

A Simple Approach to Prepare Metal Oxides Supra-Structures for LIBs

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Abstract: A variety of materials have been investigated as potential electrode materials for LIBs. Electrodes including Fe, Co, Ni or Cu have more Lithium ion storage capacity (more than 600 mAh/g) comparing to graphite (about 372 mAh/g). Recently, much effort has been focused toward achieving 3-dimensional hollow spheres with high surface area and porous for better capacity performance. In this study a simple spray drying approach has been introduced to synthesize porous CuO and Co₃O₄ microspheres. The results revealed that uniform structures of the nanoparticles microspheres were achieved. Then their cyclic performance were analyzed and compared to their commercial counterparts. The porous CuO microspheres and Co₃O₄ microspheres exhibited high capacity retention (86.2% of the discharge capacity of the second cycle after 60 cycles) and (89.8% of the discharge capacity of the second cycle after 40 cycles) at a current density of 400 mA/g, respectively. The excellent electrochemical properties could be attributed to their unique porous structures. The electrochemical results showed that microspheric electrode materials are able to manifest superior electrochemical properties compared to their commercial counterparts.

Keywords: Co₃O₄, CuO, Porous microspheres, Anode material, Lithium ion battery, Spray drying method

1. INTRODUCTION

Low cost, high performance energy storage systems are required for the implementation of renewable energy systems which reduce our reliance on environmentally polluting fossil fuels [1]. Lithium-ion batteries (LIBs) are predominantly used as the power storage for many portable electronic devices and have great potential for use in large-scale storage applications such as electric vehicles and stationary energy backup systems [2-4]. Efforts to increase the energy storage capacity of LIBs have focused on the development of new electrode materials with various compositions and structures. Nanostructured metal oxides MO_x (M = Cu, Mn, Fe, Co, Ni, etc.) have attracted particular attention as anode materials for high performance LIBs due to their high theoretical capacities, low cost and controllable fabrication[5,6].

Several recent studies have demonstrated control over size, shape and structure of nanostructured metal oxides to achieve unique properties for LIBs [7]. Structures such as nanofibers [8], mesoporous particles threaded with carbon nanotubes [9], hollow

octahedra [10], nanowires [11], pillow-shaped porous structure [12], zero-dimensional nanoparticles [13], one dimensional nanowires [14-16], nanorods [17-18], nanotubes [18-19], nanoneedles [20], and nanoflakes [21] have been investigated. The preparation of these materials however typically relies on complicated methods with multi-step procedures which limit commercial scalability [19-20, 22]. The development of facile industrially applicable approaches for the synthesis of new anode materials remains a great challenge. Spray drying is an industrially scalable method for the preparation of particles [23]. In this study, porous copper oxide and cobalt oxide microspheres have been prepared using the industrially scalable spray drying method and their electrochemical performances were analyzed and compared with commercially available nanoparticles. The morphology and electrochemical properties of the prepared anode active materials were also investigated in detail.

2. EXPERIMENTAL SECTION

2.1. Preparation of CuO and Co₃O₄ Microspheres

To synthesize CuO and Co₃O₄ microspheres, 10 mmol of CuO

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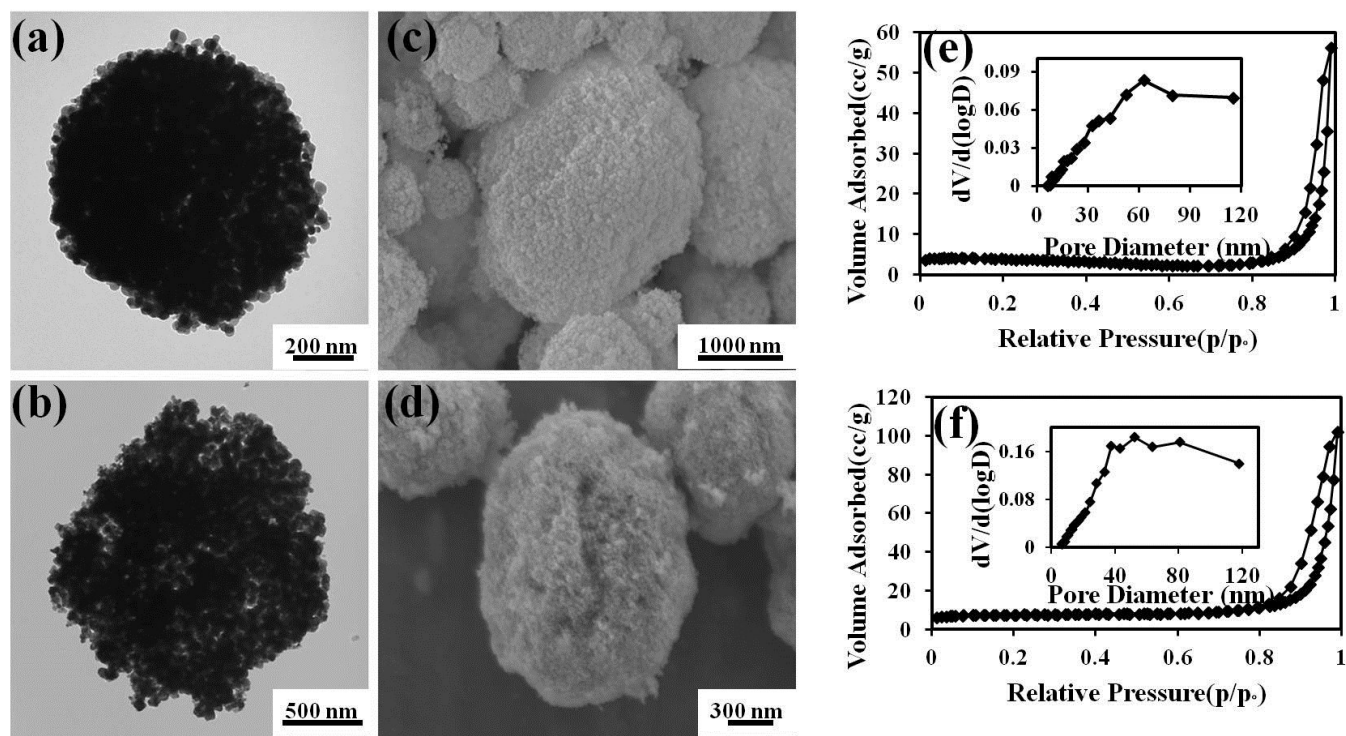


Figure 1. (a, b)TEM images, (c, d)SEM images, and (e, f) N_2 adsorption-desorption isotherms of copper oxide and cobalt oxide microspheres respectively.

nanoparticles and 3.3 mmol of Co_3O_4 nanoparticles (size up to 25 nm) which were purchased from Sigma-Aldrich, separately were mixed in 100 ml distilled water and after sonication for 2 h, were spray dried at $220^\circ C$. The as-made product heated in furnace up to $400^\circ C$, $2^\circ C/min$ in air for 5 h.

2.2. Characterization

The morphological and structural characteristics of the as-synthesized CuO powders were analyzed directly by powder X-ray Diffraction (XRD, Model Rigaku Miniflex X-ray diffractometer with Co radiation) pattern and Transmission electron microscopy (TEM) (Model Philips Tecnai F20 and JEOL 1010). Scanning electron microscopy (SEM) images were obtained on JEOL JSM 7800 microscope operated at 15 kV. N_2 adsorption isotherms were determined at 77 K using a nitrogen adsorption apparatus (ASAP Tristar II 3020 surface area and porosity analyser, Micromeritics) after degassing the samples at $180^\circ C$ for 6 h.

2.3. Electrochemical measurement

To prepare positive electrodes for the electrochemical tests, a mixture of prepared microspheres (70 wt.%), carbon black (20 wt.%), and polyvinylidene fluoride (10 wt.%) in *n*-methyl pyrrolidone was cast onto a Cu foil. After eliminating the solvent in a vacuum oven at $120^\circ C$ for 12 h, Swagelok-type half-cells were assembled in an argon filled glove box. Lithium chips were employed as the counter electrode. The electrolyte was a mixture of 1 M $LiPF_6$ in ethylene carbonate, dimethyl carbonate, and diethylcarbonate (1:1:1 by volume). The cell performance was evaluated galvanostatically at a current density of 400 mA/g for both charge

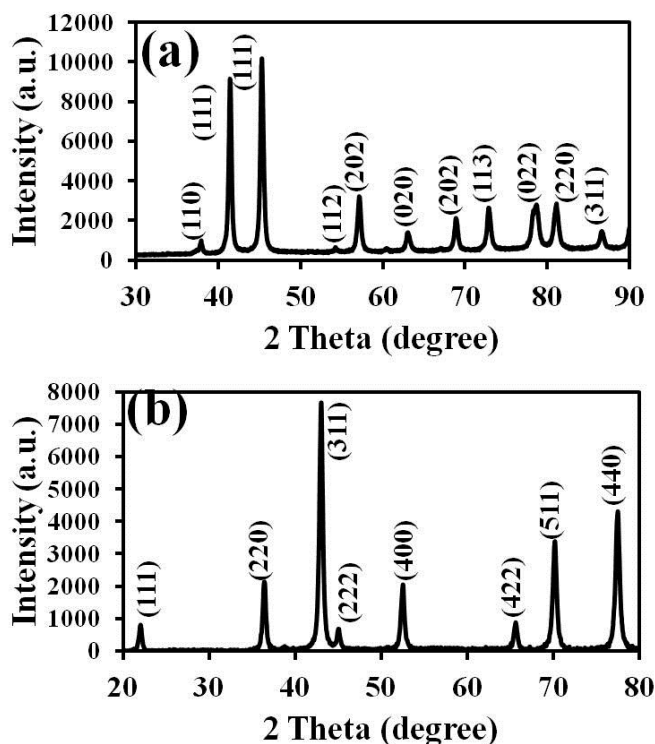


Figure 2. XRD pattern of (a)copper and (b)cobalt oxide microspheres.

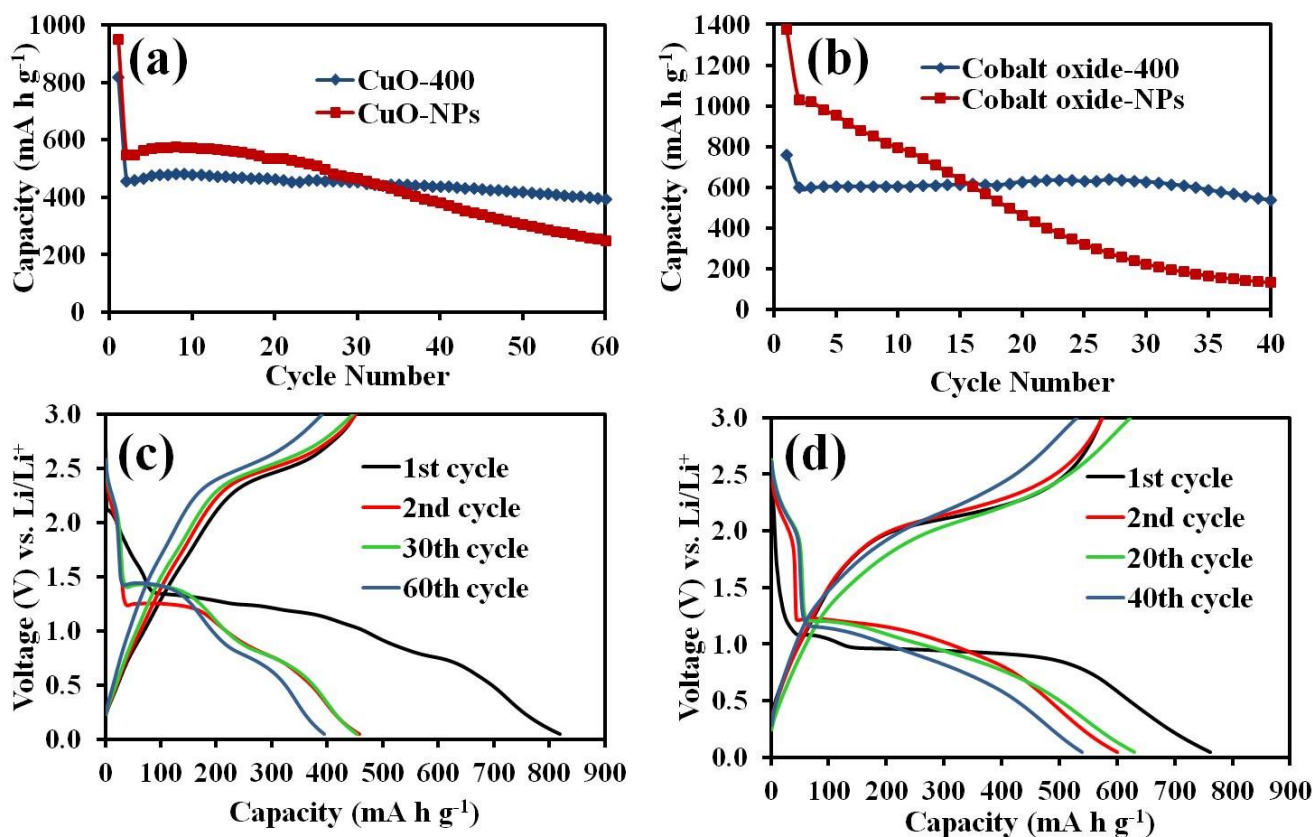


Figure 3. Cyclic performance (a,b) and Galvanostatic charge-discharge profiles(c,d) of copper oxide and cobalt oxide microspheres respectively.

and discharge at room temperature. The cells were cycled in a voltage range of 0.05-3.0 V.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of CuO and Co₃O₄ Microspheres

In the present work, CuO and Co₃O₄ microspheres were successfully synthesized using the facile spray drying method. The morphologies and structure information of synthesized CuO and Co₃O₄ microspheres were investigated using TEM and SEM. From TEM (Fig. 1- a,b), a spherical structures measuring approximately 1-5 μm formed by the clustering of smaller nanosized particles are visible. Small void spaces are observed throughout the microsphere clusters which can be attributed to the interparticle spaces formed by the aggregation of nanoparticles during spray drying.

The SEM micrographs (Fig. 1- c,d) clearly show a spherical morphology with a rough and porous surface. SEM images also indicate the existence of quite large inter-particle voids on the surface of the microspheres. N₂ adsorption-desorption isotherms (Fig. 1- e,f) of the CuO and Co₃O₄ microspheres confirm the highly porous structure of the aggregate spheres. Using the Brunauer-Emmette-Teller (BET) method, the surface area is measured to be 10.67 m²/g and 23.46 m²/g for CuO and Co₃O₄ microspheres, respectively. According to the BJH pore size distribution and the isotherms, the primary pore size distribution ranges from 40 to 60

nm for the both samples. The pore volume is calculated to be about 0.09 cm³/g and 0.16 cm³/g for CuO and Co₃O₄ microspheres respectively. These results confirm the TEM findings indicating the microspheres contain relatively large (>40 nm) pores. Fig. 2 shows an X-ray diffraction pattern of (a)CuO and (b)Co₃O₄ microspheres.

Distinct diffraction peaks are observed for the two samples, which can be indexed to the standard XRD pattern of CuO (JCPDS card No. 48-1548) and Co₃O₄ (JCPDS card No. 43-1003), respectively. No obvious peaks corresponding to other copper oxides and cobalt oxides are observed in the diffraction pattern which is indicative of the formation of phase-pure CuO and Co₃O₄ NPs. The particles size for the CuO sample is calculated by the Scherrer formula to be about 18.59 nm. This relatively small size is beneficial for reducing the lithium ions and electron diffusion distances. The particles size calculated by the Scherrer equation for the Co₃O₄ is about 22.57 nm. Based on these characterisations, the as synthesized materials were expected to exhibit enhanced electrochemical properties. The high phase purity indicated by the XRD pattern is known to be a key factor for achieving stable performance of electrochemically active materials while the large pore size could favorably accommodate the volumetric changes of the electrode materials during charge/discharge cycles. The relatively low surface area of the synthesized particles on the other hand could minimize the electrolyte decomposition and increase the Coulombic efficiency [24].

3.2. Electrochemical Analysis

Fig. 3 shows the cycling performance of the copper oxide and cobalt oxide microspheres compared to their respective commercial counterparts, when cycled between 0.05 and 3.0 V vs. Li/Li⁺ at a current density of 400 mA/g. The initial discharge and charge capacities of the copper oxide microspheres are of 820 mAh/g and 450 mAh/g, respectively, while the commercial CuO samples showed capacities of 952 mAh/g and 539 mAh/g for the discharge and charge cycles, respectively. The cobalt oxide microspheres on the other hand displayed discharge and charge capacities of 762 mAh/g and 574 mAh/g, respectively. This was much higher than the capacities obtained for the commercial Cobalt oxide. The capacity decrease in the first cycle in the both samples can be due to the formation of the SEI layer and the consumption of electrolytes. The cycling performance of copper oxide and cobalt oxide microspheres is relatively stable for the initial 60 cycles and 40 cycles, respectively.

The porous copper oxide microspheres also exhibited high capacity retention (86.2% of discharge capacity of the second cycle after 60 cycles) at a current rate of 400 mA/g which is higher than that of pillow-shaped porous cupric oxide (CuO) [12]. The porous structures within the microspheres could be a facilitating factor for the electrolyte penetration and also provide extra sites for lithium surface storage. The results also show that the synthesized cobalt oxide microspheres have a much better initial Coulombic efficiency (75%) when compared to that of the cobalt oxide nanomesh in other study [22]. Electrochemical measurement demonstrates that the cobalt oxide microspheres as anode materials for lithium-ion batteries exhibit an initial capacity of 762 mAh/g with a reversible capacity of 539 mAh/g after 40 cycles at a current rate of 400 mA/g. While the reversible capacity for the commercial cobalt oxide nanoparticles is about 135 mAh/g. Fig. 3(c, d) show the charge-discharge behaviour of (c) copper oxide microspheres and (d) cobalt oxide microspheres at a current of 400 mA/g between 0.05 and 3.0 V when assembled as an anode in a Swagelok-type Li-ion cell. It can be seen that the studied cells show high irreversible capacity loss during the first charge-discharge cycle and improvement of stability during the subsequent cycles. Copper oxide microspheres generally show a voltage plateau at about 1.4V during the first discharge, corresponding to the reaction of Li-ions and copper oxide and formation of the surface films. The plateau shifts to about 1.5V in 30th and 60th charge-discharge cycles and becomes smaller in prolonged charge-discharge cycling. The peak at 2.3V during the charge cycle corresponds to the reverse reaction of formation of CuO from Cu and Li₂O. In regards to the cobalt oxide microspheres, two voltage plateaus at about 1.1V and 1V during the first discharge can be observed which shift to about 1.2V in subsequent charge-discharge cycles and becomes smaller in prolonged charge-discharge cycling. The peak at 2V during the charge cycle corresponds to the reverse reaction of formation of Co₃O₄ from Co and Li₂O.

These conclusions are consistent with the several other studies about the effect of morphology on the nanoparticles properties. For example in a report it was found that the fibrous morphology formed by nanoscopic copper oxide particles could increase the electrode/electrolyte contact area and also enables the facile partial reduction of Cu₂O into metallic particles (Cu⁰) [8]. Also in several other studies it has been reported that the morphology of the cobalt

oxide nanomaterials significantly affect their capacity, rate capability, and capacity retention [19-20, 22]. It is also known that in the nanostructured systems, the overall capacity could be influenced by lithium surface storage [25].

4. CONCLUSIONS

In summary, copper oxide and cobalt oxide microspheres were synthesized using a facile spray drying method. Such an approach is suitable for the mass production of anode active materials. This study shows that improvement in battery cyclability has been achieved while using synthesized microspheres instead the commercial nanoparticles. Extra sites for the lithium surface storage during cycling can be attributed by the pores within the microspheres, thus higher capacity larger than the commercial nanoparticles are delivered.

5. ACKNOWLEDGMENTS

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REFERENCES

- [1] Liu, C., et al., *Advanced Materials*, 22, 28 (2010).
- [2] Armand, M. and J.-M. Tarascon, *Nature*, 451, 652 (2008).
- [3] Debart, A., et al., *J. Electrochem. Soc.*, 148, 1266 (2001).
- [4] Poizot, P., et al., *Nature*, 407, 596 (2000).
- [5] Wu, C., et al., *Journal of Physical Chemistry*, B110, 17806 (2006).
- [6] Sahay, R., et al., *J. Phys. Chem. C*, 116, 18087 (2012).
- [7] Ko, S., et al., *Advanced Materials*, 24, 4451 (2012).
- [8] Wu, R., et al., *J. Mater. Chem. A*, 1, 11126 (2013).
- [9] Chen, L.B., et al., *Electrochimica Acta*, 54, 4198 (2009).
- [10] Wan, M., et al., *Inorganic Chemistry Communications*, 14, 38 (2011).
- [11] He, T., et al., *Chem. Mater.*, 17, 4023 (2005).
- [12] Li, Y.G., B. Tan, and Y.Y. Wu, *Nano Letters*, 8, 265 (2008).
- [13] Lou, X.W., et al., *J. Mater. Chem.*, 18, 4397 (2008).
- [14] Du, N., et al., *Adv. Mater.*, 19, 4505 (2007).
- [15] Xue, X.Y., et al., *Chem. Commun.*, 47, 4718 (2011).
- [16] Yao, Y., et al., *Int. J. Electrochem. Sci.*, 8, 3302 (2013).
- [17] Du, N., et al., *Advanced Materials*, 19, 4505 (2007).
- [18] Verdurmen, R.E.M., et al., *Lait Dairy-Journal Edp Sciences*, 82, 453 (2002).
- [19] Li, H., et al., *Adv. Mater.*, 21, 4593 (2009).
- [20] Wang, Y., et al., *Energy Environ. Sci.*, 4, 1845 (2011).