

Article

Effects of Carboxylates on the Performance of Zn Electrode

Yongli Li, Zhuan Hu and Jinqing Kan *

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China; 15705279695@163.com (Y.L.); 1822590211@139.com (Z.H.)

* Correspondence: jqkan@yzu.edu.cn; Tel.: +86-514-8797-5590 (ext. 9415); Fax: +86-514-8797-5590 (ext. 8410)

Academic Editor: Hugo F. Lopez

Received: 28 June 2016; Accepted: 21 July 2016; Published: 26 July 2016

Abstract: Zinc is widely used as a negative electrode material for batteries due to its excellent electrochemical properties. Zinc is prone to corrosion and the formation of zinc dendrites cause short circuits of the battery, which leads to reduced battery capacity and shortens the battery's life, hindering its use in weak acidic electrolytes (for example, aqueous Zn-polyaniline batteries). The effects of carboxylates (sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate, disodium malonate, and disodium succinate) and their concentrations on zinc electrode performance were studied with electrochemical methods to improve the zinc electrode activity for long-life Zn-polyaniline batteries. It was found that the ability of inhibiting corrosion of the zinc electrode is better in the aqueous electrolyte containing 0.2 M disodium malonate. The charge/discharge performance of a Zn-polyaniline battery electrodeposited with polyaniline on a carbon substrate is carried out in the aqueous electrolyte. The results show that the initial discharge specific capacity of the polyaniline in the Zn-polyaniline battery is as high as $131.1 \text{ mAh} \cdot \text{g}^{-1}$, and maintains a discharge specific capacity of $114.8 \text{ mAh} \cdot \text{g}^{-1}$ and a coulombic efficiency over 92% after 100 cycles at a charge/discharge current density of $1 \text{ A} \cdot \text{g}^{-1}$ in the voltage range of 1.5–0.7 V.

Keywords: zinc; weak acidic electrolyte; hydrogen evolution; carboxylate; polyaniline

1. Introduction

In recent years, the role of zinc in the field of science and technology has been a subject of intense research [1,2]. Zinc is widely used as a negative electrode material of batteries (such as Zn-Mn and Zn-Ag batteries) owing to the advantages of low equilibrium potential, high specific energy density, being an abundant resource, having low cost, and being environmentally friendly [3]. Conducting polymer polyaniline (PANI) [4,5] has attracted researchers' interest as a cathode active material of rechargeable batteries in aqueous [6–8] and non-aqueous electrolytes [9–12] (such as Zn-PANI secondary battery [13–17] and Li-PANI secondary battery [18–20]). A significant portion of these studies has been devoted to PANI that exhibit excellent electrochemical activity and environmental stability. PANI is easy to synthesize by the chemical or electrochemical oxidative polymerization of aniline [21], and it is also the first commercially-cheap conducting polymer available [22].

The excellent performances of zinc and PANI have inspired the interest in their use as electrode materials of electrochemical power sources. According to Rüetschi, and elaborated by Fritz Beck and Paul Rüetschi, determining factors of the battery system success are a “three E” criteria: energy (high-energy content with respect to unit weight and volume), economics (low manufacturing costs, low maintenance during use, long service life), and environment (free of toxic materials, safe, low energy consumption during manufacture and uses, long service life, high reliability, and easy to recycle) [23,24].

The aqueous Zn-PANI secondary battery based on the abundant and cheap metal (Zn) as negative electrodes, safe and nontoxic conducting polymers (polyaniline) as the positive electrodes, and clean and non-polluting aqueous-based electrolytes, have the potential to accomplish most of the three E' criteria.

For an aqueous Zn-PANI secondary battery, the aqueous electrolyte was mainly the mixture of ZnCl_2 and NH_4Cl or ZnSO_4 and $(\text{NH}_4)_2\text{SO}_4$ [16,17] at pH 4.0–5.5. pH 4.0–5.5 was chosen as a trade-off between a decreased electrochemical activity of PANI at higher pHs and increased Zn corrosion in acidic solutions. It is well known that the zinc electrode is prone to hydrogen evolution corrosion, which leads to reduced battery capacity and shortens the lifecycle of the zinc electrode, which impedes zinc's use in a weak acidic electrolyte.

in this paper the influences of carboxylates as the additives of an aqueous electrolyte on the performance of the Zn electrode are studied. The results show that the new electrolyte can effectively eliminate the hydrogen evolution corrosion of the zinc electrode and improve the discharge capacity and the cycle life of Zn/PANI secondary batteries.

2. Materials

All chemicals used were analytical grade. Sodium formate, sodium acetate, sodium propionate, disodium succinate and succinic acid were purchased from the Shanghai Titan Scientific Co., Ltd. (Shanghai, China). Trisodium citrate was offered by the Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Sodium butyrate, sodium valerate, zinc chloride, ammonium chloride, hydrochloric acid, ethanol and aniline were obtained from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Disodium malonate ($\geq 98\%$) was purchased from the Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). Zinc sheet (0.33 mm) was offered by Hai'an Chunjia Metal Products Co., Ltd. (Jiangsu, China). Other chemicals were used as received without a further treatment. All of the aqueous solutions were prepared with doubly distilled water.

2.1. Preparation of Aqueous Electrolyte Solution

The aqueous electrolyte solution is prepared, which contains the zinc chloride, ammonium chloride, disodium succinate, and trisodium citrate. Suitable hydrochloric acid was added to the electrolyte solution in order to adjust pH to 4.0. By the same method, the disodium succinate was respectively replaced by other carboxylates (sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate, and disodium malonate) in the above solution for preparing different kinds aqueous electrolyte solution.

2.2. Preparation of Electrodes

The electrochemical polymerization of the aniline was performed on a CHI 660D electrochemical workstation with a three-electrode system, a 17×30 mm graphite plate electrode, a 50×50 mm graphite plate electrode and a saturated calomel electrode (SCE) as the working electrode, the counter electrode, and the reference electrode, respectively. All potentials recorded are referred to SCE. PANI films were synthesized by the current-time curves with constant potential of 1.0 V in an aqueous 1.0 M HCl solution with 0.2 M aniline. After the electrochemical polymerization of the aniline, the PANI electrode obtained was repeatedly washed with acetone and doubly-distilled water until the washing liquid was completely colorless to remove small molecular-weight contaminants generated during polymerization. Finally, the PANI electrode was dried at 60°C .

The zinc electrode was polished with fine emery paper to remove oxides on its surface. Second, it was repeatedly washed with acetone and the doubly distilled water to clear dirt. Finally, the interface between the zinc sheet and the solution was covered with nail oil as a coating to prevent the zinc sheet being corroded by the air.

2.3. Characterization

Cyclic voltammograms (CV) were recorded on a CHI 660D electroanalysis apparatus (CHI Instruments, Austin, TX, USA) and electrochemical impedance spectroscopy (EIS) powered by an electrochemical workstation (AutoLab, Nova 1.9, Metrohm, Utrecht, The Netherlands) was used to compare the electrochemical activities of the zinc or PANI in different aqueous electrolytes, respectively. The cyclic voltammograms of the zinc electrode were recorded and the potential range was from -1.4 to -0.9 V at $50 \text{ mV} \cdot \text{s}^{-1}$ for 10 cycles in the electrolytes. EIS of the zinc electrode were obtained in the electrolyte with 10×10 mm zinc film as work electrode. The superimposed sinusoidal voltage signal was set up to 10 mV amplitude. Data were collected within the frequency range from 10^5 to 10^{-1} Hz. The CV and EIS were performed in a standard three-compartment three-electrode cell with zinc electrode or PANI electrode, Pt foil and saturated calomel electrode (SCE), which served as a working electrode, a counter electrode and a reference electrode, respectively. The surface morphologies of the zinc sheet were studied by using a scanning electron microscope (SEM, SUPRA 55-4828, Oberkochen, Germany).

3. Results and Discussion

3.1. Electrochemical Performance of the Zinc Electrode in the Aqueous Electrolyte Containing Different Monocarboxylates

Figure 1 shows the CV of the zinc electrode in the aqueous electrolyte containing different monocarboxylates, respectively. Figure 1 shows that the zinc electrode has higher peak current and larger peak area in the electrolyte containing sodium propionate, and it also has better symmetry. This indicates the zinc electrode has good reversibility and high electrode capacity in the aqueous electrolyte containing sodium propionate. Figure 2A shows the EIS of the zinc electrode in the aqueous electrolyte containing different monocarboxylates. The semicircle in Figure 2A is attributed to charge transfer resistance in combination with the double layer capacity of the electrode. The diameter of the semicircle represents the charge transfer resistance (R_{ct}). Figure 2A displays that R_{ct} of the zinc electrode is at a minimum in the electrolyte containing sodium propionate, which is about 50 ohms. This is because the carboxylate molecules were attracted to the surface of the zinc sheet and formed an adsorption layer. The hydrogen ions in the carboxyl of the carboxylate molecules are mutually exclusive with the free hydrogen ions in aqueous solution or the lone pair electrons of oxygen atoms in the carboxyl form hydrogen bonds with hydrogen ions in aqueous solution. Consequently, they obstruct the zinc atoms to get in touch with hydrogen ions, inhibiting the hydrogen evolution on the Zn electrode. The alkyl chain lengths in sodium formate and sodium acetate are too short to form dense adsorption layers on the zinc electrode. A longer alkyl chain may be twisted, which will lead to the formation of the cracks that cannot effectively prevent the zinc sheet coming into contact with free hydrogen ions in aqueous solution, resulting in the easier formation of hydrogen evolution (Figure 2C). The alkyl chain length of the sodium propionate is more suitable to form the dense adsorption layers on the zinc electrode than that of other monocarboxylates (Figure 2B), so the zinc electrode has better stability in the aqueous electrolyte containing sodium propionate.

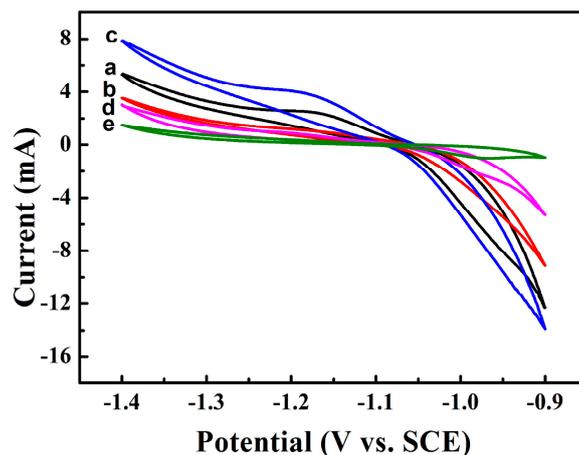


Figure 1. The CV of the zinc electrode in the aqueous electrolyte containing different monocarboxylates from -1.4 to -0.9 V at $50 \text{ mV} \cdot \text{s}^{-1}$. (a: sodium formate; b: sodium acetate; c: sodium propionate; d: sodium butyrate; and e: sodium valerate).

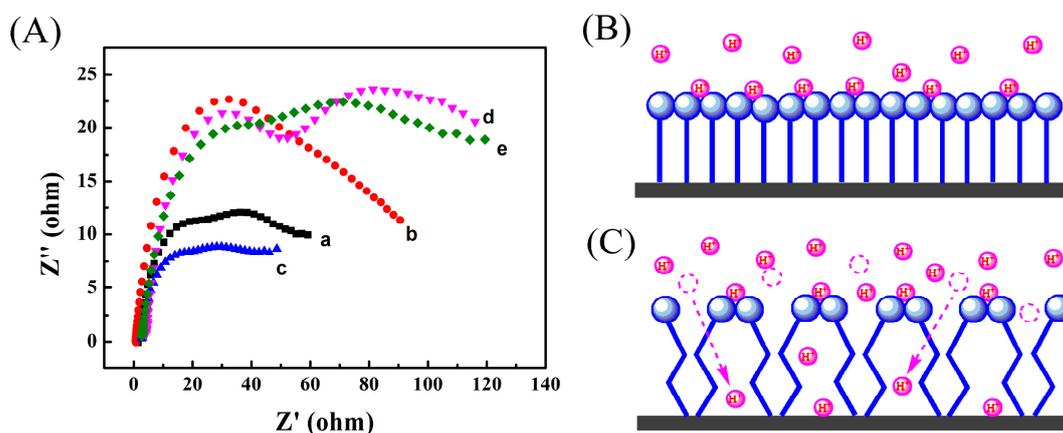


Figure 2. EIS (A) of the zinc electrode in the aqueous electrolyte containing different monocarboxylates within the frequency range from 10^5 to 10^{-1} Hz. (a: sodium formate; b: sodium acetate; c: sodium propionate; d: sodium butyrate; and e: sodium valerate). (B,C) show structure sketches of the different adsorption layers of the zinc electrode.

3.2. Electrochemical Performance of the Zinc Electrode in the Aqueous Electrolyte Containing Different Dicarboxylates

Figure 3 shows the CV of the zinc electrode in the aqueous electrolyte containing different dicarboxylates, respectively. Sodium oxalate was not as additive because it can react with zinc ions forming zinc oxalate, which is hardly dissolved in water. The dicarboxylates with more than the chain lengths of glutaric acid are more difficult to be dissolved in water. Some dicarboxylates have an irritating odor or are harmful to the human body and the environment, thus only disodium malonate and disodium succinate of dicarboxylates are discussed. Figure 3 shows that the zinc electrode has higher peak current and larger peak area in the aqueous electrolyte containing disodium malonate. Figure 4 displays EIS of the zinc electrode in the aqueous electrolyte containing different dicarboxylates. The result shows the R_{ct} of the zinc electrode in the aqueous electrolyte containing disodium malonate is smaller than that of disodium succinate, which is consistent with the result from Figure 3.

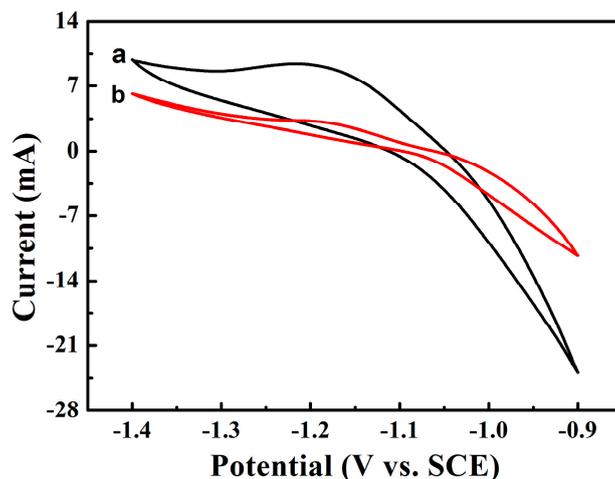


Figure 3. CV of the zinc electrode in the aqueous electrolyte containing different dicarboxylates (a: disodium malonate; and b: disodium succinate).

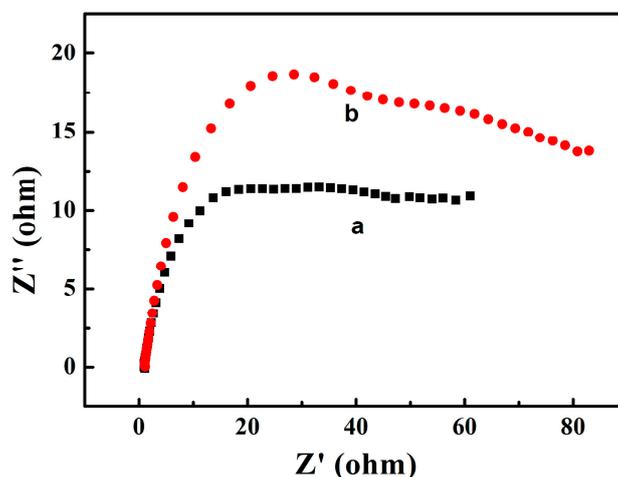


Figure 4. EIS of the zinc electrode in the aqueous electrolyte containing different dicarboxylates (a: disodium malonate; and b: disodium succinate).

3.3. Electrochemical Performance of the Zinc Electrode in the Aqueous Electrolyte Containing Different Concentrations Sodium Propionate or Disodium Malonate

The Figures 1–4 results prove that the zinc electrodes have better activity in the aqueous electrolyte containing sodium propionate or disodium malonate. The concentration of sodium propionate or sodium malonate were, respectively, changed in order to obtain their optimum concentration. The results of CV and EIS show that zinc electrodes have better electrochemical activity in the electrolyte containing 0.1 M sodium propionate (Figure 5) or 0.2 M disodium malonate (Figure 6). Figure 5A shows that zinc electrode has higher peak current and larger peak area in the electrolyte containing 0.1 M sodium propionate. Figure 5B displays the charge transfer resistance of the zinc electrode is less than that of other concentrations. From Figure 6A, it shows that the zinc electrode has higher peak current and larger peak area in the aqueous electrolyte containing 0.1 M disodium malonate, but its charge transfer resistance is maximum in Figure 6B. The charge transfer resistance of the zinc electrode is smaller and its capacitance is larger in the aqueous electrolyte containing 0.2 M disodium malonate than that of other concentrations. Obviously, the zinc electrodes have excellent electrochemical performances in the aqueous electrolyte containing 0.1 M sodium propionate or 0.2 M disodium malonate.

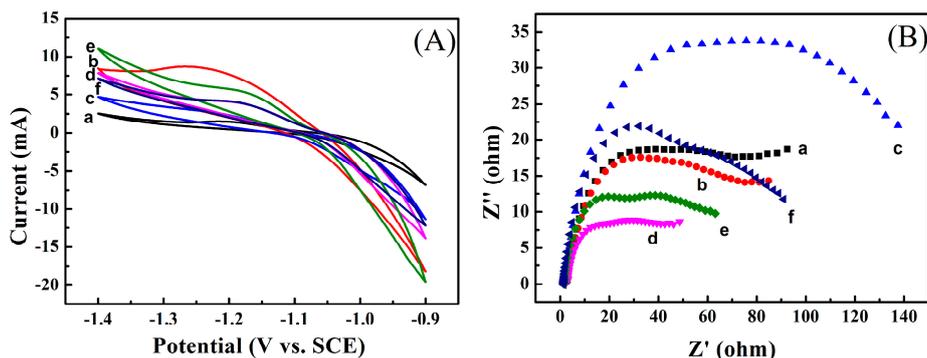


Figure 5. CV (A) and EIS (B) of the zinc electrode in the aqueous electrolyte containing different concentrations of sodium propionate (a: 0.05 M; b: 0.10 M; c: 0.15 M; d: 0.20 M; e: 0.25 M; and f: 0.30 M).

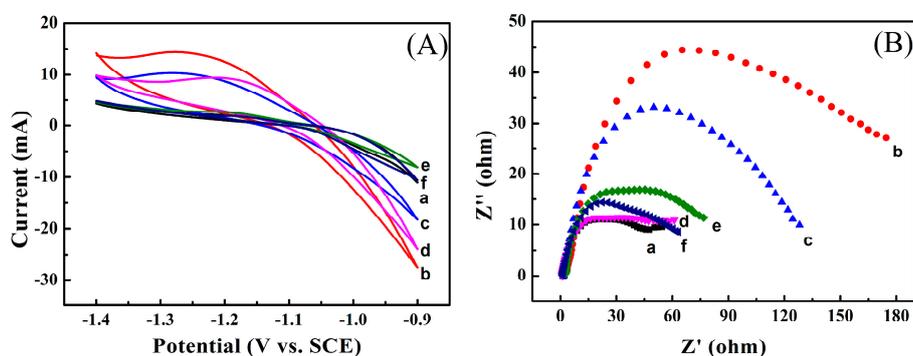


Figure 6. CV (A) and EIS (B) of the zinc electrode in the aqueous electrolyte containing different concentrations of disodium malonate (a: 0.05 M; b: 0.10 M; c: 0.15 M; d: 0.20 M; e: 0.25 M; and f: 0.30 M).

3.4. Comparing the Electrochemical Performance of the Zinc Electrodes in the Aqueous Electrolyte Containing 0.1 M Sodium Propionate or 0.2 M Disodium Malonate

compared with electrochemical activity in the aqueous electrolyte containing 0.1 M sodium propionate, it is found from Figure 7 that the zinc electrode has better electrochemical activity in the aqueous electrolyte containing 0.2 M disodium malonate (curve b) as the zinc electrode has higher peak current, larger peak area, and smaller charge transfer resistance in the system. The aqueous electrolyte containing 0.2 M disodium malonate is more appropriate for Zn electrodes.

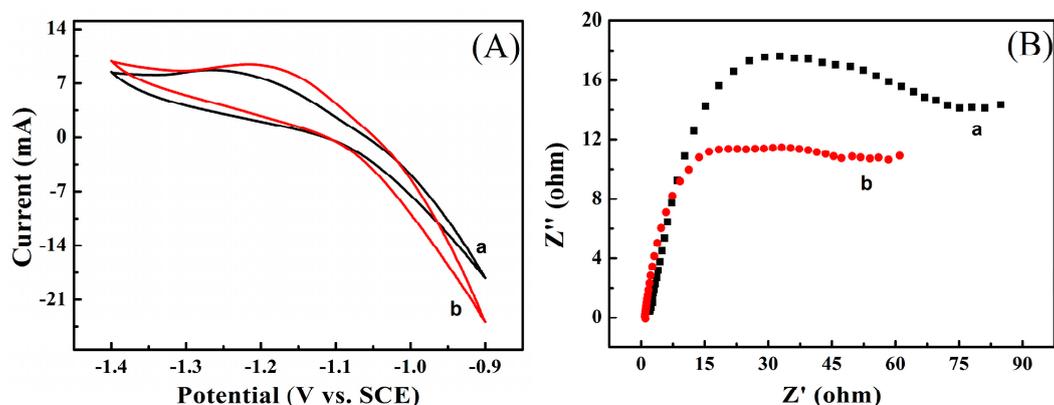


Figure 7. CV (A) and EIS (B) of the zinc electrode in the aqueous electrolyte containing 0.1 M sodium propionate (curve a) or 0.2 M disodium malonate (curve b).

3.5. Studying on the Corrosion Performance of the Zinc Sheet by SEM in the Aqueous Electrolyte Containing 0.2 M Disodium Malonate

Figure 8 displays SEM images of the zinc sheet before soaking (A), after soaking two days (B), and 30 days (C) in the aqueous electrolyte containing 0.2 M disodium malonate, respectively. From Figure 8, the scratches were left on the surface of the zinc sheet when polished with fine emery paper. When the zinc sheet was soaked for 30 days in the aqueous electrolyte, it was found that the scratches on the zinc surface can still be clearly seen from Figure 8C. It shows that the aqueous electrolyte containing 0.2 M disodium malonate is good to inhibit the corrosion of the zinc sheet. The result is consistent with that the zinc electrode has better electrochemical properties in the aqueous electrolyte containing 0.2 M disodium malonate.

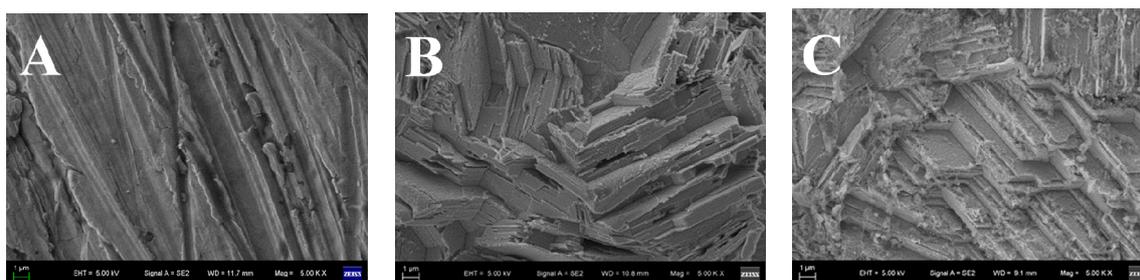


Figure 8. SEM of the zinc sheet before soaking (A) and after soaking 2 days (B) and 30 days (C) in the aqueous electrolyte containing 0.2 M disodium malonate.

3.6. Effect of Carboxylates on Properties of PANI

Figure 9 shows CV, Tafel curves, and EIS of PANI in the aqueous electrolyte containing different carboxylates, respectively. From Figure 9, it is found that PANI has higher peak current, larger peak area, higher open circuit potential, and smaller resistance in the aqueous electrolyte containing disodium malonate. Figure 10 shows electrochemical performances of PANI in the aqueous electrolyte containing different concentrations disodium malonate. From Figure 10A, it is that the PANI has better symmetry and larger peak area and smaller resistance (about 2.5 ohm) in the aqueous electrolyte containing 0.05 M or 0.25 M disodium malonate. However, PANI has also higher open circuit potential and its charge transfer resistance is also smaller (about 3 ohm) in the aqueous electrolyte containing 0.2 M disodium malonate.

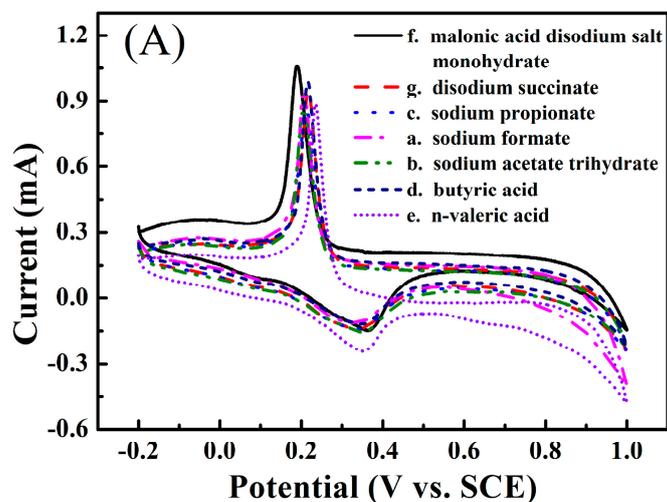


Figure 9. Cont.

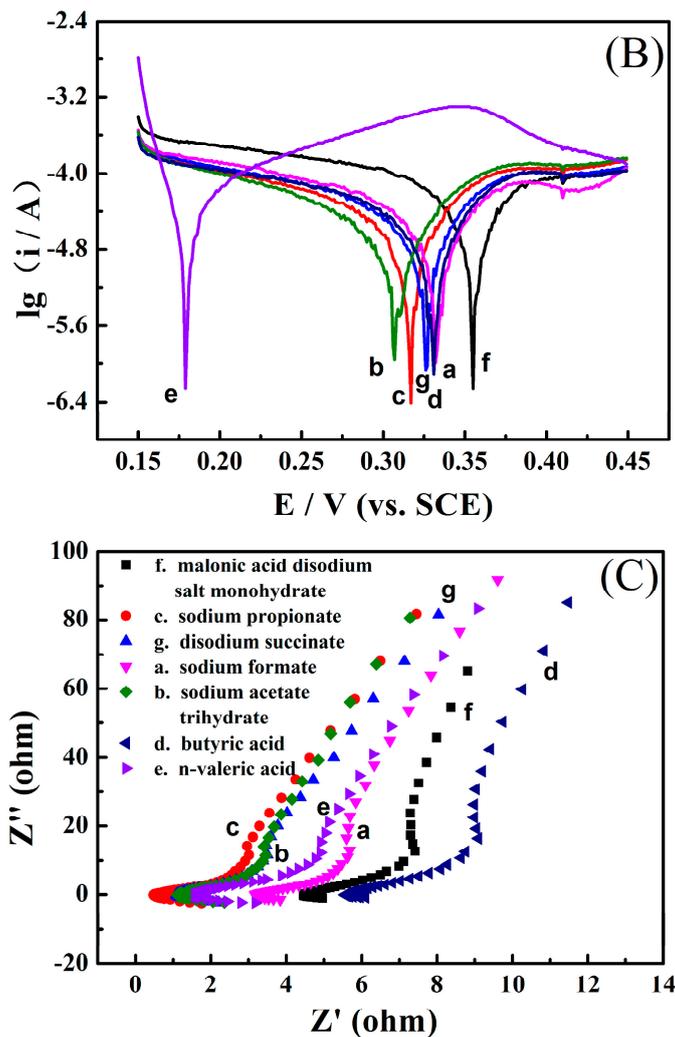


Figure 9. CV (A), Tafel curves (B), and EIS (C) of polyaniline in the aqueous electrolyte containing different carboxylates (a: sodium formate; b: sodium acetate; c: sodium propionate; d: sodium butyrate; e: sodium valerate; f: disodium malonate; and g: disodium succinate).

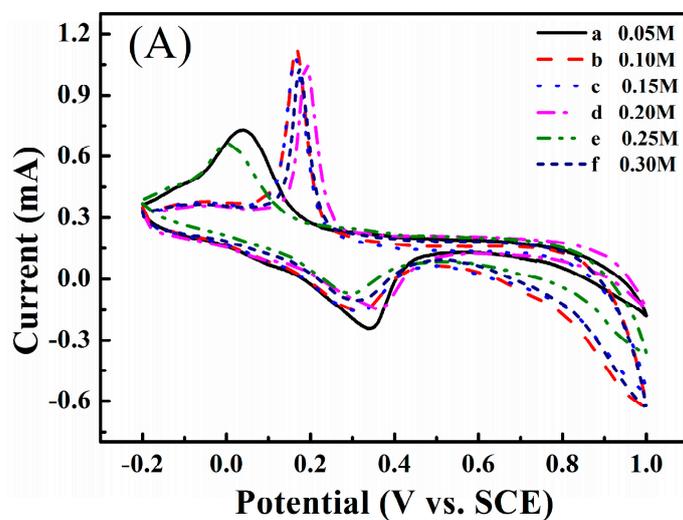


Figure 10. Cont.

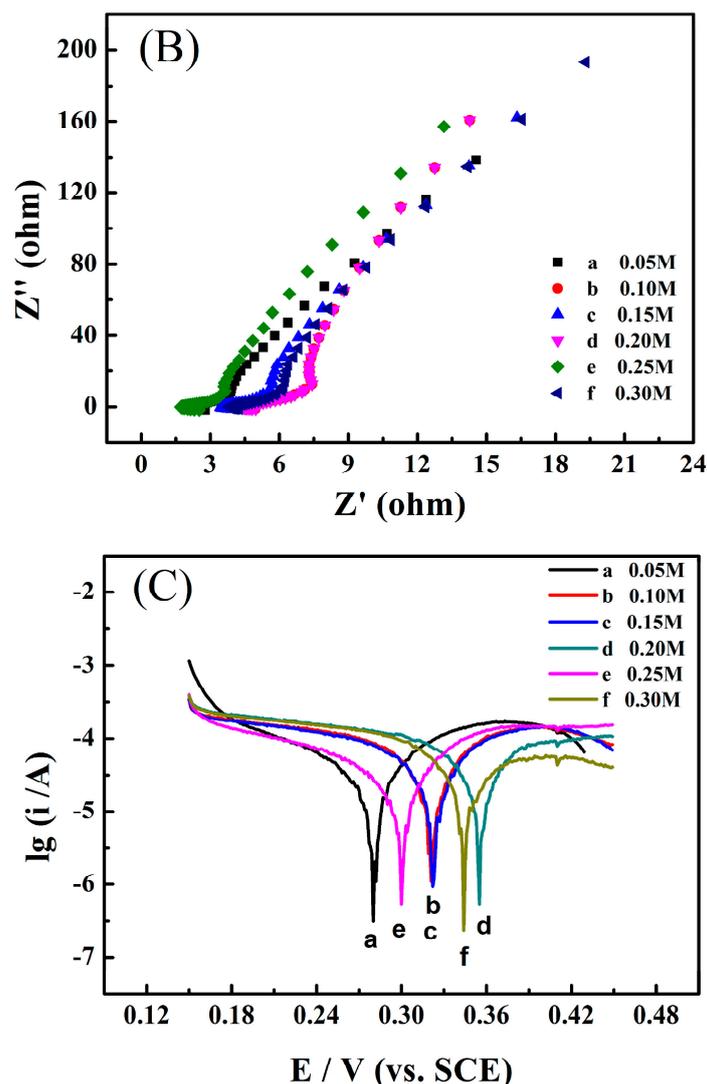


Figure 10. CV (A), EIS (B), and Tafel curves (C) of PANI in the aqueous electrolyte containing different concentrations disodium malonate (a: 0.05 M; b: 0.10 M; c: 0.15 M; d: 0.20 M; e: 0.25 M; and f: 0.30 M).

From the above results, the zinc electrode and PANI electrode both have better electrochemical properties in the electrolyte containing 0.2 M disodium malonate. Consequently, the aqueous electrolyte containing 0.2 M disodium malonate was selected as the Zn/PANI secondary battery electrolyte.

3.7. Charge-Discharge Performance Testing of Zn/PANI Secondary Battery

Figure 11 shows the charge-discharge performance of a Zn/PANI secondary battery with electrodeposited polyaniline on a carbon substrate in 0.2 M $ZnCl_2$ and 0.5 M NH_4Cl aqueous electrolyte containing 0.20 M disodium malonate. Figure 11A shows the specific capacity and the coulombic efficiency of the Zn-PANI battery vary with the number of cycles. The discharge specific capacity of the polyaniline is as high as $131.1 \text{ mAh} \cdot \text{g}^{-1}$, which is higher than that of the polyaniline electrodeposited on a Pt substrate ($108 \text{ mAh} \cdot \text{g}^{-1}$, reported by Akira Kitani) [25]. the discharge specific capacity of the polyaniline is still maintained at around $114.8 \text{ mAh} \cdot \text{g}^{-1}$ and the coulombic efficiency was close to 92% after 100 cycles in the voltage range from 1.50 V to 0.7 V with the constant current density of $1 \text{ A} \cdot \text{g}^{-1}$. Figure 11B,C show the charge and discharge curves of the 10th cycle and the 100th cycle, respectively. The good symmetry of the curves indicates that the redox performance of the battery is excellent and it also shows that the reversibility of the battery is almost unaffected by the number of cycles.

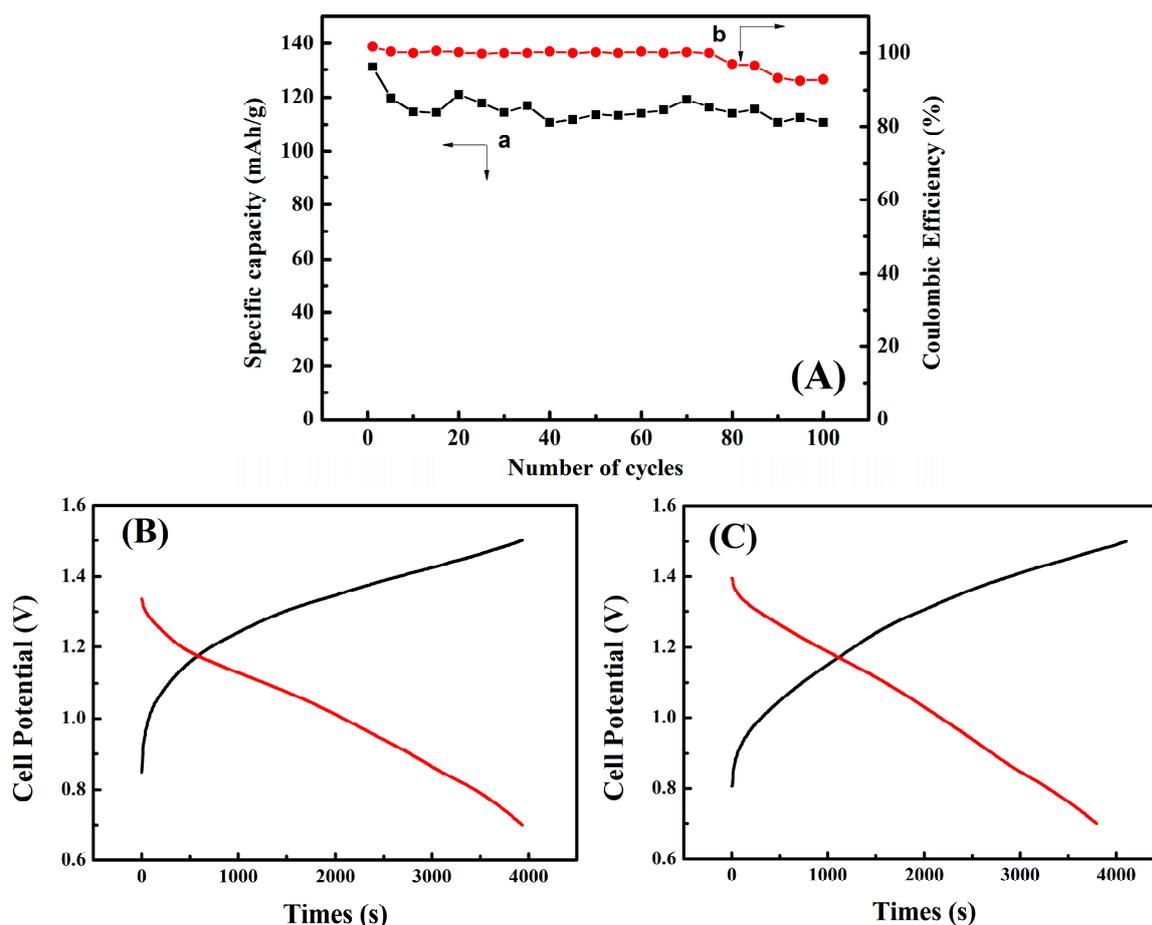


Figure 11. In 100 cycles, the specific capacity and the coulombic efficiency of the Zn-PANI battery vary with the number of cycles (A), the charge and discharge curves of the 10th cycle (B) and the 100th cycle (C).

4. Conclusions

In conclusion, the hydrogen evolution corrosion of the zinc electrode can be effectively inhibited by 0.2 M disodium malonate. The results of CV show that the zinc electrode has higher peak current and larger peak area in the aqueous electrolyte containing 0.2 M disodium malonate. The discharge specific capacity of polyaniline electrodeposited on a carbon substrate has as high as $131.1 \text{ mAh} \cdot \text{g}^{-1}$, and that of the polyaniline was still maintained at around $114.8 \text{ mAh} \cdot \text{g}^{-1}$, and the coulombic efficiency was close to 92% after 100 cycles in the voltage range from 1.50 V to 0.7 V with the constant current density of $1 \text{ A} \cdot \text{g}^{-1}$.

Acknowledgments: This project was supported by the National Science Foundation of China (No.20873119), and by the Priority Academic Program Development of Jiangsu Higher Education Institutions. Part of the data was from the Testing Center of Yangzhou University.

Author Contributions: All authors conceived, designed the study. Yongli Li wrote the paper. All authors reviewed, edited, read and approved the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Ollig, J.; Kloubert, V.; Weßels, I.; Haase, H.; Rink, L. Parameters Influencing Zinc in Experimental Systems in Vivo and in Vitro. *Metals* **2016**, *6*, 71. [[CrossRef](#)]

2. Lee, S.H.; Kwon, O.; Yoo, K.; Alorro, R.D. Removal of Zn from Contaminated Sediment by FeCl₃ in HCl Solution. *Metals* **2015**, *5*, 1812–1820. [[CrossRef](#)]
3. Yin, Y.; Liu, C.; Fan, S. A new type of secondary hybrid battery showing excellent performances. *Nano Energy* **2015**, *12*, 486–493. [[CrossRef](#)]
4. Han, J.; Wang, L.; Guo, R. Reactive polyaniline-supported sub-10 nm noble metal nanoparticles protected by a mesoporous silica shell: Controllable synthesis and application as efficient recyclable catalysts. *J. Mater. Chem.* **2012**, *22*, 5932–5935. [[CrossRef](#)]
5. Li, S.; Tan, Y.; Wang, P.; Kan, J. Inhibition of benzoic acid on the polyaniline-polyphenol oxidase biosensor. *Sens. Actuators B Chem.* **2010**, *144*, 18–22. [[CrossRef](#)]
6. Chen, C.; Hong, X.; Chen, A.; Xu, T.; Lu, L.; Lin, S.; Gao, Y. Electrochemical properties of poly (aniline-co-N-methylthionine) for zinc-conducting polymer rechargeable batteries. *Electrochim. Acta* **2016**, *190*, 240–247. [[CrossRef](#)]
7. Mak, W.F.; Wee, G.; Aravindan, V.; Gupta, N.; Mhaisalkar, S.G.; Madhavi, S. High-energy density asymmetric supercapacitor based on electrospun vanadium pentoxide and polyaniline nanofibers in aqueous electrolyte. *J. Electrochem. Soc.* **2012**, *159*, A1481–A1488. [[CrossRef](#)]
8. Dalui, B.C.; Basumallick, I.N.; Ghosh, S. Zinc-poly (aniline) rechargeable battery assembled with aqueous electrolyte. *Indian J. Chem. Tech.* **2008**, *15*, 576–580.
9. Li, Y.; Hu, Z.; Ding, Y.; Kan, J. Characteristics of the electrolyte containing ethylene carbonate and dimethyl carbonate in zinc-polyaniline battery. *Int. J. Electrochem. Sci.* **2016**, *11*, 1898–1906.
10. Guerfi, A.; Trottier, J.; Boyano, I.; de Meatza, I.; Blazquez, J.A.; Brewer, S.; Zaghbi, K. High cycling stability of zinc-anode/conducting polymer rechargeable battery with non-aqueous electrolyte. *J. Power Sources* **2014**, *248*, 1099–1104. [[CrossRef](#)]
11. Fusalba, F.; Gouérec, P.; Villers, D.; Bélanger, D. Electrochemical characterization of polyaniline in nonaqueous electrolyte and its evaluation as electrode material for electrochemical supercapacitors. *J. Electrochem. Soc.* **2001**, *148*, A1–A6. [[CrossRef](#)]
12. Varela, H.; Torresi, R.M. Ionic exchange phenomena related to the redox processes of polyaniline in nonaqueous media. *J. Electrochem. Soc.* **2000**, *147*, 665–670. [[CrossRef](#)]
13. Zhao, Y.; Si, S.; Liao, C. A single flow zinc / polyaniline suspension rechargeable battery. *J. Power Sources* **2013**, *241*, 449–453. [[CrossRef](#)]
14. Ghanbari, K.; Mousavi, M.F.; Shamsipur, M.; Karami, H. Synthesis of polyaniline/graphite composite as a cathode of Zn-polyaniline rechargeable battery. *J. Power Sources* **2007**, *170*, 513–519. [[CrossRef](#)]
15. Rahmanifar, M.S.; Mousavi, M.F.; Shamsipur, M.; Heli, H. A study on open circuit voltage reduction as a main drawback of Zn-polyaniline rechargeable batteries. *Synth. Met.* **2005**, *155*, 480–484. [[CrossRef](#)]
16. Rahmanifar, M.S.; Mousavi, M.F.; Shamsipur, M.; Ghaemi, M. What is the limiting factor of the cycle-life of Zn-polyaniline rechargeable batteries? *J. Power Sources* **2004**, *132*, 296–301. [[CrossRef](#)]
17. Sima, M.; Visan, T.; Buda, M. A comparative study of zinc-polyaniline electrochemical cells having sulfate and chloride electrolytes. *J. Power Sources* **1995**, *56*, 133–136. [[CrossRef](#)]
18. Liu, L.; Tian, F.; Zhou, M.; Guo, H.; Wang, X. Aqueous rechargeable lithium battery based on polyaniline and LiMn₂O₄ with good cycling performance. *Electrochim. Acta* **2012**, *70*, 360–364. [[CrossRef](#)]
19. Manuel, J.; Kim, J.K.; Matic, A.; Jacobsson, P.; Chauhan, G.S.; Ha, J.K.; Ahn, J.H. Electrochemical properties of lithium polymer batteries with doped polyaniline as cathode material. *Mater. Res. Bull.* **2012**, *47*, 2815–2818. [[CrossRef](#)]
20. Rehan, H.H. A new polymer/polymer rechargeable battery: Polyaniline/LiClO₄ (MeCN)/poly-1-naphthol. *J. Power Sources* **2003**, *113*, 57–61. [[CrossRef](#)]
21. MacDiarmid, A.G.; Epstein, A.J. Polyanilines: A novel class of conducting polymers. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317–332. [[CrossRef](#)]
22. Anand, J.; Palaniappan, S.; Sathyanarayana, D.N. Conducting polyaniline blends and composites. *Prog. Polym. Sci.* **1998**, *23*, 993–1018. [[CrossRef](#)]
23. Rüetschi, P. Energy storage and the environment: The role of battery technology. *J. Power Sources* **1993**, *42*, 1–7. [[CrossRef](#)]

24. Beck, F.; Rüetschi, P. Rechargeable batteries with aqueous electrolytes. *Electrochim. Acta* **2000**, *45*, 2467–2482. [[CrossRef](#)]
25. Kitani, A.; Kaya, M.; Sasaki, K. Performance study of aqueous polyaniline batteries. *J. Electrochem. Soc.* **1986**, *133*, 1069–1073. [[CrossRef](#)]



© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).