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RESEARCH PAPER

Co_3O_4 Nanoparticles : Synthesis, Characterization and Its Application as Performing Anode in Li-Ion Batteries

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ABSTRACT

In this research, a convenient, simple and rapid route for the preparation of Co_3O_4 nanoparticles using the calcination of $Co(NO_3)_2{\cdot}6H_2O$ at the presence of benzoic acid (1:1 weight ratio) is reported. Further, the as-prepared Co_3O_4 nanoparticles were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). XRD result confirmed the Co_3O_4 nanoparticles are pure phase and the average crystallite size for Co_3O_4 nanoparticles was found 77 nm. The TEM images reveal nanoparticles with size ranging from 50 to 100 nm, which is in conformity with the calculation of average crystallite sizes from XRD patterns. Furthermore, the prepared Co_3O_4 nanoparticles were investigated as an anode material for Li-ion batteries. Results showed that the Co_3O_4 nanoparticles exhibited excellent electrochemical performance and cycling stability, a capacity of 1127 mA h g^{-1} was obtained at 100 mAg^{-1} and the samples exhibited stable discharge behavior up to 130 cycles with high rate capability.

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INTRODUCTION

Recently, study of transition metal oxide (TMO) nanoparticles and nanocomposites as cathode [1-3] or anode [4-13] materials for rechargeable Li-ion batteries (LIB) has been one of the best hot research topics, because the preparation of TMO nanoparticles is often simple, low-cost and rapid. The transition metal oxide (TMO) nanoparticles as anode materials have also excellent electrochemical performance and cycling stability [1-13]. Nanoparticles of Co_3O_4 can be prepared by various techniques, i.e. solid-state thermal decomposition [14] or carbon assisted decomposition [15,16], and show variety of properties that are favorable in applications such as degradation of organic dye [14], oxidation of alcohols [15], selective oxidation of alcohols [16] and electrocatalytic oxidation of H_2O_2 [17]. Among various transition metal oxides studied for Li ion batteries, LIB's with cobalt oxide nanoparticles as anode have higher energy density compared with the other energy storage devices [5-13]. Unfortunately, nanoparticles of Co_3O_4 show large volume changes during repeated lithiation and delithiation processes [9]. However, they have higher capacity (about 890 mA h g^{-1}) [5-13] than graphite (370 mA h g^{-1}). In recent years, various shapes of Co_3O_4 nanostructures such as nanoring, mesoporous, 3D nanofiber and nanofilms have been prepared and studied as anode materials

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extensively [5-13]. For example mesoporous Co_3O_4 network that has been prepared by Wen *et al*. *via* thermal decomposition of an amorphous metal complex exhibits excellent performance for Li storage [8]. Su et al. prepared Co_3O_4 hexagonal nanorings *via* treating Co-based metal organic frameworks [9]. Co_3O_4 hexagonal nanorings show the specific capacity of 1370 mA h g^{-1} after 30 cycles. Gurunathan et al. reported convenient synthesis route for preparation of Co_3O_4 hollow microsphere [10] that exhibited excellent electrochemical performance (915 mA h g^{-1}) and cycling stability (350 cucles).

This study is a part of our ongoing effort to prepare transition metal oxide nanoparticles and investigated them as Li-ion batteries [18,19]. Herein, we report a convenient, simple and rapid method for preparation of Co_3O_4 nanoparticles using the calcination of $Co(NO_3)_2{\cdot}6H_2O$ at the presence of benzoic acid. Served as Li-ion battery anode, Co_3O_4 nanomaterials show high electrochemical performance.

MATERIALS AND METHODS

All compounds used in this research were purchased from Merck Company and used without any purification. The XRD patterns were obtained on Empyrean powder diffractometer of PANalytical in Bragg-Brentano configuration equipped with a flat sample holder and PIXCel3D detector (Cu Kα radiation, λ = 1.5418 Å). TEM images were recorded with the transmission electron microscope Philips CM120 with a LaB6 cathode operating at 120 kV and equipped with CCD camera Olympus Veleta

Synthesis of Co_3O_4 nanoparticles

1 g of $Co(NO_3)_2{\cdot}6H_2O$ and 1 g of benzoic acid were put into a crucible and ground together for 5 min. The mixture was then annealed at 600 ºC in air for 3 h. The black products were rinsed with water and finally dried at 65 ºC for 12 h.

Electrode preparation and electrochemical test method

The active Co_3O_4 material was mixed with carbon black and PVDF at a mass ratio of 70:15:15 to form slurry with NMP as solvent. The slurry was then spread onto Cu foil by doctor-blade, and dried at 80 °C for 12 h. The disc with diameter 1.53 cm was cut from dried Cu foil, and compressed under the pressure of 10 MPa to form a working electrode. The loading of active material on Cu foil was about 1 mg cm^{-2}. Lithium metal was used as the counter and the reference electrode. The electrodes were assembled into a coin cell (CR2032) in an Ar-filled glovebox using Celgard 2400 as separator and 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/ diethyl carbonate (EC/DMC/DEC, 1:1:1 vol%) as electrolyte. A galvanostatic cycling test of these assembled half-cells was conducted on a LAND CT2001A system in the voltage range of 0.01-3.0 V (vs. Li^+/Li) at different current densities.

RESULTS AND DISCUSSION

XRD patterns

X-ray diffraction (XRD) pattern of Co_3O_4 nanoparticles is shown on Fig. 1. In this pattern, there are several peaks at 2θ ≈ 18.99º, 31.26º, 36.83º, 38.54º, 44.80º, 55.64º, 59.34º and 65.21º which indicates the spinel with cubic face centered structure of Co_3O_4 with standard diffraction data of card no. JCPDS = 01-080-1532. The structure was refined by Rietveld fit in crystallographic program Jana2006 [20] that confirmed the lattice parameter *a* = 8.085 Å. The size of crystallites was determined in the same program using fundamental parameter approach [21], which removed the instrumental part of the diffraction pattern by means of known geometry of the difractometer. The average crystallite size for Co_3O_4 nanoparticles was found 77 nm.

TEM images

The morphology of Co_3O_4 nanoparticles was characterized by TEM. The Fig. 2 shows the TEM images of the sample prepared at 600 ºC. The images reveal nanoparticles with size ranging from 50 to 100 nm, which is in conformity with the calculation of average crystallite sizes from XRD patterns.

Electrochemical properties

As shown in Fig. 3a, the reduction peak around 1.17, 0.92, 0.82 V in the first cycle can be associated with reduction of $Co^{3+} \rightarrow Co^{2+}$, $Co^{2+} \rightarrow Co$ and formation of Li_2O and solid electrolyte interface (SEI) [5, 6]. The oxidation peak around ~2.0 V can be attributed to the oxidation of $Co \rightarrow Co_3O_4$ and decomposition of the SEI. In the following cycles, the redox peaks are well overlapped which means that Co_3O_4 anode has high cycling performance

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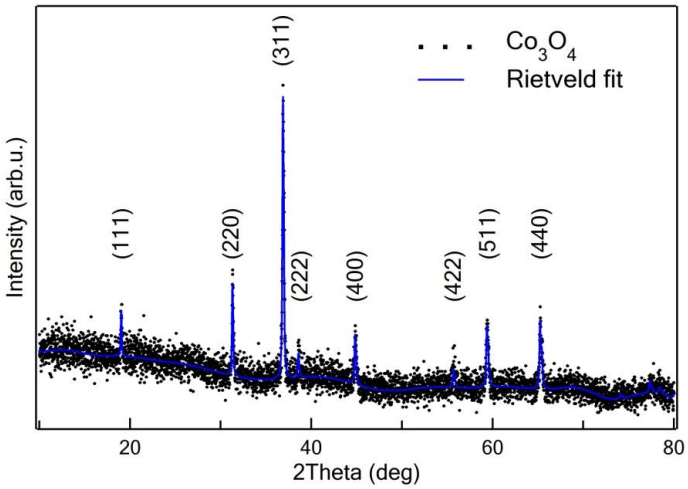

Fig. 1. XRD pattern of Co_3O_4 nanoparticles.

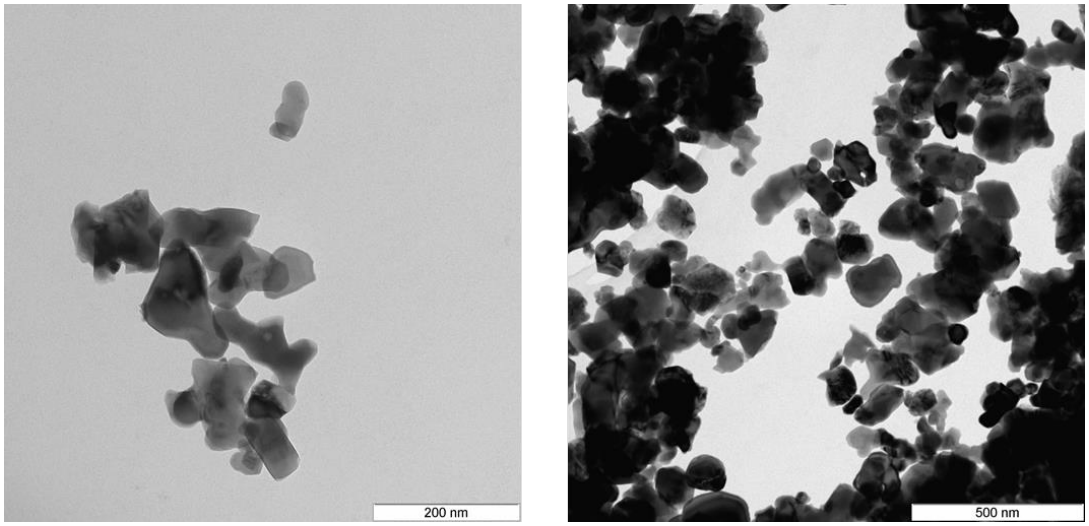

Fig. 2. TEM images of Co_3O_4 nanoparticles at different magnifications

(Fig. 3b). Fig. 4 shows capacities at different current densities of 100–1000 mA g^{-1}. Co_3O_4 sample shows 1st discharge capacity of 1996 mA h g^{-1} and charge capacity of 1127 mA h g^{-1} [22]. The irreversible capacity loss is caused by the formation of SEI and electrolyte decomposition. At current density of 1000 mA g^{-1}, the discharge capacity is 380 mA h g^{-1}. The high capacity of the Co_3O_4 electrodes can be attributed to high specific surface area which provides more active area that can react with Li^+ ions [23,24]. The cycling performance was used to prove the stability of the as-formed samples. As shown in Fig. 4, the discharge capacity is 868 mA h g^{-1} after 130 charge-discharge cycles with capacity retention of 76%, compared with reversible capacity of 1145 mA h g^{-1}. The decline of electrode performance may own to destroy of electrode materials or the change of electrode structure [25, 26].

The electrochemical impedance spectroscopy (EIS) was performed to show the resistance during electrochemical process [27]. Fig. 5 is the Nyquist plots of EIS with semicircle at high frequency and straight line at low frequency. The corresponding equivalent circuit is shown in inset of Fig. 5. The electrolyte resistance is 2.3 W. The charge transfer

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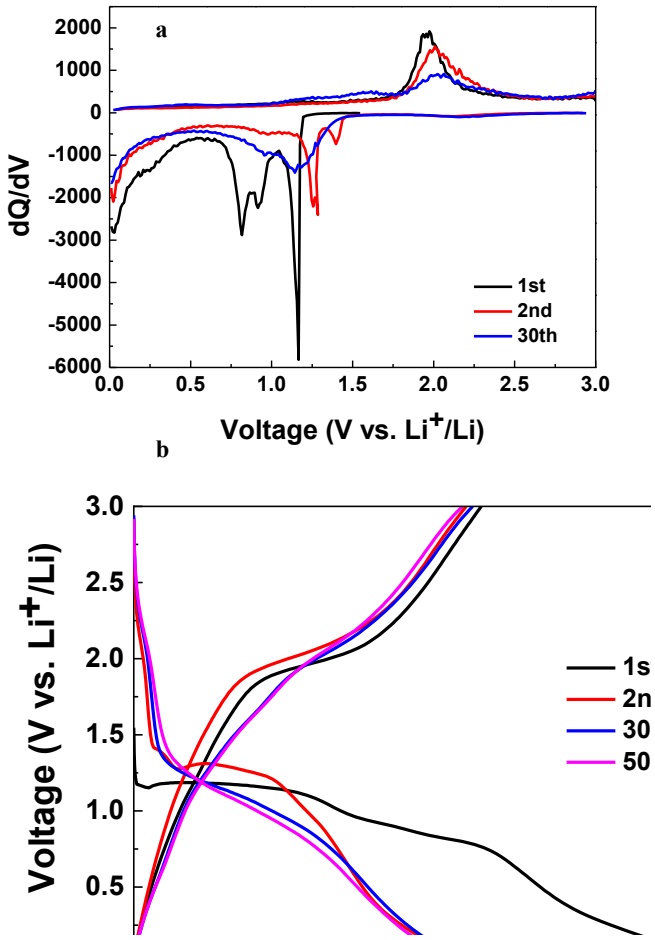

Fig. 3. Electrochemical Li-ion battery anode performance of Co_3O_4 sample. (a) discharge-charge curves at current density of 100 mA/g. (b) dQ/dV curves with different cycling numbers.

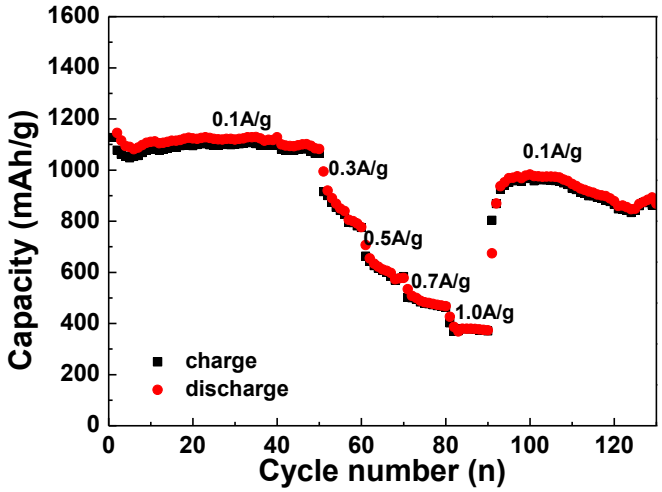

Fig. 4. Capacity of Co_3O_4 at different current densities for Li-ion battery anode.

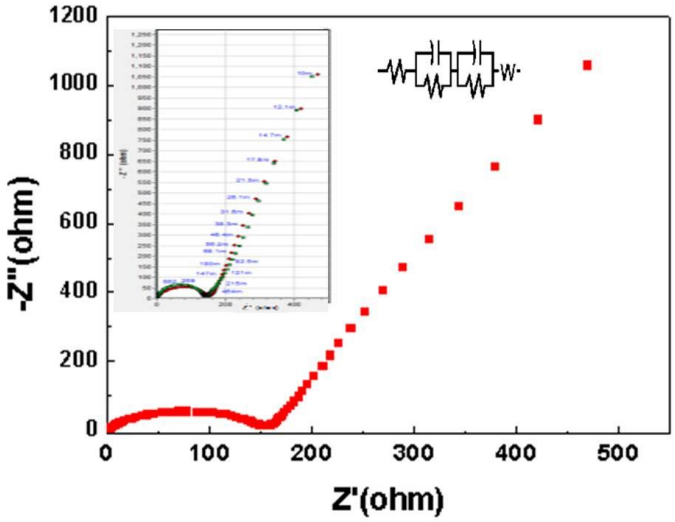

Fig. 5 Electrochemical impedance spectroscopy of Co_3O_4 sample. Insets show equivalent circuit and fitting line.

Table 1. Li-ion batteries characteristics of Co_3O_4 in literature and this work

Materials	capacity (mA h g^{-1})	Charge-discharge cycles	Ref.
Co_3O_4 nanoparticles	868	130	This work
Co_3O_4 particles	423	40	12
Co_3O_4 sheet	1245	40	28
Co_3O_4 rhombic dodecahedral	1100	6000	29
Co_3O_4 nanocages	800	30	11
Co_3O_4 Chrysanthemum-loke	450	50	30
Co_3O_4 hexagonal nanoring	1370	30	9

resistances are 130 and 907 W in first and second circuits. Two RC circuits show that two interfaces may exist in this electrochemical system, for example SEI. The straight line represents Warburg diffusion process.

These electrochemical properties of the as-prepared Co_3O_4 show that the good electrochemical performance with high storage capacity is comparable with the other previous works [9,11112,28-29]. In Table 1, previous reports about Co3O4 based Li-ion batteries with different morphology are compared.

CONCLUSION

In summary, Li-ion battery anodes based on Co_3O_4 nanoparticles show better electrochemical performance. The 1st discharge capacity was 1996 $mAhg^{-1}$ and charge capacity was 1127 mA h g^{-1}. Also, Co_3O_4 sample shows decent cycle stability with specific capacities of about 868 mA h g^{-1} at 100 mA g^{-1} after 130 charge-discharge cycles. The high capacity of the Co_3O_4 electrodes can be attributed to high specific surface area which provides more active area that can react with Li^+ ions.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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