

Homogeneous Anodic and Cathodic Ions on Battery Performance

Tat Ng H and Hsu C*

Department of Chemical and materials engineering, Lungwha University of Science and Technology, Taiwan

***Corresponding author:** Chen Hsu, Department of chemical and materials engineering, Lunghwa University of Science and Technology, 300, Sec. 1, Wanshou Rd. Guishan Shiang, Taoyuan country, Taiwan, Email: chenhsuemail@yahoo.com.tw

Research Article

Volume 3 Issue 4

Received Date: December 20, 2018

Published Date: December 31, 2018

DOI: 10.23880/nnoa-16000155

Abstract

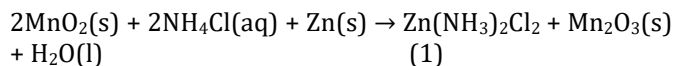
This paper proposes a novel battery with zinc oxalate (ZnC_2O_4) electrode exhibiting superior charging and rechargeable characteristics compared to an original zinc-carbon battery. ZnC_2O_4 electrode provides homogeneous anodic Zn^{+2} and cathodic $\text{C}_2\text{O}_4^{-2}$ ions. The effect of adding different percentages of ZnC_2O_4 on the charging voltage and current are investigated. The possibility of achieving charging and discharging recycles in the cell electrolyte are studied. The electrode ZnC_2O_4 was prepared by the sol-gel method. Based on the voltage, current, and energy calculations, it concludes that adding different percentages of ZnC_2O_4 to the battery electrolyte have different effects on the internal resistance of the battery.

Keywords: Zinc Oxalate; Homogeneous; Anodic Ion; Charged and Discharged; Rechargeable

Introduction

A zinc-carbon battery is one of the most simple and cheap commercially used batteries. This battery was developed from Leclanche cells [1]. The battery reaction mainly involves redox processes. The anode of this battery is a zinc can, and the cathode is a carbon rod (graphite rod), but the carbon rod is an inert electrode, acting only as an electron path. The part between the two electrodes is filled with ammonium chloride (NH_4Cl) for the electrolyte, manganese dioxide (MnO_2), zinc chloride (ZnCl_2) saturated solution, and some inert paint wet paste. When the electrode is connected, the zinc anode is oxidized to lose electrons. The lost electrons travel through the wires to the cathode, reducing NH_4^+ ions from NH_4Cl to NH_3 and thus forming hydrogen. The released hydrogen is then oxidized by MnO_2 , while the NH_3 is utilized to form the complex $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$. The

overall reaction within the battery could be expressed as follows.



A battery described in a previous study involves the application of gel electrolytes for increased capacity [2]. As the zinc shell becomes thinner over time, the paste cause leaks in the battery. When the zinc-carbon battery power is exhausted, it must be discarded because it is difficult to reuse. This is mainly because the standard reduction potential of zinc ions is smaller than the hydrogen electrode standard reduction potential. When the negative voltage is applied, the hydrogen ions are reduced to hydrogen before electrons are accepted from the zinc ions.

Rechargeable batteries are also referred to as secondary batteries; that is, they can be reused after being discharged. The current rechargeable battery types include lead-acid batteries, nickel-metal hydride batteries, nickel-cadmium batteries, and lithium batteries. Rechargeable batteries can be prepared by various methods. For example, rechargeable batteries can be used with aqueous electrolytes [3]. Rechargeable MnO_2/zinc batteries can be prepared with an alkaline electrolyte [4]. This can be explained using models of the cathode and anode processes during cycling. The Zn/ZnCl_2 dry battery can be made to be rechargeable by changing the electrode composition [5-7]. The capacity of the battery depends on the composition of the cathode material. The recharge cycles can be improved by adding a surface-active agent to the electrolyte solution. The electrode can be modified and used for the lithium secondary battery [8].

Purpose of this Work

A zinc-carbon battery offers long-term use and is rather cheap. This battery's power cannot be improved, and it cannot be used as a secondary battery. This work examined the addition of oxalate materials to the battery in order to alter its discharge characteristics. Furthermore, the study attempts to increase the stored energy density and also examined the charge and discharge cycle in order to determine the feasibility of recharging the battery.

Experimental Details

In this study, zinc oxalate (ZnC_2O_4) was prepared by the sol-gel method. The morphology of the synthesized ZnC_2O_4 was observed by scanning electron microscopy, and the structure of ZnC_2O_4 was characterized by X-ray diffraction. ZnC_2O_4 at 0 wt.%, 1 wt.%, 5 wt.%, 10 wt.%, 25 wt.%, and 75 wt.% was added to the original battery, and the discharging and charging recycle experiments were then carried out. The electrolyte was dried and weighed to be approximately 52.05 g. The electrolyte and ZnC_2O_4 were ground for 10 min. This was mixed with the electrolytic solution and ZnC_2O_4 . The porous diaphragm, graphite rod, and ZnC_2O_4 electrolyte mixture were then packed into the battery can. The graphite rod was placed in the middle of the zinc can, and pure water was then added. The metal cap and the negative metal sheet were then restored, and a sealed plastic tape was used instead of the plastic layer in order to fix the battery parts firmly.

The setup of the discharge experiment and the hardware structure of the charge and discharge cycle experiment are described as follows. There were three

components to use, for example, switches, resistors, and wires for the discharge circuit. The discharge tests were carried out at loads of 4 and 20 Ω . The current was measured after 10 mins of the discharge connection, and the battery voltage was measured after 150 sec after short of the recharging. This cycle study selected 0% and 5% of zinc oxalate batteries to carry out the charge and discharge cycle. The voltage was measured after 10 mins of the discharge test, and measured after charging 1 hr. The experiments repeated charge and discharge test for 10 times.

Results and Discussion

Figure 1(a) shows a scanning electron microscopy image of ZnC_2O_4 . ZnC_2O_4 normally exhibits an elongated tetrahedral geometry with a basic structure (i.e., $\alpha\text{-ZnC}_2\text{O}_4$) [1]. The crystal form of $\alpha\text{-ZnC}_2\text{O}_4$ is triclinic, and the adjacent metal ions are linked in a one-dimensional chain structure, but the interchain is linked in a three-dimensional network structure through hydrogen bonding. The octahedral structure through zinc cobonding is the optimal place for the insertion of impurities. Figure 1(b) shows an X-ray diffraction spectrum of ZnC_2O_4 , revealing the structure of $\alpha\text{-ZnC}_2\text{O}_4$. The powder was determined to be white and to be slightly soluble in water.

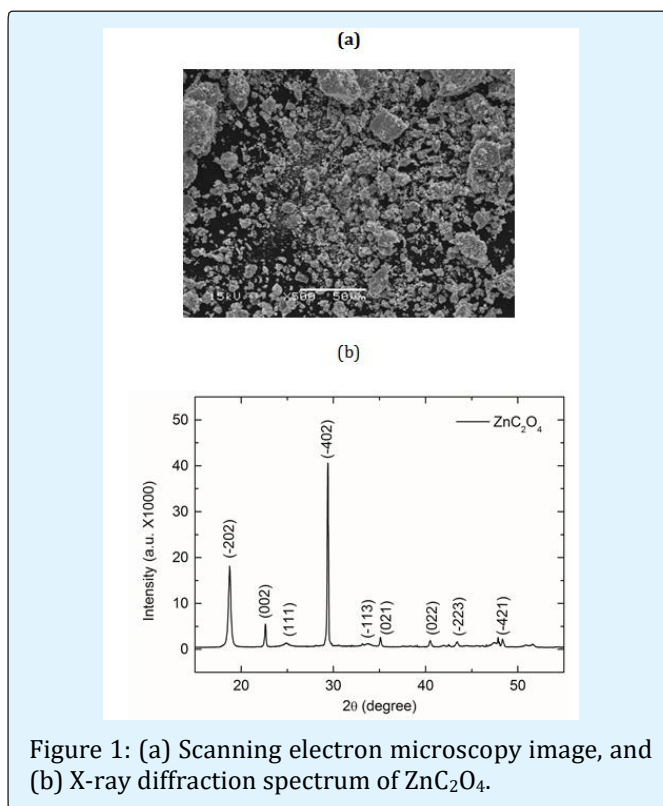


Figure 1: (a) Scanning electron microscopy image, and (b) X-ray diffraction spectrum of ZnC_2O_4 .

Figure 2(a) shows the discharge curves of the 4 Ω load with respect to time. For the 4 Ω load, the voltages decreased with time for 0 wt.% ZnC_2O_4 . For 1 wt.% ZnC_2O_4 , the voltage was higher than that in the case of 0 wt.% ZnC_2O_4 . The charge voltage was lower than 1.38 V, and it was the higher than that of the prototype after approximately 100 min. For 5–10 wt.% ZnC_2O_4 , the same tendency as that for the 0 wt.% ZnC_2O_4 was observed. The overall voltages tended to decrease for 25 and 75 wt.% ZnC_2O_4 . For the 20 Ω load, as shown in Figure 2(b), the voltage was higher than that in the case of the 4 Ω load. The voltage for 0 wt.% ZnC_2O_4 decreased with the time. The voltages for 1 and 5 wt.% ZnC_2O_4 decreased slowly as compared with that for 0 wt.% ZnC_2O_4 , whereas those for 10 and 75 wt.% ZnC_2O_4 mostly decreased with increasing time. The results for 25 wt.% ZnC_2O_4 were the same as those for 0 wt.% ZnC_2O_4 . In general, discharge tendencies for ZnC_2O_4 additions lower than 10 wt.% were determined to be quite similar.

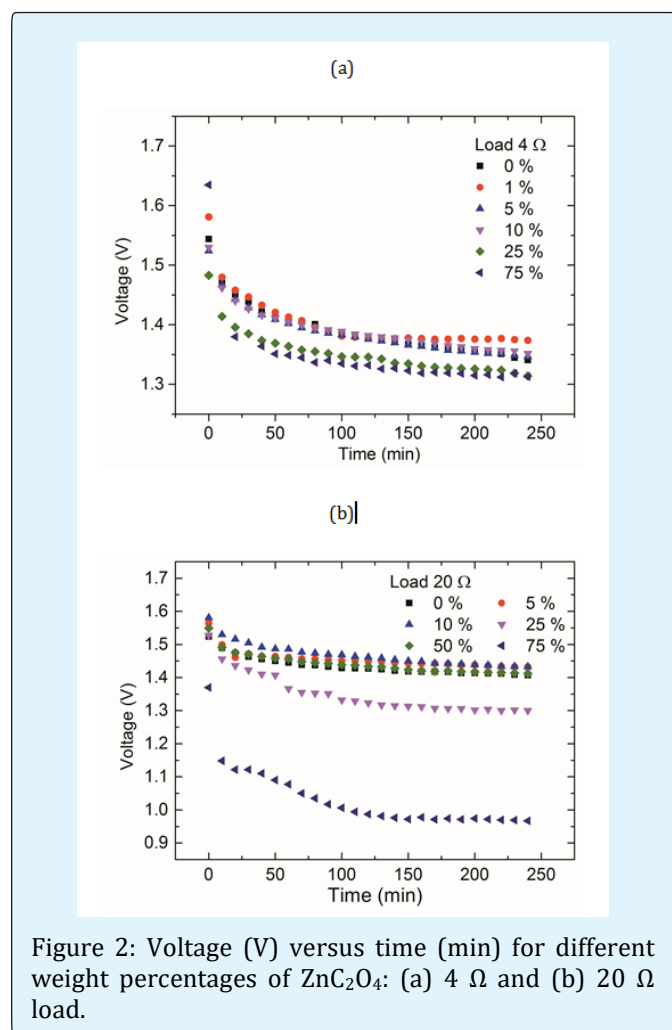


Figure 2: Voltage (V) versus time (min) for different weight percentages of ZnC_2O_4 : (a) 4 Ω and (b) 20 Ω load.

Figure 3 illustrates a graph of the discharge current versus time at the two loads. At the 4 Ω load, for 0 wt.% ZnC_2O_4 , the current decreased with time and was significantly reduced. The battery current for 1 wt.% ZnC_2O_4 was largely reduced. The battery current for 5 wt.% ZnC_2O_4 was the largest, followed by those for 0, 10, and 25 wt.% ZnC_2O_4 . At the 20 Ω load, the current generally slightly increased and remained constant or decreased. The current for the 0 wt.% ZnC_2O_4 battery was the largest. The currents for the 1 and 25 wt.% ZnC_2O_4 batteries were largely reduced, followed by those for the 5, 10, and 75 wt.% ZnC_2O_4 batteries. Clearly, as the load increased, the current decreased. The variation in the currents could be the result of the variation in internal resistance with the amounts of ZnC_2O_4 . Dissolving a small amount of ZnC_2O_4 in water could increase the conductivity until equilibrium. Subsequently added ZnC_2O_4 would dissolve and remain as solids, causing an increase in the resistivity.

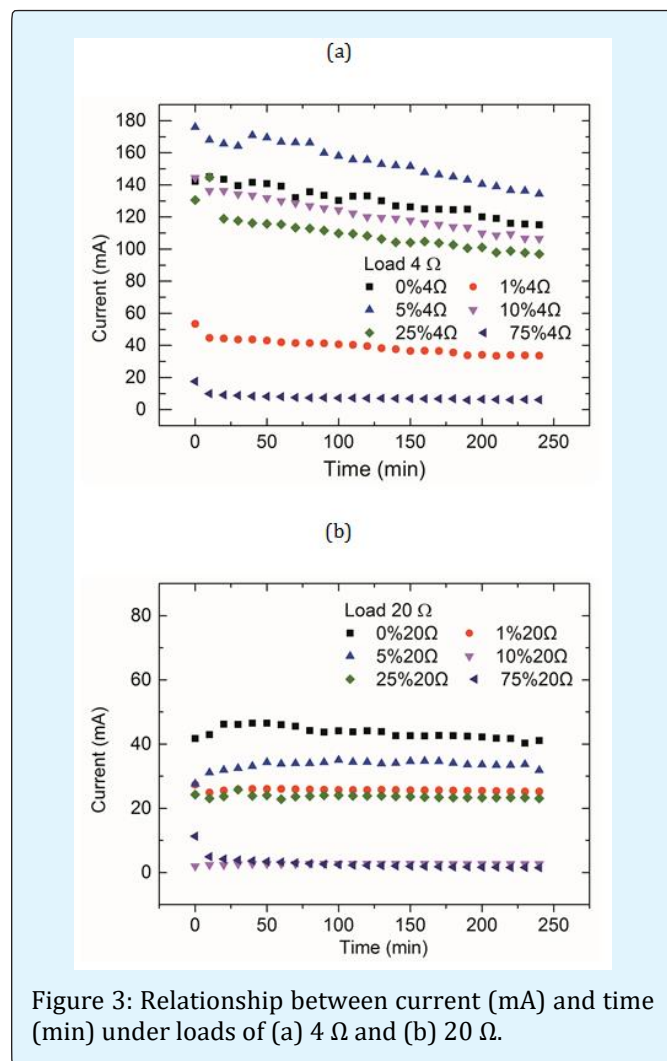


Figure 3: Relationship between current (mA) and time (min) under loads of (a) 4 Ω and (b) 20 Ω .

Figure 4 shows the relationship between voltage and time for charge and discharge cycles of 0 and 5 wt.% ZnC_2O_4 batteries; in this figure, the high point (red dot) is the voltage at which the charge is completed, and the low point (black dot) is the voltage at which the discharge is completed. For 0 wt.% ZnC_2O_4 , the charge and discharge voltage averaged at approximately 1.45 V, whereas for 5 wt.% ZnC_2O_4 , the charge and discharge voltage was nearly 0.05 V higher on average, indicating that 5 wt.% ZnC_2O_4 could increase the charge. This means that ZnC_2O_4 could increase the voltage level. The discharge cycle was slightly lower at a lower voltage, indicating a slight increase in the discharge rate. Thus, the addition of ZnC_2O_4 can increase the battery cycle life.

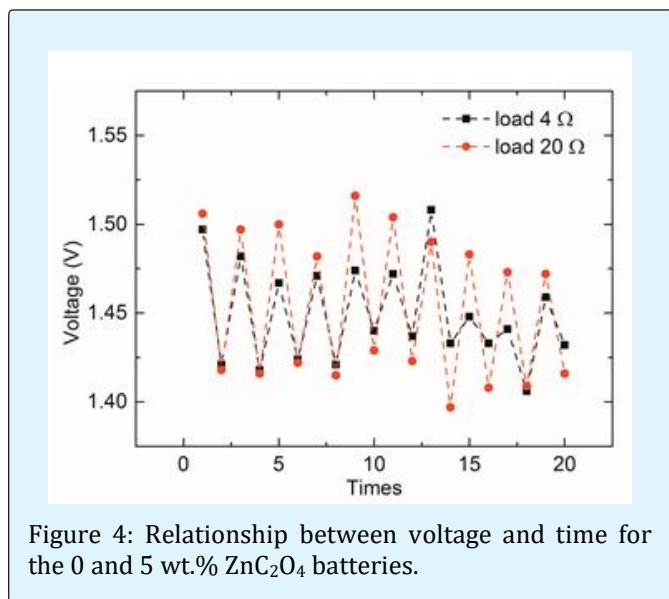


Figure 4: Relationship between voltage and time for the 0 and 5 wt.% ZnC_2O_4 batteries.

Figure 5 shows the relationship between power and time. The formula of voltage (V) \times current (mA) yields power (mW) with respect to time (min). For the 4 Ω load, the experimental results showed that the power of the 0 wt.% ZnC_2O_4 battery was lower than that of the 5 wt.% ZnC_2O_4 battery. The power of the 5 wt.% ZnC_2O_4 battery was the highest. The power levels of the 10, 25, and 75 wt.% ZnC_2O_4 batteries decreased with the amount of ZnC_2O_4 added. The power of the 1 wt.% ZnC_2O_4 battery also decreased and was higher than only that of the 75 wt.% ZnC_2O_4 battery. For the 20 Ω load, the experimental results revealed that the power decreased with the addition of ZnC_2O_4 , except for the 1 and 10 wt.% ZnC_2O_4 batteries. The power of the 1 wt.% ZnC_2O_4 battery was higher than only that of the 25 wt.% ZnC_2O_4 battery. Furthermore, the power of the 10 wt.% ZnC_2O_4 battery was similar to that of the 75 wt.% ZnC_2O_4 battery.

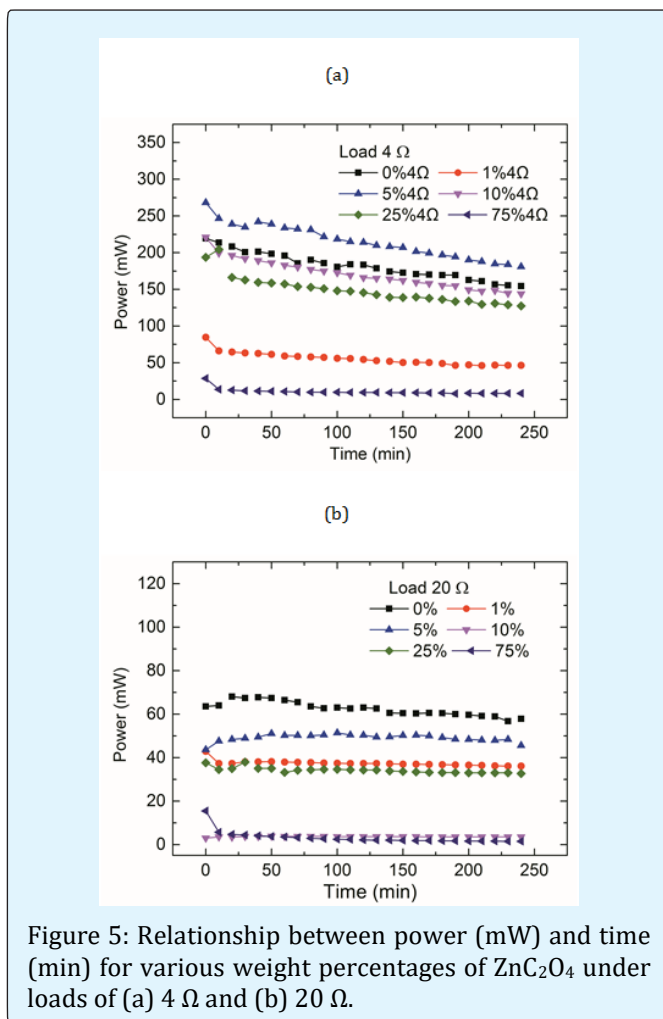


Figure 5: Relationship between power (mW) and time (min) for various weight percentages of ZnC_2O_4 under loads of (a) 4 Ω and (b) 20 Ω .

Figure 6 illustrates the energy (J/hr) persisted after 240 min with the addition of different weight percentages of ZnC_2O_4 . For the 4 Ω load, the 0 wt.% ZnC_2O_4 battery had an energy of approximately 650 J/hr after 240 min. The 1 wt.% ZnC_2O_4 battery exhausted energy to a higher extent than did the 0 wt.% ZnC_2O_4 battery. By contrast, the 5 wt.% ZnC_2O_4 battery had higher energy than the other batteries. The 10 wt.% ZnC_2O_4 battery had lower energy than the 5 wt.% ZnC_2O_4 battery. The 25 wt.% ZnC_2O_4 battery also had lower energy than the 5 wt.% ZnC_2O_4 battery. The 75 wt.% ZnC_2O_4 battery had the lowest energy. This means that the internal resistance plays an important role in the retained energy. For the 10 Ω load, the 5 wt.% ZnC_2O_4 battery had only slightly lower energy than that of the 0 wt.% ZnC_2O_4 battery. This trend is similar to that observed in the case of the 20 Ω load.

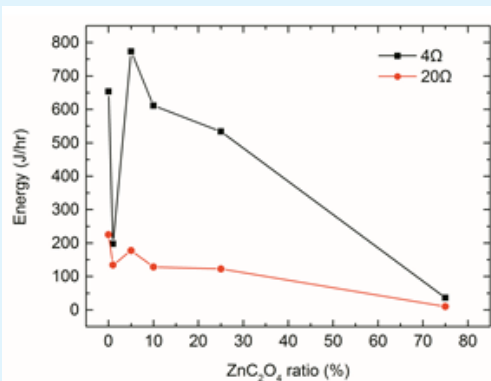
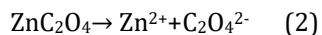


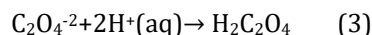
Figure 6: Energy persisted after 240 min for different weight percentages of added ZnC₂O₄.

The preceding experimental results demonstrate that the internal resistance plays a critical role in the oxalate battery performance. The 0 wt.% ZnC₂O₄ battery provided the reference energy level. The addition of 1 wt.% ZnC₂O₄ reduced the battery resistance since ZnC₂O₄ could dissolve in water until the dissolution limit was reached. Next, the addition of 5 wt.% ZnC₂O₄ crossed the maximum solubility and therefore increased the internal resistance. Subsequently, the addition of ZnC₂O₄ increased the internal resistance and caused more energy exhaustion. The 5 wt.% ZnC₂O₄ battery showed a similar discharge curve. This means that the internal resistance is quite similar to that of the zinc-carbon battery.

The high signals of the oxalate battery indicate that the battery had high capacity. This is attributable to the oxidation reaction at the anode. The voltage of this battery was observed to increase with the addition of ZnC₂O₄. ZnC₂O₄ is an open-structured substance that is slightly soluble in water. The ZnC₂O₄ reaction at the anode can be expressed by the following equation:



The reduction reaction at the cathode could decompose ZnC₂O₄ into ions. The dissolved ZnC₂O₄ involve in the reaction at both of anode and cathode. The hydrogen could be dissolved in water and transported to the oxalate ion to form oxalate, according to the following reaction:



This gives the battery its rechargeable characteristic. In this study, 10 runs of the recycle test were carried out.

This demonstrates that the ZnC₂O₄ battery can function under multiple recharge and charge cycles.

Conclusions

This study was conducted to clarify the effect of adding different weight percentages of ZnC₂O₄ on the charging voltage and current of a novel ZnC₂O₄ battery. The rechargeability of the ZnC₂O₄ battery was also discussed. The voltage and current during charge varied with the amount of ZnC₂O₄ based on the internal resistance. The experiments revealed that the optimum ZnC₂O₄ addition amount was 5 wt.%, when compared with the 0 wt.% ZnC₂O₄ battery. The discharge trend demonstrated the long life of the ZnC₂O₄ battery. The ZnC₂O₄ batteries with other weight percentages exhibited lower performance levels than that of the 5 wt.% ZnC₂O₄ battery. The high voltage of the ZnC₂O₄ battery indicate the high capacity. In the recharge test, small addition of ZnC₂O₄ (e.g., 5 wt.%) could improve the rechargeability of the ZnC₂O₄ battery.

Conflicts of Interest

There is no conflict of interest

References

1. Dell RM (2000) Batteries fifty years of materials development. *Solid State Ionics* 134(1-2): 139-158.
2. Khalid NH, Baba Isnail YM, Mohamad AA (2008) ZnCl₂- and NH₄Cl-hydroponics gel electrolytes for zinc-carbon batteries. *Journal of Power Sources* 176(1): 393-395.
3. Beck F, Rüetschi P (2000) Rechargeable batteries with aqueous electrolytes. *Electrochimica Acta* 45(15-16): 2467-2482.
4. Kordesh K, Weissenbacher M (1994) Rechargeable alkaline manganese dioxide/zinc batteries. *Journal of Power Sources* 51(1-2): 61-78.
5. Shaolin M, Jinhai Y, Wang Y (1993) A rechargeable Zn/ZnCl₂, NH₄Cl/polyaniline/carbon dry battery. *Journal of Power Sources* 45(2): 153-159.
6. Trinidad F, Montemayor MC, Fatás E (1991) Performance Study of Zn/ZnCl₂, NH₄Cl/Polyaniline/Carbon Battery. *J Electrochem Soc* 138(11): 3186-3189.

7. Mirmohseni R, Solhjo (2003) Preparation and characterization of aqueous polyaniline battery using a modified polyaniline electrode. European Polymer Journal 39(2): 219-223.
8. Lee YS, Kumada N, Yoshio M (2001) Synthesis and characterization of lithium aluminum-doped spinel ($\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$) for lithium secondary battery. Journal of Power Sources 96(2): 376-384.

