Acetate as Electrolyte for High Performance Rechargeable Zn-Mn-Deposited Zn/Ni Foam-Supported Polyaniline Composite Battery

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Increased electroactivity of polyaniline prior doped with lithium ions is observed during polymerization by cyclic voltammograms (CV) compared with pure polyaniline. The electrochemical performance of a three-dimensional nickel foam-supported polyaniline composite prepared by electropolymerization and a casting process was investigated at different low-vacuum pressures for casting the aforementioned slurry. An appropriate vacuum pressure of 3000 Pa was certified by cyclic voltammetry and scanning electron microscopy. The nickel foam-supported polyaniline composite cathode were prepared and observed with prohibited hydrogen evolution and the enhanced conductivity in a manganese acetate-zinc acetate solution electrolyte system with lithium ions additive. The deposited zinc anode prepared by co-electrodeposition of zinc-manganese exhibited with high discharge voltage and stable discharge platform. The zinc-manganese-deposited zinc/nickel foam-supported polyaniline composite battery exhibited significant improvement in the capacity density and cycle performance. A discharge capacity density of 142.3 mAh.g⁻¹ was attained by the battery, and it was maintained more than 94.7% of the original value after 60 cycles, and there was no distinct change in the coulomb efficiency with an average value of 90% over the experiment, which indicates that the present cell has promising possibility for use as an energy storage or high-performance rechargeable battery.

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Manuscript submitted August 6, 2018; revised manuscript received April 2, 2019. Published April 15, 2019.

Among the conducting polymers, polyaniline (PANI) attracts considerable interest, because of its desirable chemical stability, good redox reversibility, high conductivity, high Faradic pseudo capacitance, low cost, and environmentally friendly nature. PANI is frequently used as an alternative electrode materials that are incorporated into rechargeable energy reserve equipment, such as supercapacitors and rechargeable batteries, as well as batteries with zinc (Zn) anodes.¹⁻⁴ Compared with conventional batteries, such as lead-acid batteries⁵⁻¹⁰ and nickel-cadmium batteries¹¹⁻¹³ with high contamination, and expensive lithium-ion batteries,¹⁴⁻¹⁶ Zn/PANI has stimulated intensive interests due to its environmentally green nature, easy availability, and convenient synthesis. Thus far, however, Zn/PANI batteries have not yet commercialized on large scale. There are some main reasons for this problem. First, in the PANI film cell, only the outer material layer of the PANI film participates in the charge and discharge processes, which leads to a small discharge capacitance. Second, the low loading of active material of PANI on current collector results in low capacitance. Furthermore, because of the higher discharge current density leading to the decrease of the coulomb efficiency of the battery, the charge-discharge current density does not exceed 1mA/cm². Additionally, recent research on Zn/PANI batteries has revealed many defects, such as low utilization, diffusion and decomposition due to overcharging and zinc electrode dendrites. Those reasons result in an immense barrier that prevents industrialization and extensive application of Zn/PANI batteries.¹⁷⁻²¹ Various attempts have been made to overcome above limitations, and including the improving aniline polymerization conditions for high cell discharge capacity, changing the cell charge style to prohibit degradation, adding other metals to modify zinc electrode, supplying appropriate additives to the electrolyte for decreasing the charge/discharge time, inhibiting zinc dendrite formation, and preventing the electrode corrosion.²²⁻²³

Some effective improvement measures have been proposed. Firstly, for electrode fabrication, electrode was coated with a PANI (chemical polymerization and electrochemical polymerization) slurry which contained binder or conductive additives such as carbon powders on a cathode substrate. The slurry was compacted into the substrate to increase active materials load, which thereby elevated the conductivity of the PANI film, but simultaneously reduced the porosity of the film and formed a barrier of the internal active substances taking part in the electrochemical reactions.²⁴ In addition, at a high discharge current density, the compacting coated electrodes regularly and severely polarize, which resulted in an increased charge transfer resistance and diffusion overpotential. The PANI film can be directly electropolymerized on the cathode with aniline monomer in acidic solution, and the obtained film thickness was approximately 10 µm. However, the film couldn’t maintain the thickness due to the low total ratio of the active substance onto the substrate surface, which led to the low energy density. Thirdly, three-dimensional metal sheeting, porous metal foam, and metal fiber substrate have been used in nickel-metal hydride batteries and lithium-ion batteries. The usage of these materials has resulted in an upsurge of research attempts to develop the PANI’s electrochemical properties. The Ni foam substrate presents absolute advantages which due to three-dimensional, porous and fibrous nature, and can serve as an electron transport channel under the PANI coating layer. Although the conductivity of the PANI cathode was greatly increased with the Ni foam substrate, undesirable self-erosion and hydrogen evolution questions still exist. For the purpose of prohibiting the corrosion of the Ni foam substrate, in our previous study, cathode electrophoresis was performed to deposit a PANI film (PANI-L) on the Ni foam substrate by cathode electrophoresis for PANI-CL on the Ni foam substrate. The electrochemical performances of doped product and still porous 3D Ni foam substrate. The electrochemical behaviors and morphology of the Ni foam-supported PANI-CL were compared with a product that was doped after it underwent electrophoresis and casting. The electrochemical performances of doped product and undoped were compared, and the doping concentration of Li⁺ was also considered. For lowering the Ni foam corrosion, compared with strong acid salt, manganese acetate-zinc acetate-lithium acetate solution (MnZnLi-acet) was expected as weak acid electrolyte that gained

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a small amount of strength conductivity due to added lithium ions. Therefore, the electrochemical performances of the Ni foam-supported PANI-CL in different acetate electrolytes and various concentrations of these acetate salts were studied. Because of the presence of Mn$^{2+}$ in the Zn//Ni foam-supported PANI-CL battery electrolyte during the charging process, the codeposition of Zn$^{2+}$ and Mn$^{2+}$ was also investigated in the performance and morphology of the deposition. The discharge capacity density and the average discharge upper voltage of the Zn-Mn-deposited Zn//Ni foam-supported PANI-CL fabricated by the present method were also investigated.

**Experimental**

*Preparation of electrolyte solution.*—0.5 M ZnSO$_4$ + 0.5 M (NH$_4$)$_2$SO$_4$ (pH = 4.0) solution (coded as S$_0$) was prepared as a control electrolyte system. The solutions of 0.5 M Zn(CH$_3$COO)$_2$ + 0.1 M CH$_3$COOLi (coded as S$_1$, pH = 5.5), 0.5 M Zn(CH$_3$COO)$_2$ + 0.3 Mn(CH$_3$COO)$_2$ + 0.1 M CH$_3$COOLi (pH = 5.5, coded as S$_2$), 0.5 M Zn(CH$_3$COO)$_2$ + 0.05 M Mn(CH$_3$COO)$_2$ (pH = 5.5, coded as S$_3$), Zn(CH$_3$COO)$_2$ (pH 5.5, coded as S$_4$), Mn(CH$_3$COO)$_2$ (pH 5.5, coded as S$_5$) was generated.

Stable PANI-L powder was galvanostatically synthesized at a current density of 1 mA cm$^{-2}$ on the graphite plate for 24 h in a solution containing 0.5 M aniline, carbon powder as a conductive reagent with an average particle size of 35 nm, 1M HCl, 25 mM aloe vera as a binder, and six different concentrations of CH$_3$COOLi (0 M, 0.1 M, 0.2 M, 0.3 M 0.4 M, and 0.5 M, which are coded as PANI-L0, PANI-L0.1, PANI-L0.2, PANI-L0.3, PANI-L0.4, and PANI-L0.5) as the doping agent, without stirring and with pre-emission of oxygen by bubbling nitrogen into the electrolyte. After scratching the electrode plate with a plastic knife, the resultant PANI-L powder was collected and then successively washed with distilled HCl and distilled water several times until the filtered liquid appeared colorless. Then, the powder was subjected to grinding with a cutting mill to obtained micro sized PANI-L particles, which were then dried in a vacuum oven at 80°C for 24 h. PANI as a control sample was also synthesized by the same method described above but without dopant. In order to increase the cathode material’s electroactivity, PANI-L composites (PANI-CL) were then fabricated by evenly mixing both the obtained PANI-L and carbon powder according to a mass ratio of 10:1.

All reagents employed in these tests were analytical grade.

**Preparation of PANI-CL using electrochemical polymerization.**—Electropolymerization was conducted in a three-electrode system, with a graphite plate as working electrode, a platinum (Pt) wire as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The distance between the working electrode and counter electrode was maintained at 1.0 cm. Before the electrochemical polymerization, the graphite electrode surface was successively polished with emery papers of 800, 1200, and 1500 grade and then cleaned in a ultrasonic bath in a mixture of water and ethanol. Stable PANI-L powder was galvanostatically synthesized at a current density of 1 mA cm$^{-2}$ on the graphite plate for 24 h in a solution containing 0.5 M aniline, carbon powder as a conductive reagent with an average particle size of 35 nm, 1M HCl, 25 mM aloe vera as a binder, and six different concentrations of CH$_3$COOLi as the doping agent, without stirring and with pre-emission of oxygen by bubbling nitrogen into the electrolyte. After scratching the electrode plate with a plastic knife, the resultant PANI-L powder was collected and then successively washed with diluted HCl and distilled water several times until the filtered liquid appeared colorless. Then, the powder was subjected to grinding with a cutting mill to obtained micro sized PANI-L particles, which were then dried in a vacuum oven at 80°C for 24 h.

**Preparation of the PANI-CL cathode supported by Ni foam.**—To prepare the Ni foam, 1 g of PANI-L powder was dissolved in 50 ml acetic acid to prepare a initial PANI-CL suspension solution with mass concentration of 20 mg ml$^{-1}$. 0.3 ml of which was dispersed into 29.7 ml of N,N-dimethylformamide and then subjected to ultrasonication for 10 min in order to produce a PANI-CL powder suspension with average particle diameter of approximately 0.1 μm. The Ni foam was available as a commercially prepared conductive substrate (Kunshan Desco Electronics Co., Ltd), with thickness of 1.6 mm, higher than 95% of porosity, larger than 3500 cm$^2$.cm$^{-3}$ of specific surface area, and surface density of 500 g.m$^{-2}$. The foam was first pretreated for high adhesion and corrosion resistance, and then soaked and cleaned using heated distilled water and ethanol for approximately 10 min each. For obtaining compact PANI cathodes, the electrophoretic deposition of PANI-CL particles on the porous Ni foam was implemented at potentiotstat 20 V for 10 min with a set up of which the Ni foam acted as a PANI substrate collector, the graphite plate served as the counter electrode, a 500 W mains as DC voltage supplier, with 0.5 cm distance between two electrodes in the PANI-CL powder suspension. To avoid the Ni foam corrosion, all electrophoresis tests were conducted in non-aqueous solvent containing acetic acid and N,N-dimethylformamide at room temperature. After being dried at 80°C for 5 h, the weight of electrodeposited PANI-CL on the Ni foam substrate with or without deposits was measured. The effective geometrical area of the working electrode was 1cm$^2$.

A PANI-CL casting slurry was prepared by dispersing 15 g of PANI-CL powder in 150 ml of 1 M ZnSO$_4$ aqueous solution with 7.5 ml of 2% polyethylene glycol as an additive reagent. Under vacuum filtration, the obtained homogeneous PANI-CL slurry was cast into a porous Ni foam substrate firstly coated with an electrophoresis deposition layer, for the purpose of increasing the load capacity of PANI-CL in the Ni foam (the process is abbreviated as E-SCVF). The frequency of different vacuum filtration pressures (2000 Pa, 3000 Pa, and 4000 Pa) employed in the casting was also considered. A Ni foam-supported PANI cathode as a control electrode was also prepared by the above E-SCVF process.

Cross-sectional scanning electron microscopy (SEM) of the Ni foam-supported PANI-CL was performed relating to different vacuum filtration pressures. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) examination of the Ni foam-supported PANI-CL were carried out in different electrolytes.

**A Zn-Mn-deposited Zn anode obtained by the electrodoposition method.**—Galvanostatic deposition was employed to investigate the current efficiency of Zn-Mn co-deposition. These experiments were carried out at room temperature without stirring in a conventional three-electrode cell. The Zn plate was used as working electrode as well as the substrate material for the Zn–Mn co-deposit coating. Platinum (Pt) wire (high-purity Pt) was used as counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode mounted in a Luggin capillary. The Pt wire surface was successively abraded with emery papers of the following grade 600, 1000, and 1200, and then the wire was degreased in a saturated solution of NaOH in ethanol, pickled with 1 M HNO$_3$ for 30 s and finally rinsed with ethanol and distilled water.

**Manufacture of the Zn-Mn-deposited Zn//Ni foam-supported PANI-CL battery.**—To investigate the electrochemical performance of the Zn-Mn deposited Zn//Ni foam-supported PANI-CL battery, a reasonable cell system was designed. The prepared Zn-Mn-deposited Zn electrode was used as a cathode, and the fabricated Ni foam-supported PANI-CL composite electrode was used as a anode. Two electrodes were placed in a glass cell filled with acetate electrolyte solution composed of 0.5 M S$_2$, 0.3 M S$_4$, and 0.1 M CH$_3$COOLi for observing the charge and discharge performance of the present battery.

**Material and electrochemical characterization.**—The pH of all solutions was measured with a digital pH meter (PHS-3G, Shangh hai REX Instrument Co., China). The particle size distribution of
the PANI powder suspension was confirmed using laser particle size analyzer (Mastersizer 3000, Malvern, England). The electrical conductivity tests was implemented with conductivity meter (DDSJ-318 Shanghai REX Instrument Co., China). All electrochemical experiments were carried out using a CHI660D electrochemical analyzer (Chenhua Instrument Co., China). The working electrode was Ni foam, Ni foam-supported PANI, or a graphite plate. The counter electrode was Pt wire, and the reference electrode was a SCE. All potentials were referenced to the SCE. All charge/discharge experiments using the Zn-Mn-deposited Zn/Ni foam-supported PANI-CL battery were conducted with a BTS battery test system (Neware Ltd., China). The morphology of PANI, PANI-CL, and the Zn-Mn deposition layer was evaluated using a scanning electron microscope (JEOL JSM-6360F) coupled to an energy dispersion spectrometer (EDS) analyzer for elemental composition analysis.

Results and Discussion

**Influence of prior doping of Li⁺ on PANI.**—The CV (Fig. 1A) reflect the prior dopant concentration effect of CH3COOLi or without before compositing on the electrochemical performance of the resultant PANI by electropolymerization. With Li⁺ ions prior doping, the redox peak current of samples is steeply elevated, comparing with PANI-L0’s significantly vulnerable redox peak current without Li⁺ prior doping before composite. This result reveals that the powerful pseudo-protonation of Li⁺ ions leads to the anions embedding themselves into the sample for electrobalance.33,34 Those results bring about the enhanced conductivity of PANI which maybe due to the resultant delocalized charges on the PANI chains and the homogeneously distributed Li⁺ ions.33,34 which was confirmed by testing the electrical conductivity successively to yield the values of 1.8 and 2.2 S cm⁻¹ for PANI-L0, PANI-L0.1, samples. The mechanism may be explained by the SEM images of PANI with prior doping and without, shown in Fig. 1B. The micro morphology of PANI-L0 (Fig. 1B) appears a bulky flocculent structure with a greater number of large pores that likely interrupt the charge transfer between the substrate and the conductive materials. Fig. 1C shows a compact and scaly morphology of PANI, which indicates prior doping with Li⁺ ions not only results in pseudo-protonation, but also closely connects the conductive agent to the substrate. This morphology contributes to the electrical contact between PANI particles, which leads to a smooth charge transfer to drastically increase the redox peak current and improve its conductivity. This is consistent with the conclusion of Fig. 1A. However, Fig. 1A also shows that the concentration of CH3COOLi has less effect on peak current, probably because the Li⁺ ions in PANI were saturated at a concentration of 0.1 M during the prior doping.

**Electrochemical behavior of Ni foam-supported PANI-CL cathode in acetate electrolyte systems.**—The CV of aqueous electrolyte solution systems S₀, S₁, and S₅ were investigated using an electrochemical workstation (CHI660D) at room temperature with a three-electrode configuration using a Ni foam-supported PANI control cathode (1 cm × 1 cm) as the working electrode, Pt wire as the counter electrode, and a SCE as the reference electrode with a potential window between 0 V and 0.8 V at scan rates of 50 mV s⁻¹. The CV expresses information regarding the reversible characteristics of the electrode in an appropriate electrolyte solution and the influences of different concentrations and scan rates of dopants and electrolytes on the electrode.

As shown in Fig. 2A, Compared to S₀ and S₁ aqueous solution, the control cathode exhibits a lower redox current in the S₂ system and displays few redox peaks, which is due to the low acidity of acetate and the lack of Li⁺ ions pseudo protonation. It’s known that the redox current of PANI increase along with increasing acidity.34 However, S₅ in water will hydrolyze into the acidic HZn(OH)(CH₃COO)₂⁺, which can release protons to favor the PANI protonation, namely, H⁺ ions doping into the PANI material. The protonation can increase the electrochemical active, but there is only a small amount of ionization of the weak acid of HZn(OH)(CH₃COO)₂⁺, additionally with the feebly pseudo protonation of zinc ions. Thus, in Fig. 2Aa, the CV shows the lowest redox peak current. In the S₁ solution system, as shown in Fig. 2Ab, the cathode yields a strong electrochemical response with the highest peak current, which is attributed to stronger acidity, the pseudo-protonation of the zinc ions and the doping of the sulfate radical. However, the irregular peak shapes appear extremely asymmetrical, and the potentials of the redox peaks distinctly deviate from the original position of pure PANI, additionally with two pairs of redox peaks overlapping, which indicates that the cathode in the electrolyte system suffers from severe bad electrochemical reversibility. In contrast, in the S₂ medium, as shown in Fig. 2Ac, there are two pairs of obviously separate redox peaks with high peak current and relatively symmetrical shape, which indicates that the PANI has the best redox electrochemical property in the present system among the tested electrolytes. The first pair of redox peaks in the potential range of 0.3 V to 0.22 V relates to the oxidation from the PANI’s leucoemeraldine base (LEB) to emeraldine base (EB) and vice versa, accompanied by the doping or off-doping of Li⁺ and Zn²⁺ cations.33 Li ions provide a stronger pseudo-protonation than that of Zn²⁺ ions to increase the redox peak current, which is consistent with the conclusion of Fig. 1Ab. The second pair of redox peaks in the potential range of 0.5 V to 0.65 V relates to the redioxidation from EB to permigraniline (PE) and vice versa, accompanied by the doping or off-doping of anions. Fig. 2Ac exhibits a regular triangular shape, which suggests the present electrolyte system is a promising candidate solution for Ni foam-supported PANI composite cathode.

For the purpose of choosing a more suitable electrolyte system and an appropriate dopant for a Ni foam-supported PANI composite cathode with corrosion protection, the polarization curves of Ni

![Figure 1](https://example.com/image1.png)

**Figure 1.** Influence of prior dopant on PANI’s electrochemical properties and micro morphology. A: The CV of PANI electropolymerization before being prior doped with different concentrations of CH₃COOLi(PANI-L0, PANI-L0.1, PANI-L0.2, PANI-L0.3, PANI-L0.4, and PANI-L0.5, respectively). B: The SEM images of PANI without Li⁺ ions doping before composite. C: The SEM images of PANI that underwent prior doping of Li⁺ ions before composite.
foam-supported PANI in different electrolytes were detected in Fig. 2B. According to Fig. 2B, the corrosion potential (E_{corr}) is 0 V for S_0 system, 0.16 V for S_1 system, 0.18 V for S_1, 0.24 V for S_2. The E_{corr} positive shift of 0.16 V suggests the Ni-foam supported PANI electrode in weak acid salt solution with lower corrosion. And the positive shift of 0.18 V demonstrates that the control cathode in the electrolyte system of S_2 undergoes the lowest corrosion, which is possibly due to the higher hydrogen evolution overpotential of Mn. Simultaneously, the corrosion current (I_{corr}) for Ni-foam supported PANI in weak acid salt electrolyte systems also visibly decreases in comparison with the strong acid salt system. Thus, the Ni foam becomes stable in an acetate electrolyte system, particularly with the aid of Li and Mn^{2+} ions assistant, and with the smallest I_{corr}. So, the lowest corrosion speed can be obtained with the electrolyte system of S_2. In this regard, a more promising alternative S_5 is dopant of PANI-CL, the electrochemical performance of PANI-CL doping with Mn^{2+} ions were examined.

Fig. 2C indicates that the redox peak current of PANI-CL in the present electrolyte system relates to the concentration of S_5 among the electrolytes. As seen in Fig. 2Ca, PANI-CL doped with the 0.1 M Mn ions exerts a minor impact on the electroactivity due to the low doping quantity. Along with the rising of Mn^{2+} concentration, the peak current significantly increases. Once the doping concentration beyond 0.3 M, the Mn^{2+} concentration continues to increase, and the peak current exhibits little change, which illustrates that the Mn^{2+} ions approach to saturation status in PANI-CL. Continually adding S_5 will improve the electrochemical performance of PANI-CL. With the increase in S_5, the reduction peak potentials shift to the left, while the oxidation peaks potentials shift to the right, which enlarges the potential difference between the redox peaks. This occurs because when the current increase, the electrode polarization elevates, and the internal resistance within the circuit increases. However, the potential difference of the two pairs of redox peaks does not exceed 0.2 V, which illustrates that the electrochemical reactions exhibit excellent reversibility and high coulomb efficiency. The main effect of Mn doping on the electrical activity of PANI-CL is that the transition of the metal empty orbits combine with the imino groups in PANI. The nitrogen atoms in the PANI anthraquinone structure provide electrons for the transition metal to form π bonds. Mn ions are adsorbed on the surface of PANI and permeated into the interior of the PANI molecular chain. The doping process of Mn ions is a pseudo-protonation process. The formation of large π bonds facilitate the electron transferring in the PANI molecular chains and a resultant increase in the conductivity of PANI, which subsequently contributes to an improvement in electrical activity.

To confirm the marked advanced electrochemical performance of 0.3 M S_5 which was added to the electrolyte, electrochemical impedance spectroscopy (EIS) of the Ni foam-supported PANI-CL in different electrolytes was observed. The obtained Nyquist plots are shown in Fig. 2D. In the high frequency region, the intercept of the real axis relates to the resistance of the electrolyte solution, and the semi-circular radius represents the transmission resistance of electrons between the electrolyte solution and the PANI-CL interface. In accordance with the Nyquist diagram, the impedance spectrum of the undoped PANI in the low frequency region is a straight line at 45° to the x-axis, which indicates that the resistance is controlled by the ions diffusion process in the solution. With the concentration increase of the doping Mn ions, the equivalent series resistance (R_{ESR}) in the high frequency region cleanly drops. The slope of the straight line in the low frequency region increases and more closely resembles a pure capacitance behavior. The results show that Mn doping has a great effect on the conductivity of PANI-CL, and the conductivity of PANI-CL also increases with the increase in the Mn ion concentration, which is consistent with the conclusion of Fig. 1C. Therefore, it can be
determined that the solution of \( \text{S}_2 \) is the most suitable electrolyte system for a PANI-CL cathode.

**The effect of vacuum filtration pressures on the electroactivity of Ni foam supported PANI-CL.**—To prevent the surface corrosion of metal and implement hydrogen evolution to electrodeposit PANI-CL on Ni foam (SEM image shown in Fig. 3B) in acidic electrolyte, cathodic electroporesis was employed to form an adherent PANI-CL film on the Ni foam surface (SEM image shown in Fig. 3C) in anhydrous media. This was followed by low-vacuum casting of the PANI-CL slurry into a Ni foam skeleton coated with a thin PANI-CL film for a more compact PANI-CL cathode (namely, the E-SCVF process). It should be noted that the different vacuum degree could possibly change the electrochemical performance of the Ni foam-supported PANI-CL cathode, which was identified by the CV (Fig. 3A) of the present cathode prepared by casting under various vacuum pressures. One pair of visible redox peaks are observed around 0.59 V and 0.52 V, which is due to the partial redoxidation of PANI, and one pair of redox peaks are observed around 0.20 V and 0 V, which can be attributed to the doping/dedoping of \( \text{Li}^+ \) ions and \( \text{Mn}^{2+} \) ions into/from PANI for the Ni foam-supported PANI-CL composite cathode. However, the curve b in Fig. 3A of the present cathode cast at 3000 Pa appears a higher redoxidation peak current than that of the others. This probably occurred because many large pores remained within the present cathode structure (Fig. 3D) due to the casting with insufficient PANI-CL electroactive composite at a low degree of vacuum. The porous structure leads to a lax connection between PANI-CL particles or an incoherent interface between the Ni substrate and PANI-CL, and neither of these are conductive for charge transfer. As shown in Fig. 3F, a high casting vacuum pressure of 2000 Pa causes too dense material structure for the electrolyte solution to permeate into the internal electrode, and part of the Ni skeleton was broken, which results in a large internal resistance that occurs with low peak current (Fig. 3Ac). Seen in Fig. E, the medium vacuum casting process made large pores disappear and residual capillary pores appear. The capillary pores could facilitate the movement of the external electrolyte solution into the internal material and simultaneously occurrence with the smooth electron transmission channel which favor the high peak current (Fig. 3Ab). Moreover, the shortest distance of 0.07 V between the first oxidation peak and counter-reduced peak of PANI, as shown in Fig. 3Ab, predicts the promising reversibility of the present cathode in the charge/discharge process.

**Co-electrodeposition of Zn-Mn on a Zn anode.**—For investigating the electrodeposition behavior of \( \text{Mn}^{2+} \) and \( \text{Zn}^{2+} \) ions on the Zn anode during the charging process in electrolyte solution containing \( \text{S}_4 \) and \( \text{S}_5 \), linear sweep voltammograms (Fig. 4A) of the Zn electrode with effect surface of 1 cm\(^2\) were obtained in three solutions to certify the potential ranges where the redox reactions occur. It was finally found that \( \text{Mn}^{2+} \) and \( \text{Zn}^{2+} \) ions normally co-deposit between \(-1.55\) V and \(-1.12\) V, which is consistent with previous studies.\(^{42,43}\) The peak \( \text{C}_1 \) at approximately \(-1.15\) V represents of Zn deposition. Negative shift of 0.4 V compared to the standard \( \text{Zn}^{2+}/\text{Zn} \) potential, with higher hydrogen overpotential, indicates an increase in the anti-corrosion ability of the Zn electrode, which was due to the protective function of the Mn coating around Zn. The start potential for the peak \( \text{C}_2 \) is at approximately \(-1.35\) V, where Mn deposition begins, and is more positive than the standard \( \text{Mn}^{2+}/\text{Mn} \) potential of \(-1.42\) V vs. SCE, which suggests that the Mn deposits are accompanied by the hydrogen evolution. It should be noted that the difference between the deposition potentials was narrowed, and probably denotes the presence of acetic acid, which buffered the pH at 5.5, and thus inhibited the hydrogen formation by absorbing on the electrode surface and blocking the active center. As the \( \text{Zn}^{2+} \) ion concentration increases with a constant \( \text{Mn}^{2+} \) ion

![Graph](https://via.placeholder.com/150)

**Figure 3.** The properties of Ni foam-supported PANI-CL composite film electrode that was cast under various vacuum. A: CV of the present electrode in a solution of \( \text{S}_2 \), (a): 4000 Pa, (b): 3000 Pa, (c): 2000 Pa, at a scan rate 10 mV S\(^{-1}\). B: SEM image of pure Ni foam. C: SEM image of the Ni foam with thin PANI-CL film prepared by electroporesis without vacuum-casting the PANI-CL slurry. D: the SEM image of electrode casted at 4000 Pa. E: the SEM image of electrode casted at 3000 Pa. F: the SEM image of electrode casted at 2000 Pa.
Figure 4. Co-deposition performance of Zn-Mn on the Zn anode. A: Linear sweep voltammograms of the Zn electrode in three different solutions at a scan rate of 20 mV S$^{-1}$, (a): 0.5 M S$_4$ + 0.3 M S$_5$, (b): 0.3 M S$_4$ + 0.3 M S$_5$, and (c): 0.1 M S$_4$ + 0.3 M S$_5$. B: For Zn-Mn co-deposition, the S$_4$ content influenced (a): coulomb efficiency and (b): Mn at% in deposition layer. C: Surface morphology of the Zn-Mn deposition indicates the S$_4$ content in the solution at (a): 0.1 M, (b): 0.5 M and (c): 0.7 M. D: GDS elemental-distribution profiles of a Zn–Mn layer electrodeposited at $E_{\text{Deposition}} = -1.60$ V, SCE, from solution 0.5 M S$_4$ + 0.3 M S$_5$.

concentration of 0.3 M, the peak C$_1$ current intensity increases, while the peak C$_2$ intensity simultaneously decreases, because with a low Zn$^{2+}$ content, the Mn$^{2+}$ atomic concentration (at%) in the main salt increases, which subsequently facilitates to enhances Mn deposition and hydrogen evolution.

For the purpose of confirming the dependence of Mn at% on the deposition layer and the dependence of hydrogen evolution on the Zn$^{2+}$ ion content (which relates the at% ratio of Mn$^{2+}$ and Zn$^{2+}$) in electrolytes, without changing the Mn$^{2+}$ content, the chronocoulometry was introduced for depositing Zn-Mn with the same three-electrode system and some similar electrolytes as those used in the linear sweep voltammograms at 0.2 A cm$^{-2}$. The total hydrogen that evolved during the deposition was collected in a burette, and the hydrogen gas volume was determined and then applied to calculate the current...
density related to the hydrogen evolution reaction by using Faraday’s law. Ultimately, the current efficiency for deposition was calculated by subtracting the current density related to hydrogen evolution from the total current density employed. The relationship between current efficiency and the Zn\(^{2+}\) ions content in the electrolyte is shown in Fig. 4B. The current efficiency prominently increases along with the increase of Zn\(^{2+}\) ions content from 0 M to 0.1 M, which occurs because of the decreasing Mn\(^{2+}\) at% in the electrolyte and this contributes to the decrease in hydrogen evolution and the Mn at% in the deposition layer. Then, the current efficiency has a slight increase from 93.3% (0.3 M Zn\(^{2+}\)) to 93.7% (0.7 M Zn\(^{2+}\)), and then finally almost parallels the \(x\)-axis. The connection between the Mn at% in deposition and the Zn\(^{2+}\) ion content in the electrolyte is shown in Fig. 4Bb. The platform of Mn content at approximately 6.5 at% in deposition is related to Zn\(^{2+}\) ions concentration from 0.1 M to 0.5 M, because the stable phase formation that inhibits the Mn deposition to re-dissolve into the solution. The three SEM images of Zn-Mn deposition from three electrolytes containing 0.1 M, 0.5 M, and 0.7 M S\(_4\), are shown in Fig. 4C, respectively. Fig. 4Ca exhibits a type of platelet groups that grow in multilayers in a vertical orientation with large and small holes in the surface, which favors corrosion and hydrogen evolution. As the Zn\(^{2+}\) ion concentration increases from 0.1 M to 0.5 M, the surface morphology (Fig. 4Cb) of the deposition transforms to more compact, smooth, adherent, and fine particle. However, from the solution containing 0.7 M S\(_4\), the deposit appears to possess dendrites with trunks and branches, as shown in Fig. 4Cc. This type of structure could easily pierce the battery separator and re-dissolve in the electrolyte. Therefore, from a concentration of 0.5 M of higher content, the at% of Mn in the deposition dramatically decreases. In addition, as the at% ratio of Mn\(^{2+}\) and Zn\(^{2+}\) decreases, the Mn deposit also decreases. Taking into consideration the current efficiency, corrosion protection, hydrogen evolution, and surface morphology, the optimal concentration of S\(_4\) in the electrolyte should be determined at 0.5M.

The structure and components of the Zn–Mn alloy obtained from solution of S\(_4\) was determined by XRD and GDS, shown in Fig. 4D, the XRD diffractograms shows that the principal components of the deposit layer are a mixture of Zn(101) and \(\varepsilon\)-phase Zn–Mn (002) and \(\alpha\)-phase Zn–Mn (111). Thus, the compact morphology observed in the SEM image is essentially due to this mixture of preferred orientations. The GDS elemental distribution profiles shows that the concentration of Zn and Mn remains nearly constant and homogeneous (Zn 92.9%, Mn 6.5%) throughout the thickness of the deposit layer until to the depth of 12 μm. On going deeper into the interval layer, the concentration of Zn increased and Mn diminished, and a signal corresponding to the substrate (Zn) begun to be observed.

**Charge/discharge performance of Zn-Mn co-deposited on a Zn//Ni foam-supported PANI battery fabricated by the present method.**—In order to investigate the electrochemical response of the present Zn-Mn deposited Zn//Ni foam-supported PANI battery, the charge/discharge performance was tested by using a cell voltage ranging from 0.7 V to 1.8 V at different current densities in order to determine the large current charge/discharge capacity and cycle performance. In XRD spectrum (Fig. 5) of the prepared Zn-Mn deposition layer during the discharging process for different time, the peaks strength of Zn(101), \(\varepsilon\)-phase Zn–Mn (002) and \(\alpha\)-phase Zn–Mn (111) for 12 h reduced three times less than that of discharging process for 3 h, which indicated that Zn and Mn are simultaneously released from the layer on Zn substrate plate, and this mechanism may involve a dual ion battery system. During the charging process, Zn\(^{2+}\) and Mn\(^{2+}\) cations deposit on the Zn plate, while PANI is oxidized with the doping of CH\(_3\)COO\(^{-}\). The cell reaction is shown in Equation 1:

\[
\text{mZn} \text{(yMn)} + 2x\text{Li}^+ + (\text{oxidized} \ 2(y+x) \ \text{PANI} \text{(CH}_3\text{COO})^\text{-})_{2y+x} \\
\leftrightarrow \text{mZn}^{2+} + (\text{reduced} \ \text{PANI})_{y+x} \text{(Mn}^{2+})_x \text{(Li}^+)_{2x} + 2(x+y) \ \text{CH}_3\text{COO}^- \tag{1}
\]

In the reaction, because of being doped with protonic acid, the synthetic PANI carries positive charges and bonds with acetate anions in the solution. During discharge, the oxidized PANI is reduced, which is due to obtaining electrons that will be used to neutralize the positive charge, followed by de-doping of the acetate anions and doping of the Mn\(^{2+}\) and Li\(^+\) cations. During the charging process, the reduced PANI is oxidized, which is contributed to the release of electrons and Mn\(^{2+}\) and Li\(^+\) cations, and the acetate anions in the solution are bound to the oxidized PANI, which results in the solution appearing positive for electrification.

Fig. 6A shows the charge/discharge curves of the present battery at current densities of 2mA.cm\(^{-2}\), 5mA.cm\(^{-2}\) and 10mA.cm\(^{-2}\), respectively. There is a relatively high discharge upper voltage of 1.6 V, which is 0.5 V higher than that of the Zn//Ni foam-supported PANI battery. A stable discharging platform in the voltage range of 1.0 V to 1.6 V is seen, whether with large or small current discharge, which represents the present battery with high specific capacity and lower load loss. The change between the charge termination voltage and the discharge start voltage is less than 0.2 V, which indicates that the small ohmic drop (IR drop) and slight polarization were generated during the charging process. The high capacitance depends on the large specific surface of the Ni foam and results in further enhancement of the electrode storage charge capacity. The porous structure of Ni-foam contributes to the ions diffusion and a faster electrons transfer, therefore a large current charge and discharge mechanism can be used in the present battery. Fig. 6B indicates that the charge/discharge cycling performance of the present battery is still excellent at a large current density of 10 mA.cm\(^{-2}\). Therefore, large current can contribute a higher output power. The discharge capacity of the present battery in the first cycle is as high as 142.3 mAh.g\(^{-1}\), and is 142.0 mAh.g\(^{-1}\) (as calculated by the weight of PANI) after four cycles. The average discharge capacity loss is not greater than 0.06%. Therefore, the Ni foam-supported PANI-CL electrode is more stable in the acetate electrolyte. The insufficient acidic system can also be supplemented by lithium ions. Namely, the acetate electrolyte not only reduces the acidity of the bath, but also ensures the electroactivity of PANI. Additionally, the close distance between the charge curve and the discharge curve confirms the satisfactory conductivity of the electrolyte. Fig. 6B appears that the voltage of the battery gradually increases from 1.2 V to 1.8 V during the charge process, with a turning point at the charge voltage of approximately 1.4 V, and then a smooth increasing. An IR drop of approximately 0.2 V occurred at the beginning of the discharging process, and then the battery voltage swiftly shifted to approximately

**Figure 5.** XRD spectrum of the prepared Zn-Mn deposition layer during the discharging process for different time.
0.75 V, which indicates that the discharge upper voltage is approximately 1.6 V. Consequently, the average charge and discharge voltages of the cell were approximately 1.5 V and 1.3 V, respectively. The open circuit voltage was approximately 1.45 V. Thence, the present battery may offer a higher working voltage than pure Zn//Ni foam-supported PANI.

The charge/discharge cycling performance of the present battery is exhibited in Fig. 7. After 60 charge/discharge cycles at current density of 10 mA cm$^{-2}$, its discharge capacity remained at 94.7% of the original value. The coulomb efficiency showed no significant change, with an average value of 90% throughout the experiment, which demonstrated the battery in the present system possesses favorable cycle characteristics. The decrease in the coulomb efficiency and occurrence of self-discharging may result from the evolution of hydrogen on the anode and changing the experimental factors such as water evaporation that lead to solution transformation.

Conclusions

PANI-L attained higher redox peak current and improved electrochemical reversibility. A acetic salt was used as the electrolyte system, which resulted in lower corrosion of the Ni foam-supported PANI cathode. In the $S_2$ system, the pseudo-protonated behavior of Mn$^{2+}$ and Li$^+$ ions resulted in the increased electrochemical activity and strengthened stability of the system. We have demonstrated that the present system showed an improved performance of the charge/discharge process and high coulomb efficiency at high current density for a Zn//Ni foam-supported PANI battery. Co-electrodeposition was successively applied to fabricate a Zn-Mn-deposited Zn anode, of which the coulomb efficiency was significantly affected by the Zn$^{2+}$ concentration in the electrolyte. The battery tests have showed that the Zn-Mn co-electrodeposited Zn anode and Ni foam-supported PANI cathode in the $S_2$ battery system possessed good electrochemical performance and stable cycling performance. The present Zn-Mn-deposited Zn//Ni foam-supported PANI composite battery displayed an obvious improvement in cycle performance. After 60 cycles, its discharge capacity still remained at more than 94.7% of the original value, and the coulomb efficiency showed no significant change, with an average value of 90% throughout the experiment. This work indicates a feasible approach toward obtaining improved rechargeable batteries with low corrosion, prohibited hydrogen evolution and high discharge capacity by prior doping, acetic electrolyte, and Zn-Mn co-deposited Zn electrode.

Acknowledgments

The authors are grateful to the Nature Science Foundation of China (No. 21727810), the Nature Science Foundation of Hunan Province of China (No. 2018JJ5024) and the Nature Science Foundation of Hunan Chemical Vocational Technology College (No. HNHY2017011) for financial support.

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