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Cr Doping of Li₄Ti₅O₁₂ by Sol-Gel Method for High Power **Lithium-Ion Batteries**

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1. Introduction

Along with the rapid development of electric vehicles, the demand for lithium-ion batteries with high rate performance is dramatically booming. Li₄Ti₅O₁₂ has attracted attention on account of its high potential (1.55 V), which provides good stability, and its zero-strain characteristics, which allows high-speed charging and discharging.[1-3] Compared with carbon negative-electrode materials, it can improve the rate capability and cycling life. A main drawback, however, is that its electronic conductivity is very low because of its intrinsically wide band gap of about 2 eV.[4-6]

Various ways have been taken to increase the performance of Li₄Ti₅O₁₂ experimentally and theoretically. High temperature solid-phase method failed to make nanomaterials, but sol-gel did the good job.[7-11] Transition metals, such as chromium, gallium, magnesium, and non-metallic heteroatom, take N, P as examples, could change its electronic properties effectively, which had also been confirmed by the first principle calculations.[12-17] Coating with carbon or graphene to increase the electronic conductivity were also been tried.[18-22] For example, Song et al. modified Li₄Ti₅O₁₂ by doping Cr^{3+} , confirming that stable Cr^{3+} can effectively act as a donor.[23] Sun et al. reported that in situ carbon coating inhibits dimensional expansion and thus nano-Li₄Ti₅O₁₂ could be obtained.[24] Although they have improved the performance of Li₄Ti₅O₁₂ much more, it still can't satisfy the commercial demand for negative-electrode materials. Different cheating agent have been used to control the size of Li₄Ti₅O₁₂ particles, different high voltage materials have been tried to combined with Li₄Ti₅O₁₂ to see any efficient way to obtain superior performance for commercial application.[25-29] Among these research, sol-gel interested us because it can effectively smaller the particle size. Cr³⁺ was been explored mostly because it can be well inserted into the crystal structure of Li₄Ti₅O₁₂.[30-32]

The current paper presents a combined way to obtain modified Li₄Ti₅O₁₂. In this way, sol-gel synthesis and Cr^{3+} doping were used with (EO) 106(PO)70(EO)106 tri-block copolymer (F127) as chelate. This study mainly used it as sol-gel route ligand to form mixed gel under the conditions of

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strong acid and the mixed gel was dried at 60 cent degree and calcined in air atmosphere. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to characterize the physical properties, and cyclic voltammetry, charge/discharge test were used to investigate the electrochemical behavior of it. It is found that it shows brilliant rate capacity and cyclability.

2. Experiments

2.1. Synthesis of Cr-Doped LTO

The Cr-doped Li₄Ti₅O₁₂ (denoted as LTO as usual) samples were synthesized via a sol–gel route. F127, a kind of nonionic surfactant (EO) 106(PO) 70(EO) 106 tri-block copolymer, was used as chelating agent. 30.0 mL anhydrous ethanol was poured into 2.5 g F127 to dissolve them adequately. 6.0 mL HNO₃ (65 wt%) and 8.8 mL titanate isopropoxide were added in turn with vigorous stirring. Then it is time to prepare another solution. 2.50 g Li (AC)₂ • 2H₂O and 0.36 g Cr(AC)₂ • 6H₂O were added into 20.0 mL anhydrous ethanol to obtain green solution with vigorous stirring. Mixing these two solution and keeping stirring for 5 h to ensure adequate mixing. The final solution was dried for a week at 60°C to form a gel, which was calcined at various temperatures in air gas. The heating rate is set to 1 °C/min and the calcining time is 12 h for every sample. X-ray diffraction (XRD) was used to investigate the lattice structure of the synthesized materials in the range of 10–70 degree. Scanning electron microscopy (SEM) was taken into consideration to examine the morphology of pre-prepared samples, as well as high-resolution transmission electron microscopy (HRTEM).

2.2. Cell fabrication and electrochemical characterizations

The prepared Cr-doped LTO powder, mixed with carbon black and polyvinylidene fluoride (PVDF) to make the negative slurry with several drops of N-methyl pyrrolidinone (NMP). As usual, the weight ratio of them is 8:1:1 and the stirring time is more than 12 h to make sure no more agglomerated particles.[25] This mixed slurry was coated on copper foil using the "doctor blade" technique and then dried at 100°C for more than 12 h under vacuum conditions. The dried film was punched into 12mm round sheets to be the negative electrode for the coin type (CR2025) test cells. 1 M LiPF₆ dissolved in ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate (EC/DMC/EMC, 1:1:1 vol) was used as the electrolyte, porous polypropylene films were used as a separator and Li foil was used as the counter and reference electrodes in the assembled cells. Cyclic voltammetry, electrical impedance spectroscopy (EIS) experiments and constant current charge–discharge measurements at various rates were taken to investigate the electrochemical performance

3. Results and Discussion

Data obtained in previous studies using sol-gel method to synthesize $Li_4Ti_5O_{12}$ indicated that the size can be decreased. According to Sun et al, the grain growth of LTO was effectively restrained by the carbon generated from the carbonization of F127 in the calcination process, and a small particle size of LTO (~20 nm) was successfully obtained.[23] Besides, Song et al. revealed that the Cr^{3+} -ion doping in LTO results in the decreased structural disorder, which lead to both band gap narrowing and the increased ionic diffusivity.[24] In this paper, Cr-doped LTO was obtained using sol-gel method, using F127 as the chelating agent. Figure 1 shows the XRD results.



Figure 1. XRD pattern of the Cr-doped LTO calcined at different temperatures.

As can be seen, all peaks of Cr-doped LTO calcined from 600 °C to 800 °C were perfectly matched with the spinel structure of the Fd3m space group without any side peaks, implying that a single-phase spinel structure was prepared. The XRD pattern of pure Li₄Ti₅O₁₂ (JCPDS 49-0207) was shown and there is a small difference between 550 °C when $2\theta = 25.3^{\circ}$, which is exactly the typical peak of precursor.[14] This precursor is anatase TiO₂, which has been pointed out in previous research.[23]



Figure 2. Scanning electronic microscopy images of Cr-doped LTO samples calcined at different temperatures: a)600°C, b) 700°C, c) 750°C and d) 800°C.



Figure 3. a, b) High-resolution transmission electron microscopy images of Cr-doped LTO

Figure 2 shows SEM images of Cr-doped LTO powders at different temperatures. It is apparent that the cubic morphologies of Cr-doped is familiar with undoped LTO.[23] However, the samples calcined at 750°C showing a quite uniform particle size distribution and the average particle size is about 100 nm. The particles calcined at other temperatures tend to link together rather than form integrated crystal particles. The size of Cr-doped LTO becomes larger along with less dimensional consistency when the calcined temperature is increasing. Transmission electron microscopy (TEM) was examined and the HRTEM images were shown in Figure 3. The uniform particle size distribution is consistent with the SEM images ranging from 80 nm to 200 nm. The average grain diameter is about 100 nm, and the lattice fringe is 0.48 nm, which is consistent with the (111) atomic planes of the spinel structure.

To demonstrate electrochemical performance when the synthetized Cr-doped LTO is used in lithium-ion batteries, electrochemical measurements were applied for the assembled cells with Crdoped LTO negative electrode, which were shown in Figure 5. The redox peaks were centrosymmetric about the voltage of 1.55 V, which means the intercalation/de-intercalation process is reversible and it is the most important condition for cycling performance. As shown in Figure 4b, the EIS spectra consist of a semicircle and a straight line, which is perfect allied with the fitting curve. They refer to the charge transfer reaction (R_{ct}) and the diffusion of Li^+ in the bulk electrode respectively. By analysing the fitting curve, this R_{ct} is less than 30 Ω and it is smaller than previous research.[14, 25] The first charge/discharge curves and the cycling performance of the as-derived samples at different current rates were shown in Figure 4c and Figure 4d respectively. The specific capacity of first charge/discharge is 255 mAh/g, which is higher than the previous studies for about 50 mAh/g.[23] Additionally. the specific capacity of this synthetized material is 208, 193, 189,179, 175 and 167 mAh/g at 0.1, 0.5, 1, 5, 10 and 40 C respectively. This guite excellent performance is out of a clear sky, especially for that it can maintain more than 150 mAh/g at 40 C. As shown in Figure 4d, a very stable cyclability is observed for Cr-doped LTO, even at a high current rate of 40 C. at all measured current rates. the capacity loss is less than 0.01% per cycle, which means that the as-derived Cr-doped LTO owns high stability in repeated cycles. From 40 C to 0.1 C, the specific capacity returns 201 mAh/g, indicating superior rate capacity. Moreover, the coulombic efficiency of Cr-doped LTO approaches 100% for each cycle.



Figure 4. Electrochemical properties of Cr-doped LTO: a) CV curve measuring from 1.0 to 2.5 V, b) EIS curve including the fitting curve at the voltage of 1.55 V, c) charge and discharge curves at different rates and d) cycling performance at various current rates: 1st-10st, 10st-20st, 20st-30st, 30st-40st, 50st-60st and 60st-70st at the rate of 0.1C, 0.5C, 1C, 5C, 10C, 40C and 0.1C respectively.



Figure 5. a) Cycling performance at the rate of 1C for 100 cycle numbers, b) at the rate of 5C for 500 cycle numbers.

In order to investigate cycling performance further, a very stable cycling ability was observed for Cr-doped LTO. Cycling for 100 loops at 1C, even cycling for 500 loops at 5C, coulombic efficiency remains at close to 100% and they were shown in Figure 5. These results demonstrated that the Cr-doped LTO has an excellent reversibility and stability.

4. Conclusion

 $Li_{4-x/3}Ti_{5-2x/3}Cr_xO_{12}$ (x=0.25) sample was successfully synthesized by sol-gel method in air atmosphere. XRD patterns demonstrated that Cr-doping did not alter the spinel structure or change the fundamental electrochemical reaction mechanism of LTO. The as-prepared samples had an average particle size approximate 100 nm. The electrochemical properties of Cr-doped LTO, especially the rate capability was significantly improved in this work. Experimental results showed that the charge/discharge

specific capacity reached 167 mAh/g at 40C and the coulombic efficiency is almost 100%, showing brilliant high-rate performance for lithium-ion batteries.

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