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Microwave-assisted citric acid aided synthesis and electrochemical performance of nanosized Co_3O_4

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ABSTRACT

Electrochemical performance of Co_3O_4 in lithium-ion batteries is briefly reviewed. Co_3O_4 samples are synthesized via microwave-assisted solid state and citric acid aided methods. It is shown that the latter method leads to disperse nanosized materials having discharge capacity close to the theoretical value. Several electrolytes are probed so as to minimize capacity losses upon cycling, and the one containing lithium bis(trifluoromethane)sulfonimide in a mixture of fluoroethylene carbonate and dimethyl carbonate is selected. High-rate tests reveal that capacity retention of the samples obtained is well comparable with the best existing data, and at the current load of 5340 mA g^{-1} (6C) all materials studied retain more than 50% of initial capacity.

1. Introduction

Widely employing numerous cathode materials in commercial lithium-ion batteries (LIBs), contemporary battery technology is almost exclusively oriented to anodes made of graphite [1]. Significant efforts have been undertaken by scientists so as to find a replacement for graphite with higher specific capacity and energy density. The discovery of the anodic function of transition metal oxides in 2000 [2] has made a great stir in electrochemical community and since that time, numerous papers deal with this intriguing phenomenon [3]. Oxide anodes differ from common electrode materials whose electrochemical activity is due to reversible processes of insertion and deinsertion of lithium ions, and belong to the so-called conversion anodes, where a metal oxide undergoes electrochemical reduction in the presence of Li^+ forming a metal and lithium oxide. This means that instead of a single-phase reduction product characteristic of insertion materials, the electrochemical reduction of transition metal oxides in the presence of lithium ions leads to a two-phase mixture of the transition metal and lithium oxide.

Among transition metal oxides, cobalt oxide Co_3O_4 attracts special interest due to its high theoretical specific capacity [4]. According to the reaction

$$Co_3O_4 + 8Li^+ + 8e^- \leftrightarrow 3Co + 4Li_2O, \qquad (1)$$

it is of 890 mAh g^{-1} and 2.39 times exceeds that of graphite. However, the practical use of Co_3O_4 in LIBs is hampered by a number of drawbacks. The main ones are poor cyclability and rate capability arising from low conductivity and large volume change (ca. 100%) accompanying the electrochemical reaction. In addition, an essential problem is a large irreversible capacity of the first cycle, which is connected with the process of the solid electrolyte interface formation.

The main way to improve electrochemical characteristics of Co_3O_4 upon cycling is the regulation of its structure, dispersity and morphology by means of various synthetic methods. At the same time, special attention is paid to obtaining of nanosized Co_3O_4 [3,5]. This is due to the advantages of nanoscale materials, namely, high surface area and reducing of transport path of lithium ions and electrons in the electrode volume, thereby increasing their cycling ability and resistance to high current densities [6]. Application of various techniques, such as spray pyrolysis, co-precipitation, template synthesis, sol-gel synthesis allowing to obtain Co_3O_4 powders of different morphologies in the form of nanoparticles, nanocubes, nanofibers, nanotubes, nanoplates, mesoporous and composite nanostructures, etc. [5,7–12], in most cases improves the electrochemical characteristics of oxide materials. Actively studied are hollow structures of Co_3O_4 with internal voids compensating volume expansion upon cycling [13–15].

In Appendix, we summarize the results of the papers on the subject published during the past five years dividing them into two groups in accord with the synthetic methods and sorting by the

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specific capacity at a minimal current load. The first group represents the data on single-phase Co_3O_4 samples; the second group summarizes the results for numerous nanocomposite materials. It is worth mentioning that in both cases, the specific capacity of materials in question varies significantly and often exceeds (sometimes almost twice) the theoretical value marked with a dashed line. Among the reasons of such behavior reversible formation/dissolution of a solid electrolyte interface is put forward [9,16–18] and lithium confinement effects first described by Maier [19] are considered [9,20–23]. Besides, one cannot exclude effects caused by the presence of significant amounts of intercalation (carbonaceous materials [8,24–26]) and conversion anode materials ([12,27,28]), which can manifest their anodic function together with Co_3O_4. Another point to stress is uncertainty in the active material loading as in the cited papers, this parameter strongly affecting the electrochemical characteristics of LIBs is often omitted. Being mentioned, it varies within very wide limits ($<1\,mg\cdot cm^{-2}$ [26,29], $1\text{-}2\,mg\cdot cm^{-2}$ [9,30–33], $\sim 4\,mg\cdot cm^{-2}$ [4,34], $10.8\,mg\cdot cm^{-2}$ [35]) making a direct comparison among the different electrodes at least somewhat questionable.

Practice poses strict requirements to materials for possible replacement of carbonaceous anodes, since the latter are able to sustain extremely great current loads [36], which can reach 100C (1C is a number which indicates the amount of current when the specific capacity Q of a cell is discharged in one hour; 100C means discharging in 1/100 h). Regretfully, the data presented in Appendix are far from expectations of technologists as specific currents employed in laboratory tests of Co_3O_4 seldom exceed 10C, whereas known cathode materials are able to sustain current loads at around 100C [37].

In order to compare the materials in question and to estimate their prospects, a value of the discharge capacity loss per the unit current rate dQ_d/dI can be used [37],

$$dQ_d/dI = (Q_d^{max} - Q_d^{min})/(I_{max} - I_{min}), \tag{2}$$

where Q_d^{max} and Q_d^{min} are discharge capacities at minimal (I_{min}) and maximal (I_{max}) discharge currents applied, I_{min} and I_{max} are measured in C units, and the smaller the dQ_d/dI value, the more capacity is retained upon the current load. Calculated dQ_d/dI for Co_3O_4 are very modest, and just a few representatives of numerous materials probed can be prospective for further manufacturing, since introducing a restriction $dQ_d/dI < 70$ one reassures that no more than seven of them could serve as candidates for high-rate applications. For such materials, the dQ_d/dI values in Appendix are marked bold. It is noticeable that all of them have been synthesized by means of quite simple, easily scalable methods prospective for further mass production.

Recently, considerable attention is aroused by the use of microwave radiation in the synthesis of electrode materials [38,39]. This is related to the peculiarities of the substance heating under microwave exposure, which lie in the rapid and uniform heating of the whole sample due to the heat generated directly in its volume as a result of interactions of particles with microwaves. In addition to a significant reduction in the duration of synthesis the use of microwave radiation promotes obtaining more finely dispersed and less agglomerated materials due to the lack of necessity of prolonged exposure of high temperatures occurring upon thermal syntheses. Therefore microwave heating is an effective tool for controlling the particles morphology [38–41].

Obtaining Co_3O_4 using microwave radiation coupled with different synthesis methods is described in Refs. [42–48]. Morphology of samples significantly varies and particle size is of several tens to hundreds of nanometers. The results of electrochemical tests at low current rates (0.1-1C) [44–48] show that materials obtained with the use of microwave radiation have a stable discharge capacity close to the theoretical value. In particular, it is shown in Ref. [48] that mesoporous Co_3O_4 nanoflakes sustain over 300 charge/discharge cycles and can be discharged at current rates up to 10C ($8900\,mA\,g^{-1}$) retaining the specific capacity of $285\,mAh\,g^{-1}$.

Another point of attraction in the synthesis of the electrode materials are routes based on the use of polybasic hydroxy carboxylic acids, particularly citric acid [49–51]. The advantages of these methods are a low decomposition temperature of precursors, high homogeneity of synthesized oxides and the possibility for obtaining nanosized materials. In the synthesis of Co_3O_4 by means of the citric acid aided method performed in Refs. [35,52,53], molar ratio of Co^{2+} ions and citric acid (CA) and annealing temperature have been shown to significantly affect the phase composition, morphology and particle size of synthesized samples. In studies of the effect of these parameters on the electrochemical characteristics of Co_3O_4 [35], the optimal ratio of Co^{2+}:CA = 1:1 and the annealing temperature of 650 °C have been suggested. However, the cycling ability of the material obtained is too low, and the specific capacity on the 20th cycle at a current density of 0.3C falls to $442\,mAh\,g^{-1}$.

Among the factors influencing electrochemical properties of Co_3O_4, the composition of an electrolyte plays a major role, especially, from the point of view of the formation of a solid electrolyte interface on an electrode material [54]. In the most papers, Co_3O_4 has been investigated in a standard electrolyte consisting of a solution of lithium hexafluorophosphate in a mixture of ethylene carbonate and dimethyl carbonate [2,4,8,11,20]. However, some authors [55,56] have found that a prolonged contact of Co_3O_4 with such electrolyte causes a gradual decomposition of its components, viz., partial dissolution of Co_3O_4 and its reduction to CoO, thereby significantly decreasing the lifetime of Co_3O_4 based systems. This indicates the necessity of optimizing the electrolyte composition, so as to maximize the performance of the anode material. Fluorinated analogues of organic carbonates introduced in the electrochemical practice in Refs. [54,57] may be of great help in solving this problem.

Based on this short survey, the aim of the present paper is manifold. First of all, being concentrated upon inexpensive synthetic methods, we try to obtain Co_3O_4 by means of solid-state and citric acid aided route combined with microwave heating and to find out experimental conditions leading to nanosized materials with the best possible electrochemical performance. Second, we compare various electrolytes so as to conclude if fluorinated analogues of organic carbonates positively influence the electrochemical performance of Co_3O_4. Third, we perform high-rate tests of the best selected samples in the most appropriate electrolyte and show their advantage over the majority of materials existing to date.

2. Experimental

2.1. Materials synthesis

Synthesis and pyrolysis of citrate precursors were carried out as described in Ref. [49] with the following modifications. In order to obtain precursors (acidic citrates [49]) 1–2 M solutions of cobalt nitrate hexahydrate (ultrapure, Reachem, Russia) and citric acid (CA) monohydrate (chemically pure, Synbias, Ukraine) were mixed at Co^{2+}:CA molar ratios of 1:0, 1:0.5, 1:1, and 1:2. Further procedures, viz., evaporation of solutions to form a glass (gel) and its decomposition at 110–120 °C to form precursors, and their pyrolysis were made using microwave heating. The microwave treatment was performed in Saturn ST-MW7154 (Ukraine) and LG MS-1949W (Korea) household microwave ovens with the