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## COMMUNICATION

## A Zn-NiO rechargeable battery with long lifespan and high energy density

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

**A Zn-NiO rechargeable battery comprising NiO nanosheet anchored with CNTs as positive electrode, zinc plate as negative one and an alkaline solution of 1 M KOH and 10 mM Zn(Ac)<sub>2</sub> as electrolyte is reported. It delivers a voltage of ~1.75 V and high energy density of 228 Wh kg<sup>-1</sup> (based on the mass of positive electrode composite and zinc) with good cycling. It is great promise for practical energy storage.**

Unremitting research efforts have been paid on renewable energy because of the rapid consumption of fossil fuels. Battery technologies provide a solution to the storage of intermittent renewable energy, playing vital roles in alleviating our dependence on fossil fuels.<sup>1,2</sup> Among rechargeable batteries, lithium ion batteries have high energy densities, but the barriers for large-scale application including poor safety and high cost should be tackled.<sup>3</sup> The limited Li<sup>+</sup> ion conductivity in aprotic electrolytes also leads to inadequate power density for lithium ion batteries.<sup>4</sup> On the other hand, traditional aqueous batteries are low in cost and safe but have limited energy densities.<sup>5</sup> Zinc-based batteries offer an alternative to lithium ion batteries because Zn has an extensive global stockpile, relatively low redox potential, high theoretic capacity (820 mAh g<sup>-1</sup>),<sup>6</sup> the innate good safety arising from non-flammable aqueous electrolytes, low cost, and specific energies that are comparable to or higher than those of lithium ion batteries such as Ag-Zn (~150 Wh kg<sup>-1</sup>) and Zn-air (up to 400 Wh kg<sup>-1</sup>).<sup>7</sup> Although they are longly established for primary (single-use) energy storage, Zn-based batteries are anticipated for use in advanced technologies such as electric and hybrid electric vehicles and smart grids.

Conventional Zn-Ni batteries are commonly assembled from Ni(OH)<sub>2</sub> delivering an energy density up to 70 Wh kg<sup>-1</sup>, which is only 20% of their theoretical value (372 Wh kg<sup>-1</sup>).<sup>8</sup> Comparatively, NiO has much higher theoretical capacity (358 mAh g<sup>-1</sup>) because of its smaller molecular weight than Ni(OH)<sub>2</sub> according to the equation  $C = (F \cdot n) / (3.6 M)$ ,<sup>9</sup> but the poor electrical conductivity and low cycling life of NiO restricted its practical applications.

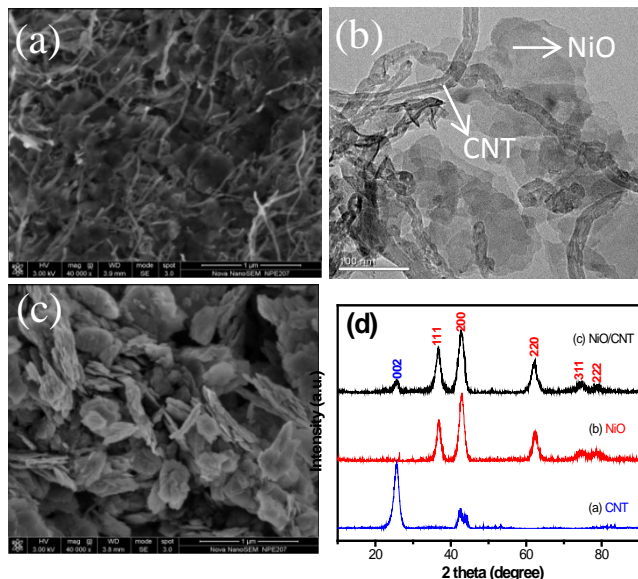
Here, we report a Zn-NiO battery consisting NiO/CNTs as positive electrode and zinc plate as negative electrode in 1 M KOH with 10 mM Zn(Ac)<sub>2</sub> as electrolyte, which features good cycling behaviour and high energy density.

The detailed preparation process of a composite of NiO nanosheet anchored with carbon nanotubes (CNTs) is presented in the electronic supplement information (ESI and Scheme S1). X-ray diffraction was carried out on a Bruker D4 X-ray diffractometer with Ni-filtered CuK<sub>α</sub> radiation. The composite or NiO was mixed with acetylene black and poly (tetrafluoroethylene) (PTFE) in a weight ratio of 8:1:1 dispersed in ethanol. After drying, the mixture was pressed into a film with an active mass loading of 3 mg cm<sup>-2</sup>, the film was cut into a disk of about 2 mg which was pressed onto Ni-grid at a pressure of 10 MPa, and finally dried at 120 °C for 12 h to act as the positive electrode. The cyclic voltammetric (CV) testing was performed in a three-electrode cell with a nickel grid and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively, by an electrochemical working station of CHI440B (Chenhua, China). The zinc plate was polished to remove the surface oxides layer prior to assembling with NiO/CNTs or pristine NiO into Zn-NiO battery in 1 M KOH and 10 mM Zn(Ac)<sub>2</sub>. The two-electrode cell was used to test the cycling and charge-discharge behaviour on a Land 2001A cell tester.

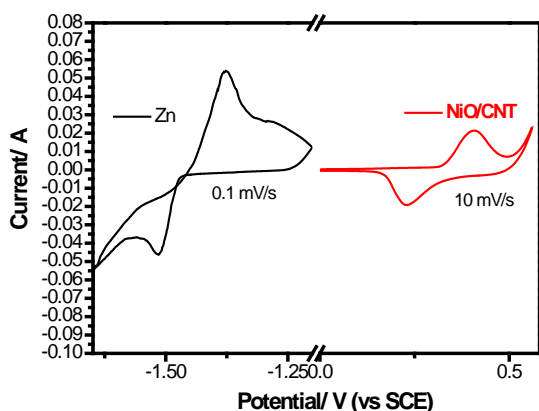
FESEM (field electron scanning microscopic) and TEM (transmission electron microscopic) micrographs of the prepared NiO/CNTs composite and the pristine NiO (Fig. 1a-c) show clearly that NiO exists as nanosheets anchored with CNTs. CNTs are utilized as templates for the growth of NiO nanosheets during the hydrothermal process. In the case of the pristine NiO, nanosheets also appear. However, their thickness is evidently much thicker. X-ray diffraction patterns (Fig. 1d) show that the as-prepared NiO/CNTs is highly crystalline, and all the peaks fit very well with the pristine NiO and CNTs, indicating that there is no crystal transformation of both NiO and CNT in the composite. The high degree of crystallinity of NiO in the composite is caused by the heat-treatment (250 °C) during the synthesis process.

CV curves of zinc plate in 1 M KOH and 10 mM Zn(Ac)<sub>2</sub> at 0.1 mV s<sup>-1</sup> and the NiO/CNT electrode in 1 M KOH aqueous electrolyte at the scan rate of 10 mV s<sup>-1</sup> are shown in Fig. 2. In the case of zinc, there is one set of redox peaks located at -1.38/-1.52 V (vs. SCE) corresponding to the redox reaction of Zn(OH)<sub>4</sub><sup>2-</sup>/Zn.<sup>10, 11</sup> Redox peaks related to the NiO/CNTs are situated at 0.40/0.23 V, in consequence of the redox reaction for OH<sup>-</sup> ions with NiO. In the case of the pristine NiO, the positions of the redox peaks are similar to

those of the nanocomposite (Fig. S1 in ESI). However, the current response is much smaller than that of the nanocomposite. Since there is a large potential difference (1.78 V) between Zn and NiO, they can be assembled into a battery system whose redox reactions during charge/discharge processes can be schematically shown in Scheme 1.



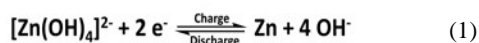
**Fig. 1** (a) Field emission scanning electron micrograph (FESEM) and (b) transmission electron micrograph (TEM) of the prepared NiO/CNTs composite; (c) FESEM micrograph of pristine NiO; (d) X-ray diffraction patterns of CNT, NiO and the NiO/CNTs nanocomposite.



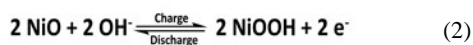
**Fig. 2** CV curves of Zn at the scan rate of  $0.1 \text{ mV s}^{-1}$  and NiO/CNTs at  $10 \text{ mV s}^{-1}$  in  $1 \text{ M KOH}$  and  $10 \text{ mM Zn}(\text{Ac})_2$ , which were tested by using nickel-grid and SCE as the counter and reference electrodes, respectively.

Their electrode and cell reactions are simplified and shown in the following:

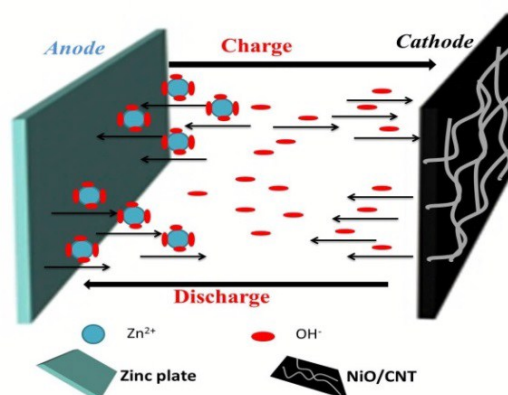
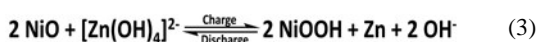
Negative electrode:



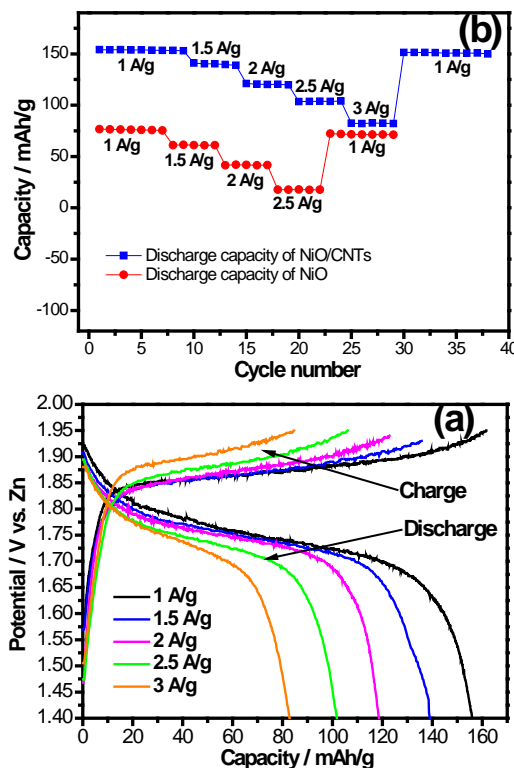
Positive electrode:



Total reaction:



**Scheme 1** Schematic illustration of the redox process for Zn-NiO battery during the charge/discharge processes.



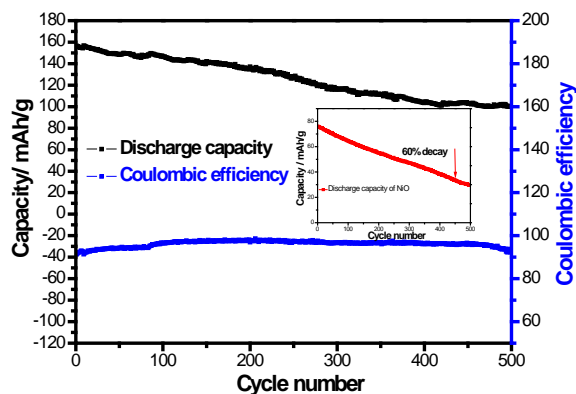
**Fig. 3** (a) Charge and discharge curves of the Zn-NiO battery at different current densities based on the NiO/CNTs composite electrode, and (b) Discharge capacity of the Zn-NiO battery at different current density between 1.4 and 1.95 V. The data were calculated based on the mass of the NiO/CNTs composite and pristine NiO.

During the charging process,  $[\text{Zn}(\text{OH})_4]^{2-}$  is turned into Zn by releasing  $\text{OH}^-$  into the electrolyte. In the meantime, NiO is transformed into NiOOH due to the reaction with  $\text{OH}^-$  from the electrolyte. The electrolyte is always kept electrically neutral. During the discharge process, Zn reacts with  $\text{OH}^-$  anions from the electrolyte to form  $[\text{Zn}(\text{OH})_4]^{2-}$  complex together with the removal of  $\text{OH}^-$  from NiOOH to become NiO, evidenced from the XRD patterns of the NiO/CNTs nanocomposite after the charging and discharging process (Fig. S2 in the ESI). It is clear that the mechanism is similar to that of  $\text{Ni}(\text{OH})_2$  since their final product after the charging process is NiOOH. However, the final product after the discharging process

is different. This indicates that the introduction of 10 mM  $\text{Zn}(\text{Ac})_2$  to the electrolyte forming  $[\text{Zn}(\text{OH})_4]^{2-}$  anions could improve the reversibility of the redox reaction of Zn, which could enhance the cycling stability of the Zn-NiO battery.<sup>12</sup>

The electrochemical performance of the Zn-NiO battery at different current densities between 1.4-1.95 V is shown in Fig. 3a. The charge/discharge voltage platforms at about 1.87/1.75 V are very clear which are consistent with the CV results. The reversible capacity of the battery is  $155 \text{ mAh g}^{-1}$  at  $1 \text{ A g}^{-1}$  based on the NiO/CNT positive electrode, which is similar to the value of the nanocomposite measured in three-electrode system in 1 M KOH. Based on the total mass of the composite positive electrode and zinc and an average discharge voltage of 1.75 V, the calculated energy density will be  $228 \text{ Wh kg}^{-1}$  at  $1 \text{ A g}^{-1}$ . This value is comparable with those of lithium ion batteries.<sup>13-16</sup>

When the charge/discharge current density increases from 1, 1.5, 2, 2.5 to  $3 \text{ A g}^{-1}$ , the discharge capacity of the NiO/CNTs nanocomposite decreases from 155, 139, 120, 102 to  $82 \text{ mAh g}^{-1}$ , respectively, much higher than those of the pristine NiO (Fig. 3b). This is consistent with the results from CV test (Fig. S2 in ESI). In this work, the design of the NiO nanosheets anchored with CNTs as the positive electrode in the Zn-NiO battery offers better electronic conductivity (Nyquist plots, Fig. S3 in the ESI), leading to better electrochemical redox kinetics and a consequent higher capacity<sup>19</sup> and good stability of the NiO nanosheets. Another reason to the higher capacity for the composite is due to the thinner NiO nanosheets and higher crystallinity of NiO. This suggests that the Zn-NiO battery can be charged and discharged fast, and can meet the rapid change of power supply and demand from the grid. However, its rate capability cannot be compared with that measured in three-electrode system, resulting from higher internal resistance in the assembly of total battery and the decline of redox reversibility of  $\text{Zn}(\text{OH})_4^{2-}/\text{Zn}$  in the alkaline electrolyte due to the formation of  $\text{Zn}(\text{OH})_2$  and  $\text{ZnO}$ .<sup>11</sup>



**Fig. 4** cycling performance of the Zn-NiO battery at  $1 \text{ A g}^{-1}$  based on NiO/CNTs composite and pristine NiO.

The cycling performance of the Zn-NiO battery at the current density of  $1 \text{ A g}^{-1}$  based on the NiO/CNTs composite (Fig. 4) shows that the coulombic efficiency is almost 100 % except in the several initial cycles, which is similar to those of lithium ion batteries. This means that the present battery supports good charge/discharge reversibility and long lifespan with 35% capacity decay after 500 cycles. In the case of the pristine NiO, there is 60% decay (inset in Fig. 4) after 500 full cycles because of better stability of the NiO/CNTs nanocomposite and the introduction of 10 mM  $\text{Zn}(\text{Ac})_2$  to the electrolyte. In the case of the electrodes instead of the batteries, the NiO/CNTs nanocomposite is very stable, and can be cycled up to

4000 full cycles with very small capacity decay, which is superior to that of the pristine NiO electrode (Fig. S4 in the ESI). In addition, the morphology of the NiO/CNTs nanocomposite keeps very stable even after 4000 full cycles (Fig. S5 in the ESI). As to the faster capacity fading of the Zn-based batteries than that of the electrodes, the main reason may be attributed to the formation of  $\text{Zn}(\text{OH})_2$  or  $\text{ZnO}$  and dendrite in the zinc negative electrode.<sup>17, 18</sup> However, it is much better than that of Zn-Ni(OH)<sub>2</sub> batteries.<sup>6,20</sup> Further research on improving the negative electrode is needed. The approach of utilizing NiO/CNTs as the positive electrode for Zn-NiO battery is superior to the enhanced stability of the Ni(OH)<sub>2</sub> in Zn-Ni battery<sup>20</sup> and other zinc-based batteries in neutral electrolyte<sup>21-23</sup> in pursuit of high energy density battery with low cost, good safety, long lifespan and environmentally friendliness.



**Fig. 4** LEDs powered by the assembled Zn-NiO batteries (Red, 1.7-2.3 V; White, 3-3.6 V).

Zn-NiO batteries were assembled with the NiO/CNTs nanocomposite as the positive electrode (about 1.5 mg). As shown in Fig. 4, a red LED and a white one are lighted on by one and two serial batteries, respectively, indicating that the battery could be cascaded efficiently and this design of Zn-NiO battery is of great promise for practical application.

## Conclusions

In summary, a Zn-NiO battery has been assembled based on NiO nanosheets anchored with CNTs (NiO/CNTs nanocomposite) as the positive electrode, zinc plate as the negative one, and an alkaline solution of 1 M KOH and 10 mM  $\text{Zn}(\text{Ac})_2$  as the electrolyte. The nanocomposite shows high specific capacity of  $155 \text{ mAh g}^{-1}$ , and the average discharge voltage of this battery is 1.75 V. The energy density of this battery can be  $228 \text{ Wh kg}^{-1}$  (based on the mass of positive electrode composite and zinc) and its capacity decay after 500 cycles at a current density of  $1 \text{ A g}^{-1}$  is 35%. Moreover, it could be cascaded efficiently. The above results demonstrate clearly that the approach of utilizing NiO/CNTs as the positive electrode to assemble a Zn-NiO battery is superior to the reported Ni(OH)<sub>2</sub> in Zn-Ni battery and other zinc-based batteries in neutralized electrolyte in pursuit of high energy density battery with low cost, good safety, long lifespan and environmentally friendliness.

Financial support from rom China National Distinguished Youth Scientists (NSFC No. 51425301) and STCSM (No. 14520721800) is greatly appreciated.

## Notes and references

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Electronic Supplementary Information (ESI) available: The preparation of NiO/CNTs and NiO, CV curves of NiO/CNTs and NiO, X-ray diffraction patterns of NiO/CNTs during charge-discharge process, Nyquist plots of NiO/CNTs and NiO, cycling behaviour of NiO/CNTs and NiO, and TEM micrograph of NiO/CNTs after 4000 full cycles. See DOI: 10.1039/c000000x/

1. C. Liu, F. Li, L. P. Ma and H. M. Cheng, *Adv. Mater.*, 2010, **22**, E28-62.
2. M. Armand and J. M. Tarascon, *Nature*, 2008, **451**, 652-657.
3. N. S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y. K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho and P. G. Bruce, *Angew. Chem. Int. Ed.*, 2012, **51**, 9994-10024.
4. K. Xu, *Chem. Rev.*, 2004, **104**, 4303-4417.
5. W. Tang, Y. Hou, F. Wang, L. Liu, Y. Wu and K. Zhu, *Nano. Lett.*, 2013, **13**, 2036-2040.
6. H. Kim, G. Jeong, Y. U. Kim, J. H. Kim, C. M. Park and H. J. Sohn, *Chem. Soc. Rev.*, 2013, **42**, 9011-9034.
7. J. F. Parker, C. N. Chervin, E. S. Nelson, D. R. Rolison and J. W. Long, *Energy Environ. Sci.*, 2014, **7**, 1117.
8. F. Beck and P. Rüttschi, *Electrochim. Acta*, 2000, **45**, 2467-2482.
9. G. S. Gund, D. P. Dubal, S. S. Shinde and C. D. Lokhande, *ACS Appl. Mater. Interfaces*, 2014, **6**, 3176-3188.
10. B. Yang and Z. Yang, *RSC Adv.*, 2013, **3**, 12589.
11. X. Fan, Z. Yang, W. Long, Z. Zhao and B. Yang, *Electrochim. Acta*, 2013, **92**, 365-370.
12. M. Gong, Y. Li, H. Zhang, B. Zhang, W. Zhou, J. Feng, H. Wang, Y. Liang, Z. Fan, J. Liu and H. Dai, *Energy Environ. Sci.*, 2014, **7**, 2025.
13. Y. Liu, Z. Wen, X. Wu, X. Wang, Y. Wu and R. Holze, *Chem. Commun.*, 2014, **50**, 13714-13717.
14. W. Tang, Y. Zhu, Y. Hou, L. Liu, Y. Wu, K. P. Loh, H. Zhang and K. Zhu, *Energy Environ. Sci.*, 2013, **6**, 2093.
15. Y. Hou, X. Wang, Y. Zhu, C. Hu, Z. Chang, Y. Wu and R. Holze, *J. Mater. Chem. A*, 2013, **1**, 14713.
16. L. Liu, Y. Hou, X. Wu, S. Xiao, Z. Chang, Y. Yang and Y. Wu, *Chem. Commun.*, 2013, **49**, 11515-11517.
17. S. Li, K. Shu, C. Zhao, C. Wang, Z. Guo, G. Wallace and H. K. Liu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16679-16686.
18. Z. Wang, Z. Wu, N. Bramnik and S. Mitra, *Adv. Mater.*, 2014, **26**, 970-976.
19. X. Wang, M. Li, Z. Chang, Y. Yang, Y. Wu and X. Liu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 2280-2285.
20. G. Abellán, M. Latorre-Sánchez, V. Fornés, A. Ribera and H. García, *Chem. Commun.*, 2012, **48**, 11416.
21. C. Xu, B. Li, H. Du and F. Kang, *Angew. Chem. Int. Ed.*, 2012, **51**, 933-935.
22. B. Zhang, Y. Liu, X. Wu, Y. Yang, Z. Chang, Z. Wen and Y. Wu, *Chem. Commun.*, 2014, **50**, 1209-1211.
23. H. Zhang, X. Wu, T. Yang, S. Liang and X. Yang, *Chem. Commun.*, 2013, **49**, 9977-9979.

## COMMUNICATION

## Table of Content

**A Zn-NiO rechargeable battery with long lifespan and high energy density**

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This battery delivers an average output voltage of 1.75 V, and an energy density of 228 Wh kg<sup>-1</sup> on the basis of the weights of the two electrodes. It is promising for environmentally friendly and low cost battery with high energy density and good cycling life.

