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Recent progress of $NiCo_2O_4$-based anodes for high-performance lithium-ion batteries

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ABSTRACT

Lithium-ion batteries (LIBs) are deemed as the most promising energy storage devices due to their high power density, excellent safety performance and superior cyclability. However, traditional carbon-based anodes are incapable of satisfying the ever-growing demand for high energy density owing to their low intrinsic theoretical capacity. Therefore, the research of post-carbon anodes (such as transition metal) for LIBs has exponentially increased. Among them, $NiCo_2O_4$ together with its composites have been widely studied by academic workers due to their high theoretical capacity and excellent electronic conductivity. In this review, the electrochemical reaction mechanism and recent progress including the synthetic method, various nanostructures and the strategies for improving performance of $NiCo_2O_4$ are summarized and discussed here. Specially, the hollow porous nanostructured $NiCo_2O_4$-based materials composed of 2D structures usually exhibit excellent capacity and stable cyclability. This review also offers some rational understandings and new thinking of the relationship between the synthetic method, morphologies, blending, current collector and electrochemical performance of $NiCo_2O_4$-based anodes. We have reason to believe that the integration of $NiCo_2O_4$ materials in these clean energy devices provides important chances to address challenges driven by increasing world energy demand.

1. Introduction

With the increasing attention to environmental contamination and global warming attributed to vast fossil-fuel consumption and the fast exhaustion of non-renewable energy resources [1–5], there has been a growing and imperative need to explore and store renewable and green energy sources [6,7]. Fortunately, notable development was made in the exploitation of renewable energy science such as solaode [8,9], tidal energy and wind energy [10,11]. But the energy offered by solar radiation, wind and waves is discontinuous and variable in time and space [12]. Thus, energy storage device is indispensable to deal with such lopsidedness. Current energy storage technologies are mainly the power network and electrochemical energy systems [13]. Electrochemical energy-storage systems are probably the handiest form of energy storage because of its portability and high-efficiency of energy conversion [14,15]. LIBs (Lithium-ion batteries) and SCs (supercapacitors) [16–19], as two main facilities for electrochemical energy storage, have been received significant concerns on account of their important roles in many fields [20]. SCs are known for high power density and faster charge/discharge course [21,22]. However, this kind of energy storage device usually suffers from high price, high internal resistance and low energy density, which hinder its practical use in our daily life [23,24]. LIBs received extensive concerns because of their higher energy density, good safety performance and excellent cyclability [25,26]. Since the 20th century, LIBs have been widely used in smart phones, notebook computers and other portable electronic devices. Lithium-ion battery as an energy reserve device is a transverter that converts chemical energy into electric energy and vice-versa. Typical LIBs involve anodes, cathodes, electrolyte and current collectors (Fig. 1a) [27]. The energy-supplying procedures occur at the phase border of the electrode/electrolyte interface. The electrolyte capacitates the transportation of lithium ions between anodes and cathodes. However, most electrochemical active materials are poor electron transporters, so the addition of conductive agent, such as acetylene black and activated carbon, is indispensable for LIBs which exhibit excellent electrochemical performance [28,29].

Today, LIBs are also used as the dominating power supply in EVs (electric vehicles), which will be required to possess better property of LIBs, such as higher energy density, low cost and more green [30]. Unfortunately, so far, the traditional intercalation-type material,

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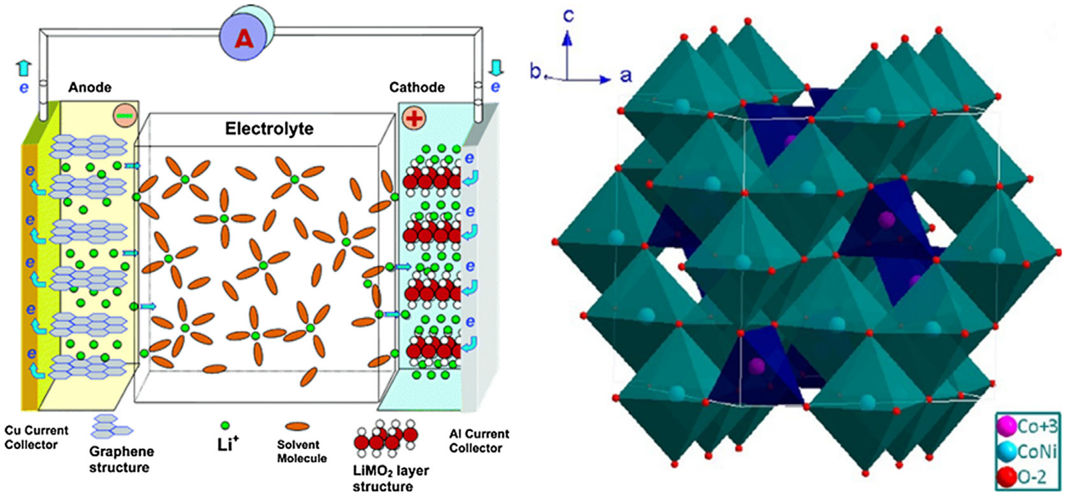

Fig. 1. (a) Schematic diagram of traditional $LiMO_2$/graphite lithium ion batteries and (b) structural representation of the $NiCo_2O_4$ space unit. Reproduced from [27,71] with permission from American Chemical Society.

graphite, is incapable of meeting these demands due to its restricted theoretical capacity (372 mA h g^{-1}) and poor rate performance, which extremely impede the micromation of portable device [31]. So it is urgent to find alternative to meet our need. Other potential anode materials, such as transition metal [32], silicium [33,34], sulfur [35,36], together with their compounds or composites explored as conversion-type anode materials have been far-ranging probed and caught the attention of academic workers because of their high theoretical capacities [37]. Among them, transition metal oxides, such as cobalt oxide [38], manganese oxide and nickel oxide [39,40], have drawn lots of attentions as anode materials with great promise, and they may replace commercial graphite on account of their high theoretical capacity, better security, and low cost. However, the actual use of transition metal oxides-based negative material is impeded by its inferior cyclability and rate capability. For example, NiO has the high theoretical capacity of 718 mA h g $^{-1}$ and a volume energy density of about 5.8 times of graphite due to its low density (6.67 g cm^{-3}) [41,42]. Unfortunately, it undergoes severe unsteadiness and poor rate performance on account of the huge volume expansion during charge/discharge course and constitutionally high electrical resistance [43].

Compared with binary metal oxides, ternary metal oxides show lower electrical resistance attributed to lower threshold energy for electron transportation between positive ions. For instance, the electrical conductivity of Co_3O_4 and $Ni_xCo_{3-x}O_4$ is 3.1×10^{-5} S cm^{-1} and 0.1–0.3 S cm^{-1} [44,45], respectively. Therefore a large amount of single-phase ternary metal oxides systems such as $MgFe_2O_4$ [46,47], $CuCo_2O_4$ [48], $MgCo_2O_4$ [49,50], $FeCo_2O_4$ [51,52], $NiCo_2O_4$ and their hybrid materials have been widely explored. Among these ternary metal oxides, the spinel $NiCo_2O_4$ that can react chemically with 8Li^+ per equation with a theoretical specific capacity of 891 mA h g^{-1} approximately, has been extensively investigated as a superior negative electrode material for LIBs [53]. Compared with monometallic nickel oxides and cobalt oxides [54–56], $NiCo_2O_4$ possesses an enhanced electronic conductivity due to the blended valences of the same positive ions in the structure [57]. Hence, $NiCo_2O_4$-based materials have been regarded as prospective materials in energy-storage materials LIBs and other fields because of their high specific capacity and environmentally friendly [58]. In addition, $NiCo_2O_4$-based materials have remarkable electrical conductivity, electrochemical activity and low operating potential. Nevertheless, the cyclability and rate capability of unmodified $NiCo_2O_4$ are difficult to achieve commercial requirements due to the large volume expansion and inherent semiconductive nature. Many strategies have been extensively applied in order to solve the abovementioned issues. First, preparing nano-scaled $NiCo_2O_4$ with special morphologies. Nano-scaled $NiCo_2O_4$ is advantageous to reduce the diffusion path of Li^+. Furthermore, $NiCo_2O_4$ with porous structures including porous 1D (one-dimensional) nanorod/nanowire [21,59], 2D (two-dimensional) nanosheet [60], and 3D (three-dimensional) porous, layered or yolk-shelled hollow nanosized construction can offer vacant space to buffer the volumetric dilatation of the oxides in time of the cyclic process [61]. Additionally, the porous structures often possess high specific surface area that brings about sufficient contact between electrodes and electrolyte and facilitates lithiation-delithiation kinetics [62,63]. Second, synthesizing nickel cobaltite-based modified anodes, which exhibit highly enhanced battery performances on account of the synergetic effects of $NiCo_2O_4$ and composites. Third, fabricating $NiCo_2O_4$ with different morphology directly on conductive substrate (like nickel foam [64,65], carbon cloth and stainless-steel mesh [66–68]) without additional binder.

In this review, the impacts on the electrochemical performance of a chain of modified strategies (such as methods of preparation, special morphologies, composites) acceptable to $NiCo_2O_4$, as well as the impact of substrates, are summarized and analyzed.

2. Structure of $NiCo_2O_4$

As a promising anode for LIBs, $NiCo_2O_4$ possesses a ferrimagnetic cubic spinel construction with mixed redox states [69], and low electric resistance as a p-type semiconductor with band energy of 2.1 eV [70]. As shown in Fig. 1b [71], the oxygen atoms in a spinel are distributed in a cubic close-packed construction, and the cations of cobalt atoms and nickel atmos occupy some or all of the octahedral and tetrahedral sites in the lattice. $NiCo_2O_4$ employs a spinel-type structure, in which the Ni cations take up merely octahedral interstices, while the Co cations are spread about among the tetrahedral and octahedral interstices [72]. One view is that $NiCo_2O_4$ could be just deemed to a nickel atom replacing one of the cobalt atoms in Co_3O_4. Compared with Co_3O_4, the improved physicochemical properties of $NiCo_2O_4$ is attributed to the inlet of the nickel atom with similar ionic radius to cobalt ion. This substitution brings about a delicate variation in the crystal structure, in which the flaws may take some surprising impacts on electrochemical performance [73]. However, due to the lack of theoretical studies on $NiCo_2O_4$, aforementioned statement have not been confirmed by other researcher and more analysis and proof need to be test and find in future researches. The reaction mechanisms of $NiCo_2O_4$ during the discharge and charge processes can be described by the following equations [71]:

$$NiCo_2O_4 + 8Li^+ + 8e^- = 2Co + Ni + 4Li_2O \quad (1)$$