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The synergic effects of Na and K co-doping on the crystal structure and electrochemical properties of $Li_4Ti_5O_{12}$ as anode material for lithium ion battery

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ABSTRACT

The effects of Na and K co-doping on the crystal structure and electrochemical properties of $Li_4Ti_5O_{12}$ have been comprehensively investigated by means of X-ray diffraction (XRD), neutron diffraction (ND), scanning electron microscope (SEM) and galvanostatic charge–discharge tests. Rietveld refinements of XRD and ND data indicate that the lattice parameters increase with the doping of Na and K, and Na or K prefers to take 8a site (tetrahedral site) in $Li_{3.98}K_{0.01}Na_{0.01}Ti_5O_{12}$. The lattice parameter and unit cell volume of $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ are even larger than that of $Li_{3.98}Na_{0.02}Ti_5O_{12}$ and $Li_{3.98}K_{0.02}Ti_5O_{12}$ indicating a cooperative effect of Na and K co-doping on the enlargement of lattice parameters and unit cell volume. The electrochemical property results demonstrate that Na and K co-doped $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ has a larger reversible capacity and rate capability as anode material for lithium ion battery compared to un-doped $Li_4Ti_5O_{12}$, Na-doped $Li_{3.98}Na_{0.02}Ti_5O_{12}$ or K-doped $Li_{3.98}Ka_{0.02}Ti_5O_{12}$, which indicates the significant synergic effect of Na and K co-doping on the improvement of the electrochemical performances of $Li_4Ti_5O_{12}$.

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1. Introduction

Lithium ion batteries (LIBs) have been widely used in cell phones, laptops, camcorders, etc since they were first discovered. Recently, hybrid electric vehicles (HEVs) or electric vehicles (EVs) have attracted wide attention because of the increasing energy consumption and the serious environment pollution problems of fossil fuels. LIBs have been regarded as promising power sources for HEVs and EVs owing to their high energy density, long cycle life, safety, lighter weight and high rate capability [1]. LIBs are mainly composed of anode materials, cathode materials, electrolyte and other supplies. The properties of anode material have a great effect on the overall performance of lithium ion battery. Among the various oxides based anode materials, $Li_4Ti_5O_{12}$ has attracted great interest as the long-life large energy storage batteries because it has several unique advantages such as negligible structural change during charge–discharge process, long and stable voltage plateau around 1.55 V versus Li^+/Li, enhanced safety and the abundant titanium dioxide raw materials. However, the rate capability of $Li_4Ti_5O_{12}$ as anode material for LIBs is very poor due to its low intrinsic electronic conductivity (~10^{-9} S cm^{-1}) [2], which restricts the wide application in HEVs or EVs.

A few approaches have been applied to improve the electronic conductivity of $Li_4Ti_5O_{12}$, such as particle size reducing [3–7], surface modification by Ag [8–10], Cu [11], carbon and carbon nanotubes [12–22], SnO_2 [23] and TiN [24], mixing with a conductive second phase [25] and doping with metal ions (K^+ [26], Mg^{2+} [27], Ca^{2+} [28], Zn^{2+} [29], Ga^{3+} [30], Cr^{3+} [31], La^{3+} [32], Mn^{4+} [33]) or non-metal ions (F^- [34], Br^- [35]). Elements doping in the $Li_4Ti_5O_{12}$ has been proved to be an effective way to improve the electronic conductivity and rate capability. The synthesis methods of $Li_4Ti_5O_{12}$ mainly include solid state [36], sol–gel [37], microwave [38], combustion [39], hydrothermal methods [40] and molten salt processes [44]. $Li_4Ti_5O_{12}$ belongs to the cubic AB_2O_4 spinel structure, where A resides on tetrahedral sites, and B on

octahedral sites within the closely packed cubic oxygen lattice. The tetrahedral position of A-type cations is completely occupied by Li^+, whereas the octahedral position of B-type cations is occupied by both titanium ions Ti^{4+} and Li^+ ions with the occupancy of 5/6 and 1/6, respectively [33].

Two elements co-doping can further optimize the crystal structure and atom environment, and might have synergic effects on the electrochemical performance of the $Li_4Ti_5O_{12}$. Though some elements have been successfully doped into $Li_4Ti_5O_{12}$ few articles are focused on the co-doping effect of two elements. In this study, we successfully prepared K and Na co-doped $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ through a facile solid-state method. For comparisons, $Li_4Ti_5O_{12}$, $Li_{3.98}Na_{0.02}Ti_5O_{12}$, and $Li_{3.98}K_{0.02}Ti_5O_{12}$ were also synthesized using the similar method. The effects of K and Na co-doping on the crystal structure, morphology, and electrochemical performances of $Li_4Ti_5O_{12}$ have been comprehensively investigated by means of X-ray diffraction, neutron diffraction, SEM and electrochemical performance tests. Na and K co-doped $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ shows a higher cycling stability and rate capability in comparison with un-doped $Li_4Ti_5O_{12}$, Na-doped $Li_{3.98}Na_{0.02}Ti_5O_{12}$, or K-doped $Li_{3.98}K_{0.02}Ti_5O_{12}$, which indicates an significant synergic effect of Na and K co-doping on the improvement of the electrochemical performances of $Li_4Ti_5O_{12}$.

2. Experiment

2.1. Sample preparation

All chemicals used are chemical pure and they are put into the furnace at 120 °C for 12 h in order to remove the absorbed water. The starting reagents of Li_2CO_3, TiO_2, Na_2CO_3 and K_2CO_3 are weighted with the stoichiometric ratio in order to get $Li_4Ti_5O_{12}$, $Li_{3.98}Na_{0.02}Ti_5O_{12}$, $Li_{3.98}K_{0.02}Ti_5O_{12}$ and $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ and mixed uniformly by the agate mortar. It should be noted that the ratio of the Li_2CO_3 should overweight 5% of the theoretic quality because the raw materials would decompose in the calcination process and part of Li_2O would volatilize. The uniformly mixed powder was then calcinated at 800 °C for 10 h and the speed of the warming and cooling process was controlled at 5 °C/min.

2.2. Structure characterization

XRD patterns were obtained using a Bruker D8 diffractometer with CuKα radiation. Neutron powder diffraction measurement was performed on PKU-HIPD of China Advanced Research Reactor (CARR) in China Institute of Atomic Energy. The wavelength is 1.48056 Å and the scanning step is 0.05°. XRD and neutron diffraction patterns were refined using the FULLPROF program based on Rietveld method [41]. Particle morphology was characterized by a field-emission scanning electron microscope (FESEM, Hitachi S4800).

2.3. Electrode preparation and electrochemical characterization

Electrochemical performance was evaluated in 2032 coin-type cells. The slurry of active material, carbon Black, and poly-vinylidene fluoride (PVDF dissolved in n-methyl pyrrolidinone weight ratio of 1:9) with a weight ratio of 7:2:1 was coated on a Cu foil substrate and dried at 80 °C for 4 h in the air and then transferred to the vacuum oven at 120 °C for 12 h. The active mass loading for the cells is about 2 mg. Li metal was utilized as counter electrode, Celgard 2300 as separator, and a mixture of 1 M LiPF6 in EC(ethylene carbonate) and DC (dimethyl carbonate) with a volume ratio of 1: 1 as electrolyte. Half-cells were assembled in a glove box ($[O_2] < 0.1$ ppm, $[H_2O < 0.1$ ppm]) with a full of argon at room temperature. The charge/discharge capacity was tested on a XIN-WEI Celltext system with cutoff voltage range from 1.0 to 2.5 V.

3. Results and discussion

3.1. Structure and morphology

The XRD patterns of bulk $Li_4Ti_5O_{12}$, $Li_{3.98}Na_{0.02}Ti_5O_{12}$, $Li_{3.98}K_{0.02}Ti_5O_{12}$, Na—K co-doped $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ obtained by solid state method are shown in Fig. 1. As shown in Fig. 1, all the diffraction peaks of the four samples can be indexed to the spinel $Li_4Ti_5O_{12}$ and no impurity phase peaks are detected indicating that a small amount of Na and/or K doping does not change the crystal structure.

Rietveld refinement of XRD patterns has been performed to calculate the lattice parameters. Fig. 2 shows Rietveld refinement of $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ indicating a good fit. The red point, black line, blue line and green short vertical line stand for the observed data, calculation data, the difference value of the experiment and calculation data and the Bragg position, respectively. The lattice parameters (a), unit cell volumes (V) and O atom positions of $Li_4Ti_5O_{12}$, $Li_{3.98}Na_{0.02}Ti_5O_{12}$, $Li_{3.98}K_{0.02}Ti_5O_{12}$ and $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ have been summarized in Table 1. As shown in Table 1, the lattice parameters and unit cell volumes of $Li_{3.98}Na_{0.02}Ti_5O_{12}$, $Li_{3.98}K_{0.02}Ti_5O_{12}$, and $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ are larger than that of pure $Li_4Ti_5O_{12}$ owing to the bigger radius of Na^+ (98 pm) and K^+ (133 pm) than Li^+ (68—70 pm) [42], which also indicates that Na and K substitute part of Li and prefer to take Li site. It also should be noticed that the lattice parameters and unit cell volumes of $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$ are even larger than that of $Li_{3.98}Na_{0.02}Ti_5O_{12}$ and $Li_{3.98}K_{0.02}Ti_5O_{12}$ indicating a synergic effect on the enlargement of lattice parameters and unit cell volume. The synergic effect of Na—K co-doping on the lattice parameters might come from the different site distribution and occupancies of Na or K. The site occupancy of the doped cations mainly depends on the ion radius, electronic structure and the volume of the crystal sites. The order of ion radius is: $K^+ > Na^+ > Li^+$. The ion radius difference of K^+ and Li^+
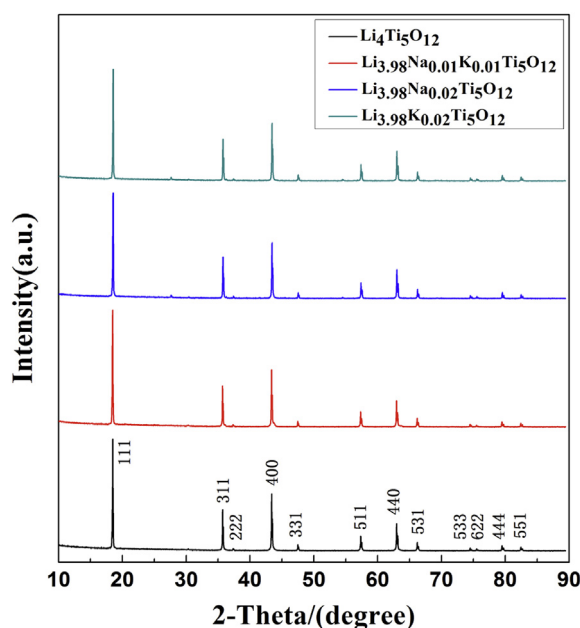

Fig. 1. XRD patterns of $Li_4Ti_5O_{12}$, $Li_{3.98}Na_{0.02}Ti_5O_{12}$, $Li_{3.98}K_{0.02}Ti_5O_{12}$ and $Li_{3.98}Na_{0.01}K_{0.01}Ti_5O_{12}$.