Electrochemical performance of $Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$ as anode materials for lithium ion batteries

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A B S T R A C T

New anode materials ($Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$) had been successfully prepared via a high temperature solid-state method. Pure phase Co-Cr replaced solid solution ($Li_3Ti_4CoCrO_{12}$) was obtained by calcinating the precursor under air atmosphere while the Co modified solid solutions ($Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$) were prepared under a reducing atmosphere. Various methods, such as XRD, SEM, EDX mapping, cyclic testing, EIS, CV, XPS and EPR were employed to characterize the powder samples and investigate their electrochemical behavior. SEM results showed spherical shape of the products with nano sized primary crystals. EDX mapping further confirmed the different existence of the Co element, uniform distribution of Co^{2+} ions within the spinel lattice and separated metallic Co on the particle surface. Cyclic tests revealed that the Co modified samples showed great promotion in their electrochemical performance. For the sample with x = 0.1, the best results with an initial capacity of 157.6 mA h/g and a capacity retention of 96.4% after 100 runs were observed. Such promotion can be explained by the improved electronic conductivity and enhanced Li^+ diffusion coefficient confirmed by the EIS and CV simulation, which was caused by the oxygen vacancy produced during the calcination under the reducing atmosphere.

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1. Introduction

Recently, the spinel lithium titanium ($Li_4Ti_5O_{12}$) has attracted more and more attention as a promising anode material for secondary lithium ion batteries [1–4]. The structure of $Li_4Ti_5O_{12}$ belongs to a cubic system with Fd3m space group, where three quarters of lithium ions occupy tetrahedral 8a sites, and the other quarter of lithium ions and Ti^{4+} are randomly distributed at octahedral 16d sites. O^{2-} ions are located at the 32e sites, and the 16c sites are left blank [5]. During the discharging process, three external Li^+ ions can be inserted into the blank 16c sites and a theoretical specific capacity can be calculated according to the above electrochemical process. At the charging process, a reverse process occurs and the extra Li ions can be removed from the spinel lattice [6]. During the whole processes, the volume change is less than 0.1% [7]. Therefore, spinel $Li_4Ti_5O_{12}$ (LTO) is a zero-strain material for Li ion intercalation/deintercalation with a theoretical

specific capacity of 175 $mAhg^{-1}$ [8,9]. Moreover, it has a discharge plateau of about 1.55 V versus Li/Li^+, which can avoid the growth of dendritic lithium on the anode surface at high charging rates [10]. Thus, LTO has excellent characteristics in regard to the safety issues [11].

Except for the advantages stated above, some problems have limited the commercialization of the $Li_4Ti_5O_{12}$ in the industry. One of the key drawbacks holding the application of $Li_4Ti_5O_{12}$ is its low electronic conductivity (about $10^{-9}Scm^{-1}$) [2] which would reduce its specific capacity during charging-discharging process. Many attempts have been devoted to enhance the electronic conductivity, such as doping with Li or Ti sites [12,13], surface coating with conductive materials [14], and reducing particle size [15–17]. Recently, X. Li et al. [18] reported that Zr-doped $Li_4Ti_5O_{12}$ displays high rate capability and good cycling stability on account of the reduced charge transfer resistance and improved conductivity. However, polluting gas will also be released due to the decomposition of CH_3COO^- and NO_4^- during the process of high temperature calcination.

In this paper, we synthesized a new anode material $Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$ through a simple solid-state process to increase both

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the electronic conductivity and the Li ion diffusion coefficient of the prepared anodic materials. The new anode material $Li_3Ti_4CoCrO_{12}$ comes from a substitution of the original $Li_4Ti_5O_{12}$ spinel structure, where Ti^{4+} ions, together with Li^+ ions, were replaced by Co^{2+} and Cr^{3+} ions. To further improve the electrochemical performance, the $Li_3Ti_4CoCrO_{12}$ anode powder was modified with different amount of metallic Co by calcinating the precursor in a reducing atmosphere. The synthesis of the target anode material of $Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$ can be summarized by the following equation:

$$Li_4Ti_5O_{12} + Co^{2+} + Cr^{3+} + 2xe^- = Co_x \Big/ Li_3Ti_4Co_{1-x}CrO_{12}$$
$$+ Ti^{4+} + Li^+ \qquad (1)$$
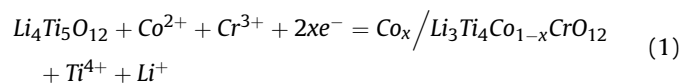
Here we report the preparation of the new anodic materials and the investigation of their electrochemical performances using XRD, SEM, EDX mapping, cyclic testing, EIS, CV, XPS and EPR. It was confirmed by the experimental results that $Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$ anode materials present excellent electrochemical performance due to the improved electronic conductivity and enhanced Li^+ diffusion coefficient, and thus is expected as potential anode material in LIBs.

2. Experimental procedures

2.1. Synthesis of the anode materials

$Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$ (x = 0, 0.05, 0.1 and 0.15) anodic powders were prepared through a solid-state process. The raw materials employed in the experiment are Lithium hydroxide (99.5%), titanium dioxide (anatase structure, 98.5%), Cobalt oxide (99.5%) and chromic oxide (99%). 5mol % of excessive Li was employed to compensate the evaporation of Li during the synthesis process at high temperatures. All the raw materials were thoroughly mixed using a ball miller for 4 h in water. Then the obtained powder was dried by a spray dryer and spherical precursor was obtained. At last, the anodic powers were obtained by calcining the precursor under 850 °C for 12 h in different atmosphere. For the pristine powder, the precursor was calcined under air atmosphere, while the $Li_3Ti_4Co_{1-x}CrO_{12}$ (x = 0.05, 0.1, 0.15)anodic materials were prepared under a mixed flow gas of $2.5\%H_2$ and $97.5\%Ar$.

Various testing methods were employed for the characterization of as prepared anodic powder. XRD profiles were collected with a TD3200 X-ray diffractometer using Cu Ka radiation. The data were monitored from 10° to 70° (2θ) using a continuous scanning mode. The surface morphology and particle size of the prepared powders were investigated via a scanning electron microscopy (SEM). The element distribution was tested using SEM-EDX. The valance states of the different elements were characterized using an X-ray photoelectron spectroscopy (XPS). The formation of oxygen vacancies was confirmed with an electron paramagnetic resonance spectroscopy (EPR).

2.2. Electrochemical testing

Electrochemical behaviors of the anodic powders were investigated with conventional methods. The working electrodes were prepared with the doctor blade method using slurry including active material, conducting carbon and PVDF as the binder. The weight ratio of the components was fixed as 8:1:1 for each component. The slurry was first pasted onto an Al sheet and then dried at 110 °C in a vacuum oven for 12 h. The thickness of coating materials is approximately 0.030 mm. The dried foil was rolled into its final thickness of 0.015–0.025 mm. Subsequently, sheet electrodes were prepared by cutting the foil into discs with diameter of 12 mm.

The electrochemical properties of the materials were tested using coin-like cells. All the cells were assembled in a glove box filled with Ar. The cells were galvanostatic charged and discharged on a Land CT2001 battery tester at the voltage of 1.0–2.5 V to investigate the specific capacity and cyclic performance. The electrochemical impedance spectroscopy (EIS) measurements were carried out in two-electrode cells using Auto Lab PGSTAT302 in the frequency range of 10^{-2} to 10^5 Hz to compare the electronic conductivity of the prepared samples. Cyclic voltammetry (CV) tests were conducted on an electrochemical workstation (CHI1000C) from 1.0 to 2.2 V (vs. Li/Li^+) with different scan rates to calculate the Li ion diffusion coefficient.

3. Results and discussion

All the samples were prepared by calcinating the precursor under 850 °C with different atmosphere. The XRD profiles of $Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$ (x = 0, 0.05, 0.1 and 0.15) samples are presented in Fig. 1. All the refractions of the samples can be identified as a spinel phase with cubic structure, indicating that Co^{2+} and Cr^{3+} have successfully incorporated into the lattice of the spinel $Li_4Ti_5O_{12}$. Meanwhile, some additional peaks appear at approximately 44.2°and 51.5° for the samples calcinated under reducing atmosphere with x = 0.05, 0.1 and 0.15. By a careful comparison, the two peaks can be attributed to the reflection from metallic Co according to PDF#04-004-8491. Such results confirm that metallic Co can be obtained by simply calcinating the precursor in reducing atmosphere, as we expected before. Therefore, both Co-Cr replaced solid solution and metallic Co modified $Li_3Ti_4CoCrO_{12}$ anodic materials were created in the experiment.

Surface morphologies observation were conducted for the pristine solid solution and Co modified samples by SEM. Fig. 2 shows the typical micrographs of the $Li_3Ti_4CoCrO_{12}$ and $Co_x/Li_3Ti_4Co_{1-x}CrO_{12}$ (x = 0.1)materials. As shown in Fig. 2a and b, it is clear that both the samples have spherically porous microstructure [19], due to the spray drying process employed in the experiment. The particle size of the spherically porous materials is about 10–15 μm. The porous microstructure of the particle should be attributed to the pyrolysis of the precursor [20]. However, the morphological differences were observed by the comparison between high magnification micrographs. Fig. 2c and d reveal the fine structure of an individual spherical particle of the powders
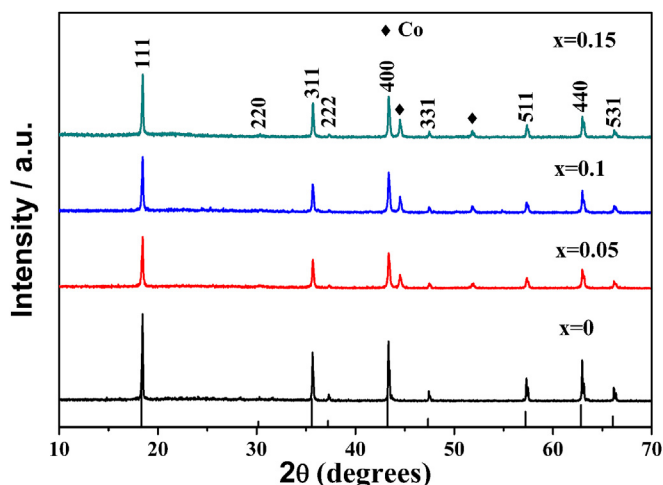

Fig. 1. XRD patterns of the as-obtained samples synthesized with different Co ratios.