Preparation of polypyrrole coated zinc anode electrode for inhibition corrosion of secondary zinc ion battery

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Abstract. In this work, polypyrrole coated onto zinc surface anode electrode was successfully prepared via cyclic voltammetry deposition. The different PPy thickness layer on zinc electrode is controlled by the different numbers of deposited cycles at 3, 5, 7 and 10 cycles. The surface morphology development of polypyrrole nano/micro structure covering on zinc surface was examined by Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy. The electrochemical activity of polypyrrole coated zinc electrode is characterized by linear polarization, cyclic voltammetry and galvanic static charge-discharge, indicating that the anti-corrosion PPy surface covering on Zn electrode can yield the highest value of corrosion inhibition efficiency of 67% and serve as high redox layer to improve the charge performance.

1. Introduction
Recently, the development of anode materials for metal ion secondary batteries (such as lithium-ion, aluminium-ion, potassium-ion, sodium-ion and zinc-ion) has attracted increasing attention. Among of them, lithium-ion are most widely materials used owning to its features, possessing high voltage, high energy density and long-life cycle. However, the price of lithium tends to increase due to the plentiful consumption of lithium in future. Thus, the study the sustainable materials for secondary batteries is necessary. Zinc (Zn) is one of the most commonly used as promising anode materials for secondary battery due to its high theoretical density energy, abundant resource and environmentally begin materials that are used [1]. Nevertheless, zinc-based anode electrode reveals some issues, including the corrosion and dendrite formation of anode electrodes during the charge-discharge process [2]. To overcome those problems, recently, conducting polymer such a polypyrrole which can form tightly on nanoparticle surface is considered as the shield to minimize the corrosion reaction of zinc electrodes and prevent the growth of zinc dendrite formation [3]. Several reports revealed the same results of the using conductive coated onto zinc particles which is not only to decrease corrosion rate but also can decrease a self-discharge behaviour enhancing the performance of zinc ion electrode [4]. However, to achieve the high efficiency of the corrosion suppression during discharge process, the design homogenous uniform layer of coating materials on zinc surface is priority to concern. Polypyrrole is
one of interesting conductive polymer with high redox reaction. Its characteristic features possess the flexible and the charge molecule offering high compatibility with metal surface. But, the use of polypyrrole as coating materials for zinc surface still has not been widely addressed. Therefore, in this work, the incorporation of polypyrrole as a conductive polymer layer coated zinc surface is purposed as shielding layer for suppressing the corrosion rate. The different amounts of polypyrrole coated zinc surface on corrosion rate was also studied simultaneously with the electrochemical performance for zinc-manganese rechargeable battery.

2. Experimental section

2.1. Preparation of bare zinc and polypyrrole coated zinc anode electrode
The bare zinc and polypyrrole coated zinc electrode were prepared by electrochemical deposition. Firstly, the electroplating technique, configured with parallel electrode consisting of nickel foam as cathode and zinc plate as anode, was used to deposit zinc layer on nickel foam with supporting electrolyte of 0.6 M zinc sulfate aqueous solution. The current density at 65 mA cm\(^{-2}\) was applied for 10 minutes using potenstat/galvanostat (PGSTAT204) [5]. The obtained zinc electrode was wash with distilled water and dried overnight. For polypyrrole coated zinc electrode, the cyclic voltammetry technique, configured with conventional three electrode systems consisting of the as-prepared zinc electrode as working electrode, Ag/AgCl as reference electrode and platinum as counter electrode, was used to deposit the polypyrrole on zinc surface electrode. The voltage between 0 to 1 V at scan rate 50 mV sec\(^{-1}\) with 3 cycle depositions was applied with supporting electrolyte of 0.1 M pyrrole aqueous solution at pH 3. In this present work, the different amounts of polypyrrole coated zinc electrode were prepared by modulating the number of deposited cycles at 0, 3, 5, 7 and 10 cycles (denoted as Zn, Zn/PPy-3, Zn/PPy-5, Zn/PPy-7 and Zn/PPy-10, respectively).

2.2. Preparation of \(\delta\)-MnO\(_2\) cathode electrode
\(\delta\)-MnO\(_2\) was synthesised by hydrothermal method as described elsewhere [6]. The cathode electrode was prepared by pasting the mixtures of 80 \%wt. of \(\delta\)-MnO\(_2\), 15 \%wt. of conductive carbon and 5 \%wt. of polytetrafluoroethylene in water/ethanol solution. The mixture slurry was pasted on Ni foam, pressed and placed in oven at 60 °C for 3 h. Finally, the as-prepared electrode was cut in size 1 cm x 2 cm.

2.3. Characterization
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 electrode was 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 10 keV.

2.4. Electrochemical measurements
To evaluate the corrosion of the as-prepared Zn coated PPy, linear polarization technique was applied to conventional three-electrode configuration with the as-prepared samples as working electrode, platinum plate as the counter electrode and Ag/AgCl as the reference electrode by scanning between -1.0 and -0.9 V vs E\(_{\text{OCV}}\) its open circuit voltage (OCV) at the rate of 0.5 mV/s. To evaluate electrochemical performance, cyclic voltammetry was determined with two electrodes consisting of the as-prepared samples as working electrode and \(\delta\)-MnO\(_2\) as the counter electrode, employing in 50 ml of 2 M zinc sulfate between 1 to 2 V at 5 mV/sec. The galvanostatic charge/discharge technique was used to evaluate the energy capacity of Zn-Mn battery. The positive electrode was the \(\delta\)-MnO\(_2\) with a much higher capacity than that of the zinc electrode three times. The negative electrode was the zinc electrode. The cells were charged 4C for 20 min and discharged at 1C rate down to 1.3 V.
3. Results and discussion

3.1. Morphology study

In this work, polypyrrole is coated on zinc surface by cyclic voltammetry deposition. Representative surface morphologies of bare zinc and polypyrrole coated zinc at different number of deposited cycles are illustrated in Fig.1. SEM evidence in Fig.1a reveals the stacking of flat plate-like structure of zinc. Obviously, the remarkable difference of the morphology in each PPy coated zinc samples can be easily recognized, demonstrating that the increase in dense growth of ppy covering on zinc surface with increase the number of cycle deposition (seen Fig. 1(b), (c), (d) and (e), respectively). Additionally, SEM-EDS evidence in Fig.1(f) reveals the nitrogen signal on bulk surface, confirming that the coating layer on zinc surface is polypyrrole.

![Figure 1. SEM images of (a) Zn (b) Zn/PPy-3, (c) Zn/PPy-5, (d) Zn/PPy-7, (e) Zn/PPy-10 and (f) SEM-EDS of Zn/PPy-3](image)

3.2. Electrochemical properties

The linear polarization curves of the bare zinc and polypyrrole coated zinc electrodes are illustrated in Fig. 2. The calculated potential and current corrosion by Tafel fit are tabulated in table 1. As seen from table 1, obviously, the bare zinc electrode possesses the highest corrosion currents at 483.17 μA/cm²,
while all polypyrrole coated zinc electrode reveal the lower corrosion currents than that of zinc, implying that the anti-corrosion performance of polypyrrole coated zinc is superior to zinc. As SEM evident support, PPy coated zinc surface can act as shielding effect to decrease the direct contact between zinc and electrolyte leading to slow down the zinc corrosion process. It can be concluded that polypyrrole coating on zinc surface can suppress the corrosion of zinc electrode. Zn/PPy-5 shows the lowest corrosion currents at 159.38 μA/cm² with the highest values of corrosion inhibition efficiency of 67.01%. The more coating surface of Zn/PPy-7 and Zn/PPy-10 electrode reveals the slight decrease in its corrosion protection. This result is ascribed to the fact that the highly dense PPy surface can limit the ion mobility and the reaction channels by trapping inside PPy layer, leading to accumulate the charge on its surface inducing in the polarisation process.

| Materials    | E_{corr} (V)  | I_{corr} (μA/cm²) | η (%)  |
|--------------|---------------|-------------------|--------|
| Zn           | -0.96165      | 483.17            | -      |
| Zn/PPy-3     | -0.95805      | 160.13            | 66.86  |
| Zn/PPy-5     | -0.95624      | 159.38            | 67.01  |
| Zn/PPy-7     | -0.95822      | 179.87            | 62.77  |
| Zn/PPy-10    | -0.95895      | 244.40            | 49.42  |

The electrochemical performance evaluated by cyclic voltammetry is displayed as seen in Fig. 3. All of polypyrrole coated zinc electrodes exhibit the enhancing in the CV area relative to bare Zn electrode, implying higher activity surface of PPy coated Zn. Galvanic static charge-discharge is used to determine the capacity of electrode at discharge rate of 1 C. As seen from Fig. 3(b), the discharge efficiency of polypyrrole coated zinc obviously reveal the better performance than that of bare zinc. The reason is that the conductivity of zinc electrode and redox reaction is improved by the polypyrrole layer. Zn/PPy-5 electrode reveals the highest capacity which is good agreement with SEM and linear polarization results. In addition, at high amount of polypyrrole coating, Zn/PPy-7 and Zn/PPy-10 exhibit the slight decrease in discharge efficiency. As evident support by SEM, Zn/PPy-7 and Zn/PPy-10 demonstrate the high thickness layer which can serve as trapping layer, causing the limitation of ion diffusion. The discharge products may retain in the electrode rather than dissolving into electrolyte leading to decrease in electrochemical capacity.

![Figure 3](image-url)

**Figure 3.** (a) Cyclic voltammograms of zinc and polypyrrole coated zinc electrodes at 5 mV/s and (b) Typical discharge curve of zinc and polypyrrole coated zinc electrodes at the rate of 1C
4. Conclusions
Polypyrrole coated zinc electrodes have been electrically synthesized via cyclic voltammetry deposition. The developed film thickness of PPy coated Zn depends on the number of deposited cycles. PPy coated Zn at 5 cycles reveals the most effective electrode for improving anti-corrosion with the highest value of corrosion inhibition efficiency of 67%. Evident results in CV and GCD reveal the better electrochemical capacity of PPy coated Zn electrode relative to zinc, especially at 5 cycles deposition. This polypyrrole coating zinc are considered as the high efficiency anode materials utilizing for zinc-ion batteries.

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