Co₃O₄ Nanoparticles: Synthesis, Characterization and Its Application as Performing Anode in Li-Ion Batteries

Aliakbar Dehno Khalaji ¹, Marketa Jarosova ², Pavel Machek ², Kunfeng Chen ³, Dongfeng Xue ³

¹ Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran
² Institute of Physic of the Czech Academy of Sciences, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic
³ State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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ABSTRACT

In this research, a convenient, simple and rapid route for the preparation of Co₃O₄ nanoparticles using the calcination of Co(NO₃)₂·6H₂O at the presence of benzoic acid (1:1 weight ratio) is reported. Further, the as-prepared Co₃O₄ nanoparticles were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). XRD result confirmed the Co₃O₄ nanoparticles are pure phase and the average crystallite size for Co₃O₄ 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 Co₃O₄ nanoparticles were investigated as an anode material for Li-ion batteries. Results showed that the Co₃O₄ 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.

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 Co₃O₄ 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 H₂O₂ [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 Co₃O₄ 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 Co₃O₄ nanostructures such as nanoring, mesoporous, 3D nanofiber and nanofilms have been prepared and studied as anode materials.
extensively [5-13]. For example mesoporous Co$_3$O$_4$ 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$_3$O$_4$ hexagonal nanorings via treating Co-based metal organic frameworks [9]. Co$_3$O$_4$ 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$_3$O$_4$ hollow microsphere [10] that exhibited excellent electrochemical performance (915 mA h g$^{-1}$) and cycling stability (350 cycles).

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$_3$O$_4$ nanoparticles using the calcination of Co(NO$_3$)$_2$·6H$_2$O at the presence of benzoic acid. Served as Li-ion battery anode, Co$_3$O$_4$ 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, $\lambda = 1.5418$ Å). TEM images were recorded with the transmission electron microscope Philips CM120 with a LaB$_6$ cathode operating at 120 kV and equipped with CCD camera Olympus Veleta

Synthesis of Co$_3$O$_4$ nanoparticles

1 g of Co(NO$_3$)$_2$·6H$_2$O 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$_3$O$_4$ material was mixed with carbon black and PVDF at a mass ratio of 70:15:15 to form slurry as solvent. The slurry was then spread onto Cu foil by doctor-blade, and dried at 80 ºC 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$^+/\text{Li}$) at different current densities.

RESULTS AND DISCUSSION

XRD patterns

X-ray diffraction (XRD) pattern of Co$_3$O$_4$ 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$_3$O$_4$ 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 diffractometer. The average crystallite size for Co$_3$O$_4$ nanoparticles was found 77 nm.

TEM images

The morphology of Co$_3$O$_4$ 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$^{3+}$ → Co$^{2+}$, Co$^{2+}$ → Co and formation of Li$_2$O and solid electrolyte interface (SEI) [5, 6]. The oxidation peak around ~2.0 V can be attributed to the oxidation of Co → Co$_3$O$_4$ and decomposition of the SEI. In the following cycles, the redox peaks are well overlapped which means that Co$_3$O$_4$ anode has high cycling performance.
(Fig. 3b). Fig. 4 shows capacities at different current densities of 100–1000 mA g⁻¹. Co₃O₄ 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 Co₃O₄ 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
Fig. 3. Electrochemical Li-ion battery anode performance of Co$_3$O$_4$ 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$_3$O$_4$ at different current densities for Li-ion battery anode.
Table 1. Li-ion batteries characteristics of Co$_3$O$_4$ in literature and this work

<table>
<thead>
<tr>
<th>Materials</th>
<th>Capacity (mA h g$^{-1}$)</th>
<th>Charge-discharge cycles</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO$_x$ nanoparticles</td>
<td>868</td>
<td>130</td>
<td>This work</td>
</tr>
<tr>
<td>CoO$_x$ particles</td>
<td>423</td>
<td>40</td>
<td>12</td>
</tr>
<tr>
<td>CoO$_x$ sheet</td>
<td>1245</td>
<td>6000</td>
<td>28</td>
</tr>
<tr>
<td>CoO$_x$ rhombic dodecahedral</td>
<td>1100</td>
<td>6000</td>
<td>29</td>
</tr>
<tr>
<td>CoO$_x$ nanocages</td>
<td>800</td>
<td>30</td>
<td>11</td>
</tr>
<tr>
<td>CoO$_x$ Chrysanthemum-loke</td>
<td>450</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>CoO$_x$ hexagonal nanoring</td>
<td>1370</td>
<td>30</td>
<td>9</td>
</tr>
</tbody>
</table>

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$_3$O$_4$ 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$_3$O$_4$ nanoparticles show better electrochemical performance. The 1st discharge capacity was 1996 mAh g$^{-1}$ and charge capacity was 1127 mA h g$^{-1}$. Also, Co$_3$O$_4$ 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$_3$O$_4$ 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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