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High-performance aqueous rechargeable batteries based on zinc anode and $NiCo_2O_4$ cathode

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Abstract. A new aqueous Zn–$NiCo_2O_4$ rechargeable battery system with a high voltage, consisting of $NiCo_2O_4$ as cathode and metal Zn as anode, is proposed for the first time. It is cheap and environmental friendly, and its energy density is about 202.8 Wh kg^{-1}. The system still maintains excellent capacity retention of about 85% after 100 full cycles at a current rate of 2 A g^{-1} between 1.5 and 1.95 V. This work not only provides a new battery system but also shows promise for application in large-scale energy storage for its low cost, good cycling and environmental friendliness.

Keywords. Rechargeable battery; aqueous electrolyte; $NiCo_2O_4$ cathode; Zn anode; energy density.

1. Introduction

The eminent global energy crisis and growing ecological concerns have led to intensive developments in the application of clean and renewable energies, as well as green transportations such as electric and hybrid electric vehicles.[1] All these applications demand low cost, safe and environment-friendly energy storage system. Battery is the most versatile means for storing electricity in the form of chemical energy. Lithium ion batteries have highest energy and highest power densities among rechargeable batteries.[2] But there still exists some disadvantages of high cost and flammable nature. On the other hand, traditional aqueous batteries are cost effective and safe but limited in energy density.[2] Therefore, new aqueous rechargeable battery systems have been attracted great attention in recent years for their good safety, high ionic conductivity and the low cost of aqueous electrolytes.

Aqueous rechargeable batteries mainly include aqueous rechargeable lithium batteries and aqueous rechargeable sodium and potassium batteries.[3] All these energy storage systems provide several advantages over the traditional energy storage systems, such as low cost, long cycle life, environmental friendliness and safety. The above characteristics are very important for these systems in storing energy for electrical grids connected with intermittent energy sources such as solar, wind and hydropower. It is also important to lower the cost and meet the stringent safety requirements of batteries for pure electric vehicles. The challenges to significantly increase the specific output power and energy density of batteries urgently need to be solved.[3]

Herein, a safe and environmental-friendly Zn–$NiCo_2O_4$ rechargeable battery in aqueous alkaline solution by taking advantage of $NiCo_2O_4$ as cathode-active material and metal Zn as anode-active material is presented. The feasibility of this battery is ensured by using a mixed LiOH/KOH aqueous electrolyte with an indispensable alkalinity for the electrode reaction of $NiCo_2O_4$ and Zn electrode.

2. Experimental

2.1 *Preparation of $NiCo_2O_4$*

In a typical procedure, 0.002 mol $Ni(NO_3)_2{\cdot}6H_2O$ and 0.004 mol $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 40 ml DI water sequentially. Then the solution was stirred for half an hour at room temperature to form a black solution, followed by a drop-by-drop addition of 28% $NH_3{\cdot}H_2O$ solution until its pH reached 9. Being kept still for 5 h, the obtained precipitate was filtered, washed with water and ethanol several times to remove the surfactant and the residual ions, and dried at 80°C for 12 h in air. Finally, the precursor was annealed in air at 300°C for 3 h with a slow heating rate of 1°C min^{-1} in order to obtain $NiCo_2O_4$ nanostructure.

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2.2 *Characterization*

The structure and composition of synthesized product was characterized by powder X-ray diffraction (XRD) obtained with a Philips X-ray diffratometer equipped with CuKα radiation (λ = 1.5418 Å). The angular resolution in 2θ scans was 0.02° over a 2θ range of 15–90°.

The working electrodes were prepared by coating slurries of active material with acetylene black and polyvinylidene fluoride (80 : 10 : 10) in dimethyl sulphoxide on carbon plates. After drying at 100°C for 12 h, the electrodes were used directly. All the electrochemical measurements were performed with a CHI760D workstation by using a three-electrode cell with Pt sheet as the counter electrode and a Hg/HgO electrode as the reference electrode. Cyclic voltammogram (CV) was measured between 0.4 and 1.6 V in an alkaline solution containing 3 mol l^{-1} KOH and 1 mol l^{-1} LiOH. The charge and discharge curves of the prepared $NiCo_2O_4$ at different rates were measured between 1.5 and 1.95 V with a two electrodes system, in which Zn metal was used as the counter electrode. The performance was evaluated by 100 full cycles at a current rate of 2 A g^{-1}.

3. Results and discussion

The XRD pattern of the prepared $NiCo_2O_4$ powder is shown in figure 1a. As shown in figure 1a, eight characteristic diffraction peaks appeared, which can be readily indexed to the planes of the cubic $NiCo_2O_4$ phase (JCPDS card no. 20-0781).[4] It is worth mentioning that the pattern shows a weak crystalline state and no other peaks are observed, which effectively confirms the purity of the obtained $NiCo_2O_4$ phase.

Figure 2 shows CVs of the zinc metal and the obtained $NiCo_2O_4$ at a scan rate of 2 mV s^{-1} in a mixed Li(OH)/KOH aqueous electrolyte. In the case of the prepared $NiCo_2O_4$, the oxidation and reduction potential peaks can be observed at 1.1 and 0.9 V (*vs.* Hg/HgO), respectively, accompanied simultaneously with corresponding proton insertion/extraction reactions.[5–7] In the case of Zn, the pair of reversible redox peaks appears at –0.54 and ~ –0.4 V due to Zn dissolution/deposition, respectively. Since there is a potential difference between Zn and $NiCo_2O_4$, they can be assembled into a battery system whose redox reaction during charge and discharge process can be schematically shown as in figure 3a.

The charge and discharge curves of the prepared $NiCo_2O_4$ at different rates using Zn metal as the counter electrode are shown in figure 3b. At the charge rate of 1 A g^{-1}, it can be seen that the average charge and discharge voltage plateaus are about 1.8 and 1.7 V, which is inconsistent with the above CV results. The reversible capacity is 112 mAh g^{-1} based on the $NiCo_2O_4$-positive electrode. The energy density of Zn metal is up to 825 mAh g^{-1}, so the energy density of this battery system is restricted by the positive electrode. The reversible capacities of $NiCo_2O_4$ are 82.5, 40.1 and 15.3 mAh g^{-1} at 2, 5 and 10 A g^{-1}, respectively. This suggests that the

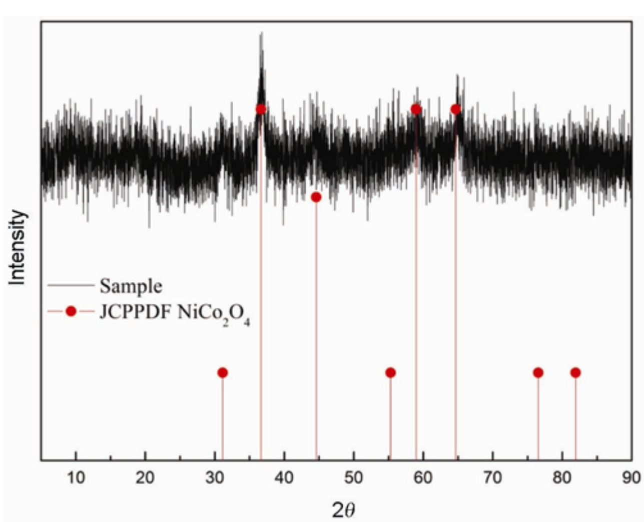

Figure 1. Representative side-angle XRD patterns of $NiCo_2O_4$ powder.

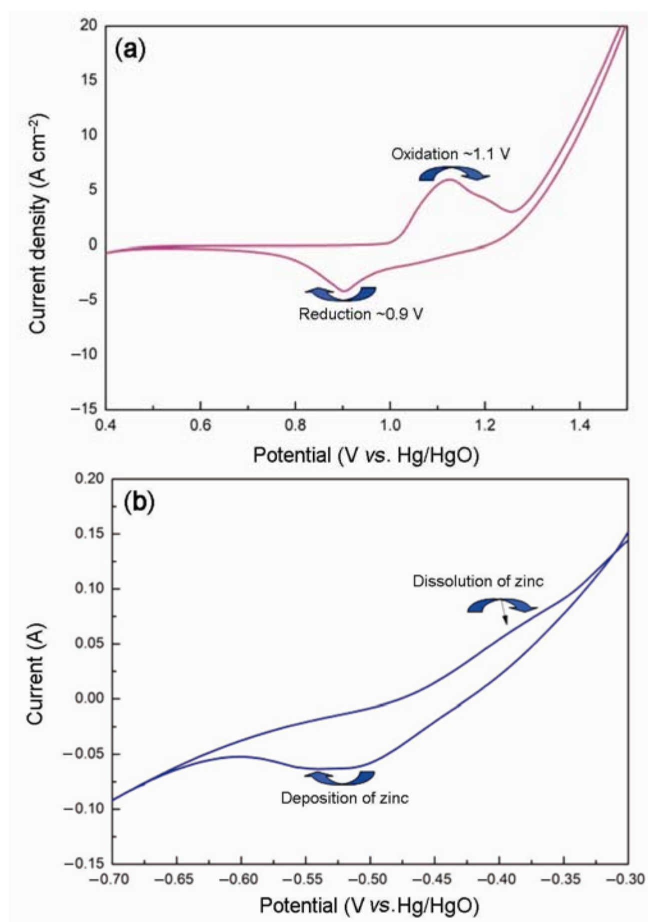

Figure 2. Typical CVs of the (**a**) zinc metal and (**b**) $NiCo_2O_4$ at a scan rate of 2 mV s^{-1}.

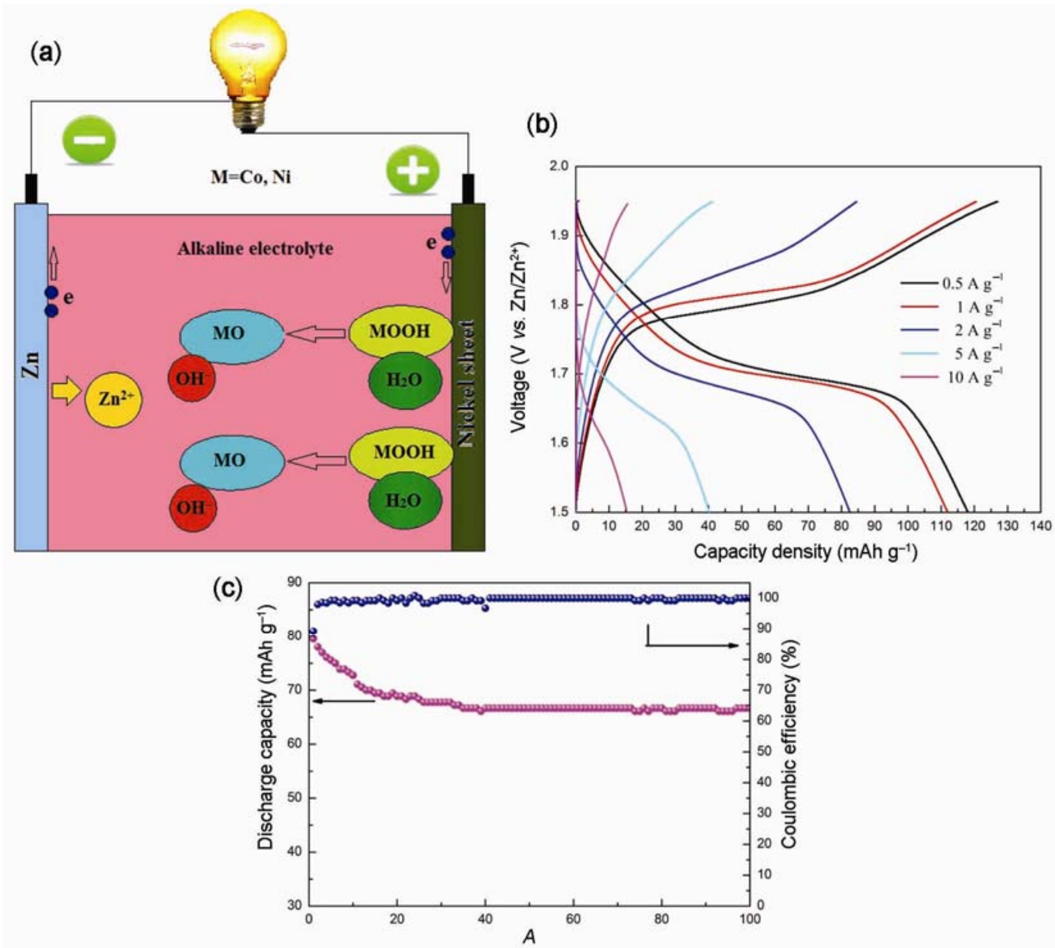

Figure 3. (**a**) Schematic representation of the electrochemical reaction process of the Zn–NiCo$_2$O$_4$ prototype cell; (**b**) charge and discharge curves of the NiCo$_2$O$_4$ at different rates using Zn metal as the counter electrode and (**c**) cycling performance of the Zn//NiCo$_2$O$_4$ prototype cell at 2 A g^{-1}.

aqueous rechargeable battery can be charged and discharged very rapidly, which can meet the rapid charge of power supply and demand from the grids. Battery is based on the solid phase reaction, the large specific surface area will be beneficial for the further improvement of the battery system performance.

The cycling performance of the Zn–NiCo$_2$O$_4$ rechargeable battery in aqueous alkaline electrolyte at 2 A g^{-1} based on NiCo$_2$O$_4$ is illustrated in figure 3c. Obviously, the prototype cell shows an excellent cycling stability. At the initial 40 cycles, the discharge capacity decreases from 79 to 67 mAh g^{-1}, and then keeps at a stable value about 67 mAh g^{-1}, maintaining excellent capacity retention of about 85%. At the first cycle, the Columbic efficiency is about 89% and then increases to about 99% at the later stage.

From the above, it can be seen clearly that the positive electrode of the prepared NiCo$_2$O$_4$ can work very well. In addition, the negative zinc electrode has a very high capacity. Both electrode materials are very cheap and have rich natural sources.[8,9] For all these characterizations, such as safe, low cost and environmentally friendly, this battery system can be a good candidate for being a power source for smart grids to store renewable energies such as solar, wind and tide. Moreover, it can also be a choice to level the valley and peak of power supply of the grids.[10,11]

4. Conclusion

In summary, an aqueous rechargeable battery system by integrating NiCo$_2$O$_4$ as cathode, metal Zn as anode and mixed aqueous LiOH/KOH aqueous solution as electrolyte was fabricated. It is a feasible strategy to combine two different electrode reaction mechanisms in aqueous alkaline electrolyte. Importantly, the fabricated Zn–NiCo$_2$O$_4$ alkaline rechargeable battery has a high operation voltage of over 1.7 V and the energy density can have values of up to 202.8 Wh kg^{-1} based on the positive electrode material. The system still maintains excellent capacity retention of about 85% after 100 full cycles at a current rate of 2 A g^{-1} between 1.5 and 1.95 V. This work not only provides a new low-cost battery system but also shows promise for application in large-scale energy storage for its low cost, good cycling and environmental friendliness.

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