

Preparation of Ag/CuO Composites as Anode for Lithium-ion Batteries

C. WANG, N. LI*, D.Y. LI and F.F. WANG

School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, P.R. China

*Corresponding author: Fax: +86 451 86418270; Tel: +86 451 86413721; E-mail: lininghit@263.net

Received: 20 June 2014;

Accepted: 9 September 2014;

Published online: 27 April 2015;

AJC-17175

An Ag/CuO composite is obtained by a facile electroless deposition process and the electrochemical performance was evaluated for lithium-ion batteries application. The Ag/CuO composite electrode exhibit excellent cycle stability, retaining the capacity of 560 mAh g⁻¹ at 0.1 C and 416 mAh g⁻¹ at 1 C after 50 cycles, respectively within the voltage range of 3-0.02 V (vs. Li⁺/Li). Furthermore, the composite electrode exhibits excellent rate capability at varying rates.

Keywords: Copper oxide, Electrochemical performance, Anode materials, Lithium-ion batteries.

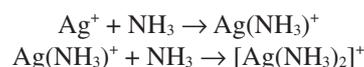
INTRODUCTION

During the past decades, extensive efforts have been dedicated to develop the advanced lithium-ion batteries with excellent electrochemical properties. Lithium-ion batteries have become the dominant power source for consumer electronics devices, electric vehicles and energy storage systems in the next generation electric power stations¹. The performances of above devices depend largely on the properties of lithium-ion batteries. However, the current commercial carbonaceous anodes have approach the theoretical capacity (372 mAh g⁻¹). As one of next-generation lithium-ion batteries promising candidates, 3d transition metal oxides (M_xO_y, where M is Cu, Fe, Ni, etc.) have been widely investigated for lithium-ion batteries due to their long life, high energy density and repetitive-use properties². Copper oxide among above transition metal oxides is of particular interest for its high theoretical capacity (670 mAh g⁻¹), inexpensiveness, non-toxicity and ease of manufacturing. However, copper oxide is a typical semiconductor with low electrical conductivity, thus resulting in poor electrochemical performance and limiting its wide practical application. To overcome these disadvantages, many efforts have been taken to improve the cycle capability and rate performance of CuO electrodes, including developing nanostructures, preparation composite electrodes¹. Comparatively, with the help of metal particles coating on electrodes can improve the electrical conductivity easily without involving complex preparation process. In the past few years, several studies have been reported that depositing/mixing noble metal on electrode (such as Li₄Ti₅O₁₂, LiMn₂O₄ and LiFePO₄) which exhibit improved electrochemical performance in lithium-ion

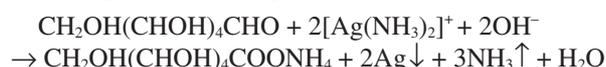
batteries³. However, the explorations on Ag modified CuO electrodes are few. In this work, we deposit Ag particles on dandelion-like CuO *via* a simple electroless deposition process. The as-prepared Ag/CuO composite is testes as anode for lithium-ion batteries and exhibits excellent reversible capacity and high-rate capability.

EXPERIMENTAL

All chemicals in the present study were analytical pure and were used as received without further purification. Dandelion-like CuO spheres was prepared as following: 4.8 mmol of copper nitrate and 14.4 mmol of urea were dissolved in 320 mL of deionized water under stirring to form a clear solution, then the solution was transferred into a 400 mL Teflon-lined autoclave and subjected to hydrothermal treatment at 180 °C for 18 h. After cooling down to room temperature, the black precipitate was collected by centrifugation and washed by distilled water and absolute ethanol and dried in a vacuum oven, followed by calcined in air at 400 °C for 2 h. Then a certain amount of Ag particle was deposited on as-prepared dandelion-like CuO in a facile electroless deposition process. Firstly, NH₃·H₂O was dropped into a certain amount of AgNO₃ solution (5 mmol L⁻¹) until the white deposit disappeared:



Then, the stoichiometry amount of glucose solution was added into above suspension under magnetic stirring at 60 °C. The following reaction took place:



The weight ratio of Ag and CuO in the composite powders was corresponding to 5 wt. % Ag in the prepared Ag/CuO composite powders.

The resulting powders were characterized by means of X-ray diffraction (XRD, D8, Bruker AXS) equipped with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). X-ray photoelectron spectroscopy measurements (XPS, K-Alpha, Thermo Fisher Scientific) were carried out for the valence state and chemical bonding information of as-prepared sample, which with using a micro-focused monochromatized Al $\text{K}\alpha$ radiation ($h\nu = 1486.7 \text{ eV}$). The morphology and micro-structure of the samples were characterized using a field-emission scanning electron microscope (SEM, Quanta 200F, FEI). The electrochemical characterization was performed with coin type cells (CR-2025) containing the CuO composite working electrode. A piece of Li metal foil was used as a combined counter and reference electrode. The CuO composite working electrodes were prepared by mixing the active materials, acetylene black and polyvinylidene fluoride binder with weight ratio of 8:1:1 in N-methyl-2-pyrrolidone. The slurry was coated onto a thin copper foil as the current collector by the "doctor blade" technique⁴. The mass of each CuO thin electrode was precisely measured with an electronic analytical balance before coin cell assembly. Test cells were assembled in an argon filled glove box, which the moisture content and oxygen level were maintained less than 1 ppm. The electrolyte was 1 M LiPF_6 in a mixture of ethylene carbonate and dimethyl carbonate (with volume ratio of 1:1) with Celgard 2300 polypropylene as separator. The cells were galvanostatically charged and discharged at a constant current density of 0.1 C (1 C = 670 mAh g^{-1}) on a battery test system for cycling and rate tests.

RESULTS AND DISCUSSION

Fig. 1 showed the XRD patterns of the Ag/CuO composite powders. Several of the detected peaks can be ascribed to the detection of CuO (JCPDS file No. 45-0937). Furthermore, some peaks can be ascribed to the detection of Ag with most noticeable the (1 1 1) plane (38.1°) and the (2 0 0) plane (44.3°)⁵.

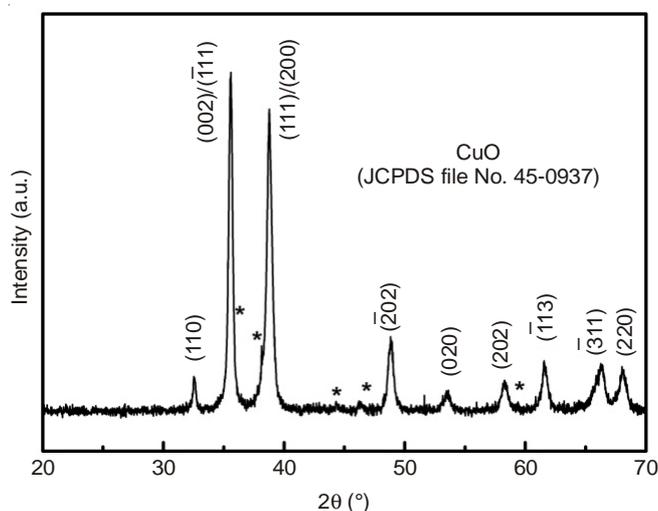


Fig. 1. XRD patterns of as-prepared Ag/CuO composite

The as-prepared Ag/CuO composite was further characterized by XPS analyses. Ag 3d and Cu 2p_{3/2} core-level spectra of as-prepared CuO sample were resolved using Gaussian curve-fitting analysis and are presented in Fig. 2ab, respectively. The main Ag 3d peak located at 368.2 and 374.2 eV, corresponding to that of the Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. This result demonstrates that the Ag metal exists as an elementary substance in the as-prepared composite. On the other hand, the main Cu 2p_{3/2} peak presents only one component. The main one is located at 934.1 eV, which is identified as Cu^{2+} characteristic of the CuO phase. The peaks at 941.7 and 944.0 eV are assigned to Cu^{2+} satellite peaks, also attesting that CuO is the main component⁶. The SEM image of the as-prepared CuO composites is shown in Fig. 3, which can be clearly observed that nanosized Ag are uniformly distributed on the surface of the CuO spheres.

In the followings, the electrochemical properties of the CuO anode were investigated by cyclic voltammetry (CV). Typical CV obtained at a scan rate of 0.2 mV s^{-1} between 3 V and 0.02 (vs. Li^+/Li) are displayed in Fig. 4. In the first cathodic scan process, peaks are observed and correspond to the multi-step electrochemical reactions (lithiation process) 7: (1) the formation of a $\text{Cu}_{1-x}\text{Cu}_x\text{O}_{1-x/2}$ solid solution with a CuO phase, (2) the formation of Cu_2O phase and (3) the decomposition of CuO into Cu and Li_2O . During the anodic scan process

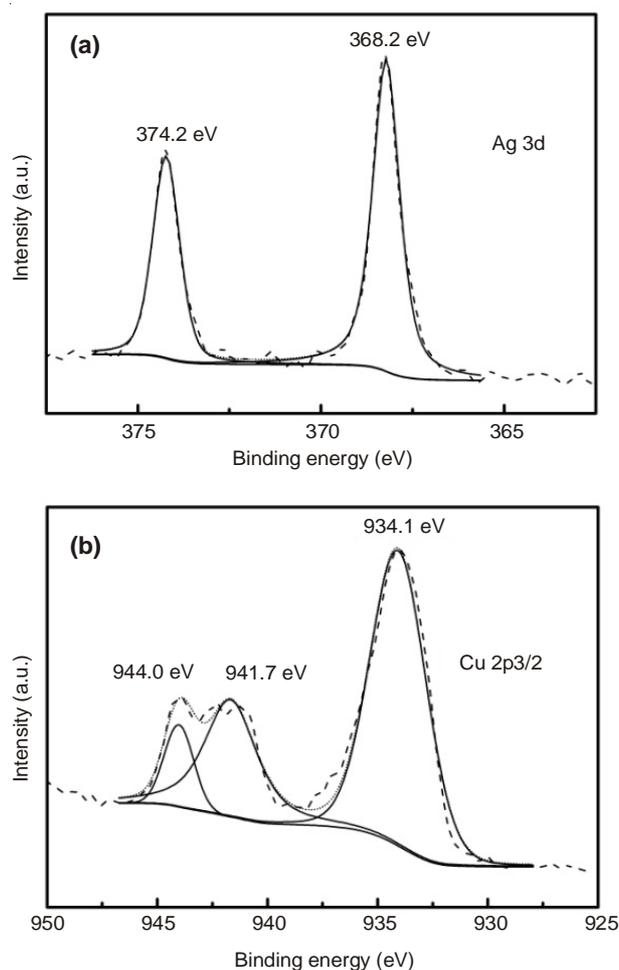


Fig. 2. XPS curve-fitting spectra of as-prepared Ag/CuO composite: (a) Ag 3d and (b) Cu 2p_{3/2}

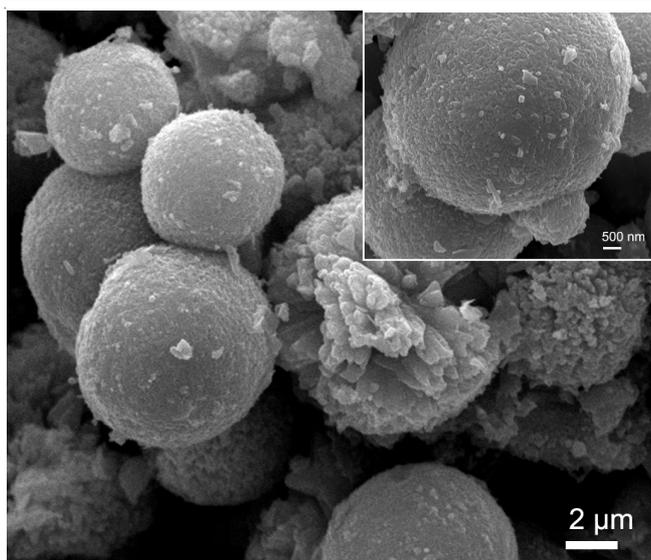


Fig. 3. SEM images of as-prepared Ag dispersed spherical CuO

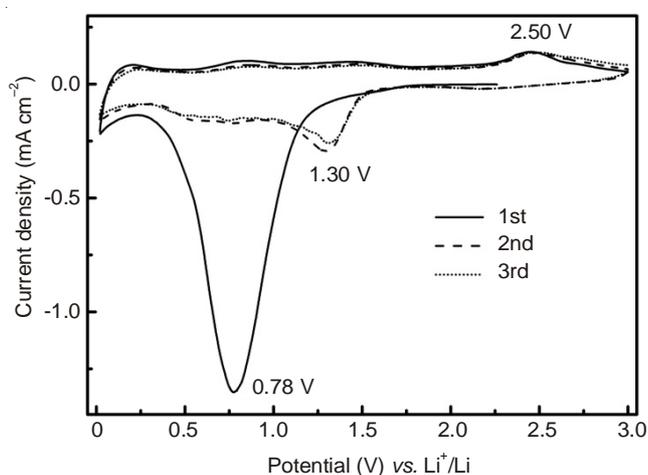


Fig. 4. Cyclic voltammograms of as-prepared Ag/CuO composite from 3 V to 0.02 V (vs. Li^+/Li) at the scan rate of 0.2 mV s^{-1}

(delithiation process), there is only one peak (2.5 V) observed which corresponds to the formation of Cu_2O and CuO . In the subsequent CV cycles, the reductive peaks shift slightly to higher potentials but the oxidative peak almost stays at the same potential. The cycling performances of Ag/CuO composite anode was evaluated at 0.1 C and 1 C in the range between 3 and 0.02 V, as shown in Fig. 5a. The Ag/CuO composite anode shows excellent cycling performance. After 50 cycles, the Ag/CuO composite anode exhibits a reversible discharge capacity of 560 mAh g^{-1} at 0.1 C and 416 mAh g^{-1} at 1 C after 50 cycles respectively which are superior to graphite based electrode (theoretical capacity 372 mAh g^{-1}), indicating the excellent cycling performance. Another excellent property of the Ag/CuO composite electrode is its high rate capability. As shown in Fig. 5b, the Ag/CuO composite electrode shows good rate capability performance. After 5 C upon decreasing the rate to 0.1 C, the reversible capacities reached 662 mAh g^{-1} . On the basis of above results, it seems scattered Ag particles

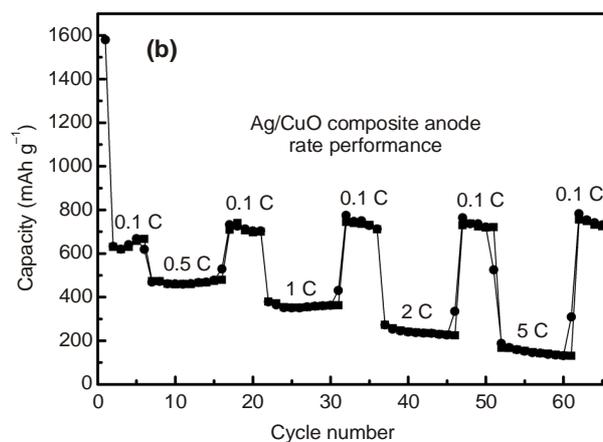
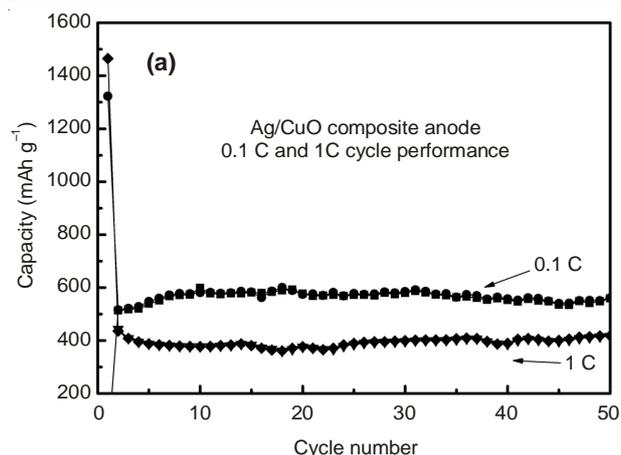


Fig. 5. (a) Cycling performance of Ag/CuO composite at a 0.1 C and 1 C rate; (b) rate performance for as-prepared Ag/CuO composite

on the as-prepared composite electrodes play an important role for excellent electrochemical performance.

Conclusion

In this work, we have developed a facile method using electroless deposition to prepare Ag/CuO composite anode for lithium-ion batteries. The Ag particles are dispersed on the surface of dandelion-like CuO and improve the electronic conductivity of electrode, which exhibit excellent cycle performance and rate performance.

REFERENCES

1. Q.Z. Zhang, K.L. Zhang, D.G. Xu, G.C. Yang, H. Huang, F.D. Nie, C.M. Liu and S.H. Yang, *Prog. Mater. Sci.*, **60**, 208 (2014).
2. J.Y. Xiang, J.P. Tu, L. Zhang, Y. Zhou, X.L. Wang and S.J. Shi, *J. Power Sources*, **195**, 313 (2010).
3. J.-G. Kim, D. Shi, M.-S. Park, G. Jeong, Y.-U. Heo, M. Seo, Y.-J. Kim, J.H. Kim and S.X. Dou, *Nano Res.*, **6**, 365 (2013).
4. F.F. Wang, C. Wang, R.Q. Liu, D. Tian and N. Li, *J. Phys. Chem. C*, **116**, 10461 (2012).
5. S. Huang, Z. Wen, X. Zhu and Z. Gu, *Electrochem. Commun.*, **6**, 1093 (2004).
6. C. Wang, Q. Li, F.F. Wang, G.F. Xia, R.Q. Liu, D.Y. Li, N. Li, J.S. Spendlow and G. Wu, *ACS Appl. Mater. Interfaces*, **6**, 1243 (2014).
7. S.Q. Wang, J.Y. Zhang and C.H. Chen, *Scr. Mater.*, **57**, 337 (2007).