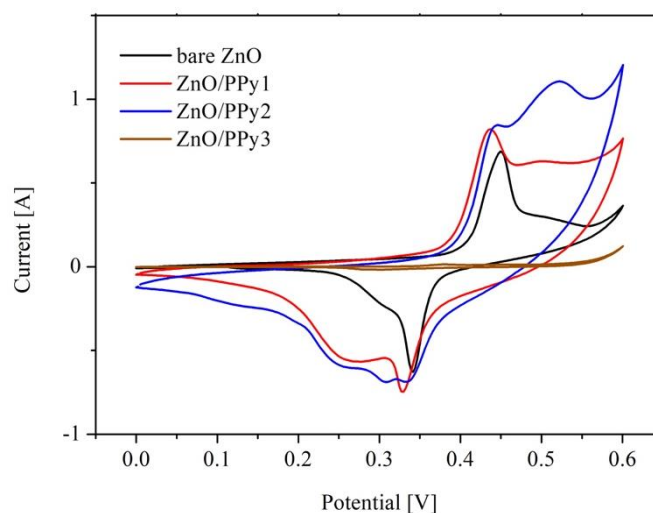


Figure 4. Cyclic voltammograms of bare ZnO and PPy coated ZnO electrodes

4. Summary

PPy/ZnO composites have been successfully synthesized at different PPy/APS ratio by aiding of ultrasonic irradiation. The use of very low concentration of APS as oxidizing agent exhibits the homogenous layer covering onto ZnO nanoparticle surface. Interestingly, the appropriate PPy features such a quantity and morphology can suppress the corrosion reaction in 7 M KOH medium. The synthesized ZnO/PPy electrode at PPy to APS ratio of 1:1 can yield the highest value of corrosion inhibition efficiency of 73.50 %. Evident results in CV manifestly demonstrates the better electrochemical active surface of PPy coated ZnO electrode at PPy to APS ratio of 1:1 relative to bare ZnO. This novel electrode is expected to utilize as an anode electrode in secondary ZnO battery for further study.

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