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CuO nano hexagons, an efficient energy storage material for Li- ion battery application

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ABSTRACT

Transition metal oxides (TMO) with admirable theoretical capacity acquired by their conversion reaction have been studied extensively as anode materials for Li-ion batteries. In the current inquisition, Cuo nano hexagons are synthesized by rapid hydrothermal method and characterized through various analytical techniques viz XRD, FESEM, TEM, FT-IR, and XPS analysis. Electrochemical cycling performance of CuO as anode material for Li-ion batteries is elucidated at different current densities between 215 mA g^{-1} and 4.3 A g^{-1}. Nano CuO anode exhibits stable discharge performance of ~575 mAh g^{-1} at current density of 215 mA g^{-1} with low irreversible capacity of 265 mA g^{-1} in the first cycle which is lesser than several reported values obtained from different nano morphological CuO and composites of CuO with conducting additives. Further, nano CuO anode exhibits high rate capability up to the current density of 4.3 A g^{-1} and resumes the initial capacity of 572 mAh g^{-1} at 215 mA g^{-1} current density and remains stable even beyond 100 cycles with zero capacity fading. These ensuing performance characteristics demonstrate nano CuO as a prospective anode material for lithium ion battery.

1. Introduction

In this epoch of electronics, lithium ion batteries are the major powerful energy storage for portable electronic devices [1]. In commercial Li- ion batteries, graphite is the universal anode material by virtue of its high cycling stability and abundance in nature [2–5]. Many scholars intensified their efforts to substitute commercial graphite anode on account of its low theoretical capacity (372 mAh g^{-1}) and poor cycling performance at high current rate. Nowadays, lithium titanium oxide (LTO) is also used in commercial Li-ion batteries in light of its zero strain property [6–8]. Alloying anodes like Sn [9–11], Sb [12,13] and Si [14–17] are acquiring significance in view of their high specific capacities of 994, 660 and 4200 mAh g^{-1} respectively. However, large volume expansion associated with alloying-dealloying mechanism during cycling confines their usage as commercial anode materials. Reversible metal displacement reaction of transition metal oxides with lithium was reported by Tarascon et al., in 2000, inspired the researchers to study extensively TMOs as negative electrode in Li-ion batteries. This conversion mechanism can accommodate more lithium ions and offer high specific capacity [18]. At present, different morphologies of transition metal oxides (TMO) with formula MO, MO_2, M_2O_3 and M_3O_4 (M = Fe, Co, Ni and Cu) evoke greater enthusiasm as commercial anode material for secondary lithium ion batteries considering their enthralling theoretical capacity and reversible conversion mechanism [19–23]. Ge-doped transition metal oxides and mixed metal oxide anodes [24,25] are also found to be exhibiting excellent Li-ion storage performance. Amid all, CuO has been exclusively studied by many researchers due to its captivating properties like high theoretical capacity (674 mAh g^{-1}), low cost, and environment sustainability. The major hindrances of CuO as anode material are poor electronic conductivity, large volume expansion of about 174% associated with Li insertion and extraction during cycling leading to capacity fading. These complications are nullified by amending morphologies of CuO resembling leaf shaped, hollow dandelion-like spheres, nano flower, nano rod, nano tube, shuttle and caddice clew like particles [26–31]. Liu et al., have reported hierarchical CuO architecture synthesized through hydrothermal method exhibits stable reversible capacity of 466 mAh g^{-1} after 50 cycles. The better electrochemical capacity is attained due to its specified morphologies and facets of CuO [32]. Leaf-like mesoporous CuO delivered

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490 mAh g^{-1} even at 2 A g^{-1} current density. Mesoporous nano structure reduces the diffusion path length of electrons and lithium ions. Moreover it increases the electrode electrolyte contact area and enhances electrochemical performance [33]. Xu et al., investigated carbon coated CuO as anode exhibits 486 mAh g^{-1} after 100 cycles shows that carbon coating not only increases the conductivity but also reduces the pulverization of active material and shows good electrochemical performance and better cycling stability [34]. Hu et al., studied hollow CuO polyhedrons as anode material fabricated from metal organic frame work templates delivering reversible capacity of 740 mAh g^{-1} at 100 mA g^{-1} till 250 cycles, much higher than its theoretical capacity. This excellent electrochemical performance is achieved by fascinating hollow/porous shell architectures [35]. R. Wu et al. studied porous CuO hollow architectures exhibiting a reversible capacity of 470 mAh g^{-1} after 100 cycles. CuO hollow octahedral ensures efficient electrolyte penetration and enhances the contact area. Hollow structures act as a buffer matrix to accommodate the associated volume expansion and contraction during cycling without ruining the structural integrity [36].

However, the above synthesis processes [31–39] require long reaction time and involve specific size directing agents like amino acids, malic acids and surfactants to derive CuO particles of different morphologies in nano scale. In this exposition, nano dimensional Cuo hexagons have been synthesized by rapid hydrothermal method; a novel, economical and rapid synthesis process suitable for large scale preparation as the reaction time is only an hour and does not incorporate any size directing reagents to attain the desired morphology. Physical characterization of the synthesized nano CuO hexagons is carried out via XRD, FESEM, TEM, FT-IR, and XPS techniques. The electrochemical nature of the morphologically transformed CuO and its operational efficiency as an anode material in Li-ion batteries are elucidated.

2. Experimental details

Nano structured CuO is synthesized by rapid hydrothermal method. In detail, 0.5 M Cu $(NO_3)_2 \cdot 3H_2O$ is dissolved in 50 ml deionised water. pH of the solution is adjusted to 9–9.5 by adding 1.5 ml of NH_3 solution. The resultant blue colour solution is transferred to 100 ml Teflon lined stainless steel autoclave maintained at 150 °C for 1 h in favour of hydrothermal reaction. The resultant black precipitate is collected by filtration. The precipitate is washed with water for several times and then with ethanol for purity. Schematic representation of CuO synthesis is given in Fig. 1. X-ray diffraction pattern of CuO is recorded in X'Pert PRO PAN analytical PW3040/60X'Pert PRO using CuKα radiation (l = 1.5418 Å) at room temperature. Surface morphology and elemental composition is analysed using Zeiss FESEM analyser. TEM images are recorded using FEI-Tecnai 20 G2 model transmission electron microscope. FT-IR spectrum is recorded through Nicolet 5DXFTIR spectrometer using KBr pellet in the range of 400–4000 cm^{-1}. XPS analysis of the synthesized CuO particles is carried out using Thermo scientific MULTI 2000 X –ray Photoelectron Spectrometer.

2.1. Electrochemical studies of CuO electrodes

CuO electrode is prepared by a slurry coating procedure over copper foil. The slurry is obtained from a mixture comprising of synthesized CuO active material, conductive material and PVDF binder taken in the proportion 80:10:10 with *N*-methylpyrrolidone as slurring agent. The coated foil is dried at 80 °C in hot air oven and then rolled in a hot roll press. 16 mm diameter electrode is blanked out to assemble 2032 coin cell against Li-foil as reference and counter electrode. Active material loading in the coated electrode is typically 0.032 mg 1 M $LiPF_6$ in 1: 1 EC: DMC is used as electrolyte. Electrochemical charge-discharge studies carried out using Arbin automatic battery cycler unit in the potential range of 0.01–3.0 V at different current densities of 215 mA g^{-1} (0.1 C), 430 mA g^{-1} (0.2 C), 1075 mA g^{-1} (0.5 C), 2150 mA g^{-1} (1 C) and 4300 mA g^{-1} (2 C). Electrochemical impedance spectroscopy is carried out using VMP3- based Biologic Impedance analyser from 10 mHz to 100 kHz. Cyclic voltammetry analysis carried out by VMP3- based Biologic cyclic voltammetry analyser between the potentials 0.1 and 3.0 V at a scan rate of 1 mV s^{-1}. After cycling, the cells are opened carefully and the electrodes are subjected to ex-situ XRD and FESEM analysis.

3. Results and discussion

X-Ray diffraction pattern for the synthesized material is given in Fig. 2. The diffraction peaks are observed at 2θ = 32.590°, 35.6010°, 38.7756°, 46.277°, 48.8015°, 51.7593°, 53.5630°, 58.4179°, 61.5528°, 66.3773°, 68.0917°, 72.4608° and 75.44° corresponding to (110), (−111), (002), (111), (200) (−112) (−202), (112), (020), (202), (−113), (−311), (220), (311) and (004) planes respectively. The obtained XRD pattern is assignable to monoclinic CuO matching with ICCD card no. 01-080-1268. The two major high intensity peaks observed at the 2 theta values 35.6010° and 38.7756° indexed as −111, 002 and 111, 200 planes are the characteristic peaks of pure monoclinic CuO. The intensity of $I_{(-111)} > I_{(111)}$ shows that the obtained CuO is highly crystalline in nature. Absence of characteristic peaks for Cu_2O, $Cu(OH)_2$ and Cu confirms that the synthesized CuO material is phase pure. The unit cell parameters are calculated

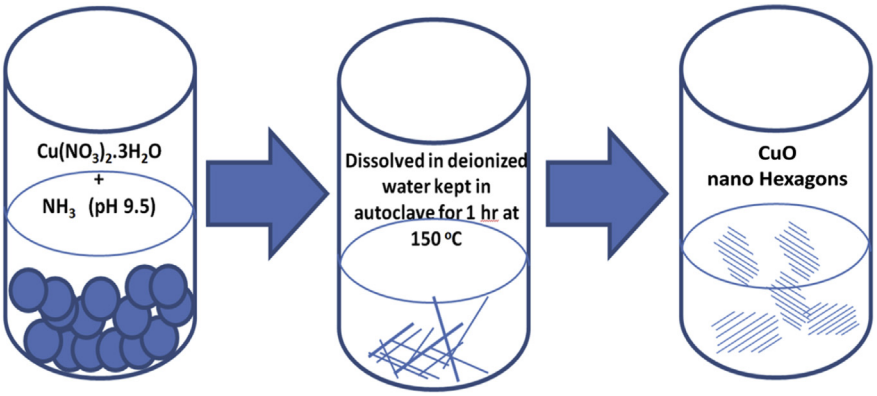

Fig. 1. Schematic representation of nano CuO synthesis.