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Nanofibers-NiCo₂O₄: Fabrication and Li-Storage Properties

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Abstract. Nano-size particles and composites as anode materials have been explored in recent years in order to reduce the cost, improve the capacity as well as cycle-life of the Lithium ion batteries (LIBs). In view of same, the nanofibers of spinel-NiCo₂O₄ are prepared by easy, viable and cost effective electrospinning technique. The as spun nanofibers composed of polymer solution and metal precursors are sintered at various temperature, and 500°C. 2h is found to be the appropriate to get best crystalline nanofibers of spinel-NiCo₂O₄. The structural, morphological and thermal characterizations are carried out by XRD, FESEM, TGA, respectively. The Li-storage and cycling properties of optimized nano-fibers of NiCo₂O₄ are examined by means of galvanostatic cycling and cyclic voltammetry. The spinel-NiCo₂O₄ delivers the first discharge and charge capacities of 1220(±10) mAhg⁻¹ and 910(±10) mAhg⁻¹ that corresponds the consumption of 11.0 and 8.2 mole of Li, respectively. The cyclic voltammetry studies reveal the average charge and discharge potentials of ~2.2 and ~0.9 V, respectively. Based on galvanostatic cycling, cyclic voltammetry and ex-situ studies like XRD, TEM and SAED, a plausible reaction mechanism is proposed.

Keywords: Nano-materials, Oxides, Anodes, Li-ion Batteries, Electrospinning

PACS: 82.47.Aa

INTRODUCTION

Rechargeable lithium ion batteries (LIBs) are the popular choice for electronic appliances like cell-phones, notebook computers, camcorders and other portable appliances. A good operating voltage of 3.6 V, moderate energy density, wide range of operating temperature (-15 to +50 °C), excellent cyclability and fair degree of safety in operation are the other advantages of the LIBs. Lithium intercalation materials as the positive (cathode) and negative (anode) electrodes are being used and liquid or gel-type Li containing salt as electrolytes. The Li-ions shuttle between the electrodes during charge-discharge cycling. The preferred cathode is the mixed oxide, LiCoO₂ whereas the anode is graphite [1]. Nano-architected particles, composites with different morphologies as cathode and anode materials have been explored in recent years of in order to reduce the cost, improve the capacity as well as cycle-life of the LIBs [1,2-5]. The nano-structured oxides can perform better due to their large surface area, increased access to the electrolyte and improved charge-transfer characteristics, including Li-ion mobility. Transition metal oxides specially Co₃O₄ have been found to exhibit almost 3 times the capacity of graphite, however, the toxic and expensive Co have not been

recognized as an alternative choice. Due to their ability to exhibit high capacity, Co-based compounds are still receiving a considerable attention. To reduce the Co-content from the spinel-Co₃O₄, nano-fibers of NiCo₂O₄ are prepared and studied as anode materials for Li-ion batteries. Due to page restriction, the results are discussed briefly.

EXPERIMENTAL

Nano-fibers of NiCo₂O₄ were prepared by electrospinning technique after sintering at 500 °C for 2h, and characterized by X-ray diffraction, FESEM, TGA. Li-storage and cycling studies were performed on cells fabricated with NiCo₂O₄ as cathode, Li-metal foil as anode, and LiPF₆ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) as the non-aqueous electrolyte. Polypropylene film (Celgard) was used as the separator. Galvanostatic discharge-charge cycling (up to 30 cycles) and cyclic voltammetry were carried out using computer-controlled commercial equipment. More details are given in Ref.[4].

RESULTS AND DISCUSSION

NiCo₂O₄ adopts the cubic spinel structure. Our results show that the *a* lattice parameter to be 8.14(1) Å, in good agreement with the literature reports. The morphology of as-spun PVP-Ni/Co precursors and sintered at 500°C for 2h are shown in Fig. 1. The nano-fibers with high aspect ratio are obtained. Further the results were complemented by HRTM, SAED studies

FIGURE 1. FESEM images of as-spun (a) and sintered (b) nanofibers. The bar represents 10μm and 1μm, respectively.

Both Ni and Co are electrochemically-active with respect to Li-metal, due to the conversion (displacement) reactions as described below. When nano-fibers of spinel-NiCo₂O₄ are electrochemically discharged (reacted) with Li-metal, the crystal structure destruction takes place followed by the formation of Ni- and Co-metal nano-particles and Li₂O, as per the Eqn. (1). At potentials above 1.0 V during charge-reaction (Li-removal), both Ni- and Co-metal nano-particles can reversibly react with Li₂O by the displacement reaction forming the respective nano-size metal oxides (Eqns.(2) and (3)). In the most favorable case, the bivalent Co²⁺ ions (i.e., CoO) can further react with Li₂O to form bi/tri-valent spinel-Co₃O₄ as per Eqn.(4)[3]. Thus, during charge-discharge cycling with Li, we can expect a total capacity corresponding to 7.0 or 7.33 recyclable moles of Li per mole of the starting material, NiCo₂O₄ as per Eqns. (2-4).

The voltage-capacity profiles of NiCo₂O₄ during First discharge-charge reactions are shown in Fig. 2. The voltage-plateaux regions indicate the two-phase co-existence, whereas the smoothly varying slopes indicate single-phase reaction. As can be seen, the first-discharge reaction consumed 11.0 moles of Li per mole of NiCo₂O₄, corresponding to the capacity, 1220(±10) mAhg⁻¹. The excess consumption of 3.0 moles of Li over and above the values given by Eqn. (1), are ascribed to the formation of solid electrolyte

interphase (SEI) and the polymeric-layer formed on the metal nano-particles by the decomposition of the solvents in the electrolyte. The overall first-charge capacity is 910(±10) mAhg⁻¹ (~8.2 mole of Li) instead of the expected value of 7.33 mole of Li. The extra capacity is probably due to decomposition of polymeric layer formed on the nano-particles of Ni and Co.

FIGURE 2. (a) Voltage vs. capacity profiles of nanofiber NiCo₂O₄, for the first discharge- and charge- (b) Capacity vs. cycle number

The capacity vs cycle number plot of ZnCo₂O₄ is shown in Fig. 2b. Up to 30th cycle, the discharge-capacity decreases slightly, the capacity remains fairly high, at ~730 mAhg⁻¹ (~7 moles of Li) and shows about 91% retention of theoretical capacity.

Cyclic voltammetry and ex-situ XRD, HR-TEM and SAED complement the above galvanostatic cycling data and confirm that Li-cycling occurs according to Eqns. 2-4. The average discharge- and charge-potentials are ~0.9 V and ~2.2 V, respectively. For the first time we have shown the Li-storage and cycling properties of nano-fiber of spinel NiCo₂O₄ where both Ni- and Co -ions act as mutual beneficial matrices. To conclude, nano fiber-NiCo₂O₄ is found to be appropriate materials as far as high capacity is concerned, however, high charge potential and large hysteresis between charge and discharge potential are some of the obstacles and need further investigations in order to finds it suitability as LIB anode material.

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REFERENCES

1. G. A. Nazri, G. Pistoia (Eds.), *Lithium Batteries – Science and Technology*, Kluwer Acad., NY, 2003.
2. A. S. Arico et al, *Nature Mater* **4** 366-372 (2005).
3. Y. Sharma et al, *Adv. Funct. Mater.* **17** 2855-2862 (2007)
4. T. P. Fen and Y. Sharma et al *J. Mater. Chem.* accepted, (2011).
5. Y. Sharma et al. To be submitted.