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Wet Method Preparation and Electrochemical Characterization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ / Graphite Anode Material*

HE Ze-qiang^{1,2*}, XIONG Li-zhi^{1,2}, LIANG Kai¹

(1. College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, Hunan China; 2. School of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China)

Abstract: $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite was prepared by sol-gel method using ethyl alcohol as solvent, lithium acetate and tetrabutyl titanate and graphite as raw materials. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composites were characterized by X-ray diffraction(XRD), scanning electron microscopy (SEM) combined with electrochemical tests. Results show that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite with 5% carbon mass fraction containing can be obtained by annealing the precursor at 600 °C for 6 h in Ar atmosphere. The composites can deliver a specific capacity of 167.1 mA h/g, 99.0% and 105.1% of the capacity can be retained after discharged for 80 times at 0.1 C and 2.0 C, respectively. Compared with pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite shares larger discharge capacity, better cyclability and rate performance, suggesting $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite is a promising anode material for lithium ion batteries.

Key words: lithium ion batteries; $\text{Li}_4\text{Ti}_5\text{O}_{12}$; anode; wet method

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Due to its good structural stability (zero-strain insertion material)^[1,2] and satisfactory safety (the mid-discharge voltage of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ close to 1.5 V versus Li^+/Li) in charge-discharge process, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is thought as a good anode material for asymmetrical mixed battery and lithium ion batteries with high power. However, lower lithium-ion conductivity and low electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lead to poor rate capability^[3-6]. To overcome this shortcoming, many methods have been tried, such as sol-gel, doping and nanotechnologies^[1-2,7]. Results show that an electronically conductive agent such as Ag is very useful to improve the high rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ^[8]. However, the high cost of Ag metal urges us to develop new conducting additive. To find a cheaper conducting additive is one of the keys for the practical application of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Carbon is a good conducting material and is used widely in lithium ion batteries. If $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is coated with carbon on its surface, the good conductivity of carbon can make up for the poor conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and thus improve its electrochemical properties. A. Guerfi et al^[9-10] investigated the effects of carbon black, high-surface-area carbon, graphite and carbonized polymer) on the structure, morphology and electrochemical properties. According to their results, carbons can play three roles: (1)

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Biography: HE Ze-qiang(1974-), male, was born in Hunan Province, Ph. D., associate professor. E-mail address: csuhzq@163.com; Tel: + 86 743 8563911.

as reducing agent, improves the reaction in the bulk powders and increases lithium diffusion in the particles to enhance complete transformation; (2) the carbon additive helps to reduce the particle size and produce an agglomerate of small particles in a chain-like structure; (3) to increase the inter-particle contact and disturb the undesirable particle growth. Hence, it is possible to obtain $\text{Li}_4\text{TisO}_{12}$ material with good performance by using different types of carbons.

In this paper, $\text{Li}_4\text{TisO}_{12}$ /graphite composite was synthesized by sol-gel method and the electrochemical properties, especially the high rate cycling performance were investigated.

1 Experiment

A certain quantity of tetrabutyl titanate was solved in ethanol absolute with the volume ratio of V (tetrabutyl titanate) : V (ethanol absolute) = 1 : 5. The solution of tetrabutyl titanate was added to an aqueous ethanol solution of lithium acetate stirring strongly according to the stoichiometric ratio of $\text{Li}_4\text{TisO}_{12}$ to get a clear yellow sol. A certain quantity of graphite (the mass ratio of $\text{Li}_4\text{TisO}_{12}$ to graphite is 19 : 1) used in lithium ion batteries was dispersed uniformly in this sol with ultrasonic wave and stirrers. After stirring for 2~ 3 h, a black gel was obtained. The gel was dried at 105 °C for 4 h in vacuum to get a black precursor. The precursor was calcinated at 600 °C in Ar atmosphere for 2~ 6 h to obtain $\text{Li}_4\text{TisO}_{12}$ /graphite composite.

The thermal behavior of the precursor was analyzed by thermal analysis apparatus (TGA/SDTA851e, METTLER TOLEDO). Phase identification studies of the samples were carried out by an X-ray diffractometer (XRD; Rigaku D/MAX-gA) with Cu $k\alpha$ radiation. The surface morphology and EDS analyses of carbon content in $\text{Li}_4\text{TisO}_{12}$ -C composite was done by scanning electron microscopy (SEM; JSM 5600 LV).

A slurry containing 80% $\text{Li}_4\text{TisO}_{12}$ /graphite composite (mass fraction, similarly hereinafter), 10% acetylene black and 10% PVDF (polyvinylidene fluoride) was made using N-methylpyrrolidinone (NMP) as the solvent. Electrodes with an area of 1 cm^2 for the measurements of electrochemical characterization were prepared by coating slurries (about 100 μm in thickness) on copper foils followed by drying in vacuum at 60 °C for 12 h. Electrochemical tests were conducted using a conventional coin-type cell, employing lithium foil as a counter electrode and utilizing 1.0 $\text{mol} \cdot \text{L}^{-1}$ LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC) (with an EC to DMC volume ratio of 1 : 1) as the electrolyte. The assembly was carried out in an Ar-filled glove box. The electrochemical analyses were carried out with an electrochemical analysis system.

2 Results and Discussion

Fig. 1 shows the thermogravimetric (TG) analysis and differential thermal analysis (DTA) of dry gel precursor. From the TG curve, it can be seen that about 7.44% weight of the precursor is loosed, which is due to lose of physical absorbed water on the surface of the precursor. Accordingly, an endothermic peak between 50 °C and 96 °C appears on the DTA curve. The obvious weight loss above 200 °C is caused by thermal decomposition of lithium acetate and the formation of titanium(IV)

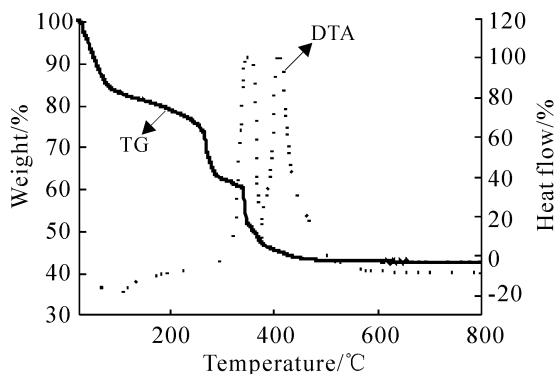


Fig. 1 TG and DTA Curves of Dry Gel Precursor

oxide from organotitanate and there are two exothermic peaks at 344 °C and 405 °C on DTA curve. When the reaction stops at 450 °C, the weight loss is 42.59%, which is close to theoretical value of 44.36%^[11]. Above 600 °C, there is no weight loss at TG curve, indicating that the decomposition is complete. TG and DTA results suggest that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite can be obtained by calcinating the precursor at 600 °C.

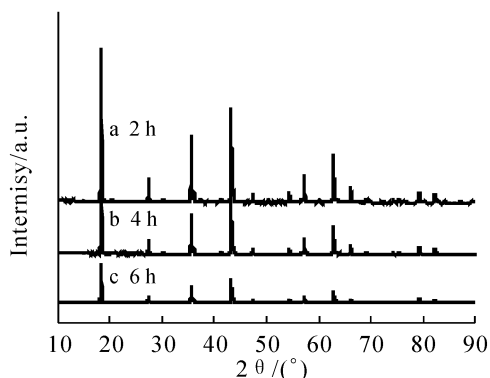


Fig. 2 XRD Patterns of Samples Calcinating at 600 °C for Various Time

Fig. 3 shows the SEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is composed of particles with single morphology and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite is composed of particles with two kinds of morphology with features corresponding to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder and graphite, respectively. As shown in Fig. 3, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles are well dispersed, while there are some aggregates between particles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite. The introduction of carbon fragments adhering to the spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles promotes the aggregation of particles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite^[10].

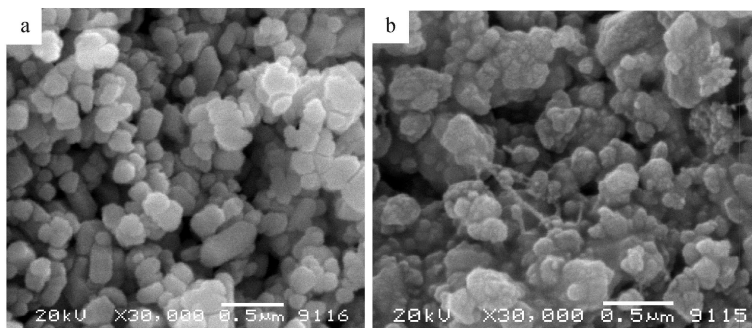


Fig. 3 SEM Images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /Graphite Composite (b) Powders

Fig. 4 presents the discharge and charge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite at 0.1 C (16.8 mA/g). $\text{Li}_4\text{Ti}_5\text{O}_{12}$ delivers a reversible discharge capacity of 146.8 mAh/g. While the reversible discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -C composite is 167.1 mAh/g, which is very close to the theoretical capacity (168 mAh/g), indicating that the active material utilization is very close to the theoretical value. Compared with $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the reversible discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -C composite is raised by about 13.8%, which is due to the improvement of lithium ion diffusion coefficient in the insertion-desertion process because of existing of carbon.

The cyclability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite is shown in Fig. 5. Cycled 80 times, the discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is 142.9 mAh/g and 97.3% of the initial capacity is retained, while the discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -C is 165.4 mAh/g and 99.0% of the initial capacity is retained. Obviously, the introduction of carbon increases the conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and improves the cycling performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphite composite.

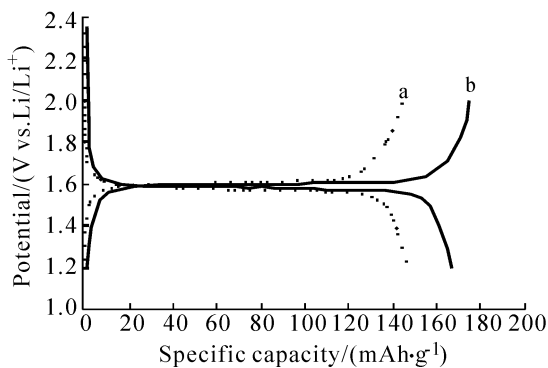


Fig. 4 Discharge and Charge Curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Graphite Composite}$ (b) Powders

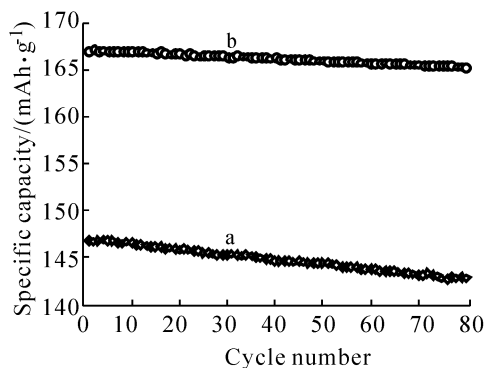


Fig. 5 Cyclability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Graphite Composite}$ (b) Powders

Fig. 6 shows the rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$. With the increase of discharge rate, the reversible capacity of both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ decreases. The reversible capacity of both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decreases from 146.8 mAh/g at 0.1 C to 116.9 mAh/g at 2.0 C, and 79.6% of the initial capacity is retained. To $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$, the reversible capacity decreases from 167.1 mAh/g at 0.1 C to 140.9 mAh/g at 2.0 C, and 84.3% of the initial capacity is retained. This result shows that the rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ is better than $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Meanwhile, it is shown from Fig. 6 that the capacity retention rate is not improved at small current rate, though it helps retain higher discharge capacity. Results show that with the increase of current rate, the cycling stability of both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ increase and the capacity retention rate keeps a higher level at higher current rate. According to our test result, the capacity retention rate of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ is the best at 2.0 C, which is 100.8% and 105.1% after cycling 80 times. It is very interesting that the capacity retention rate of both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ is more than 100% and the reason is under studying.

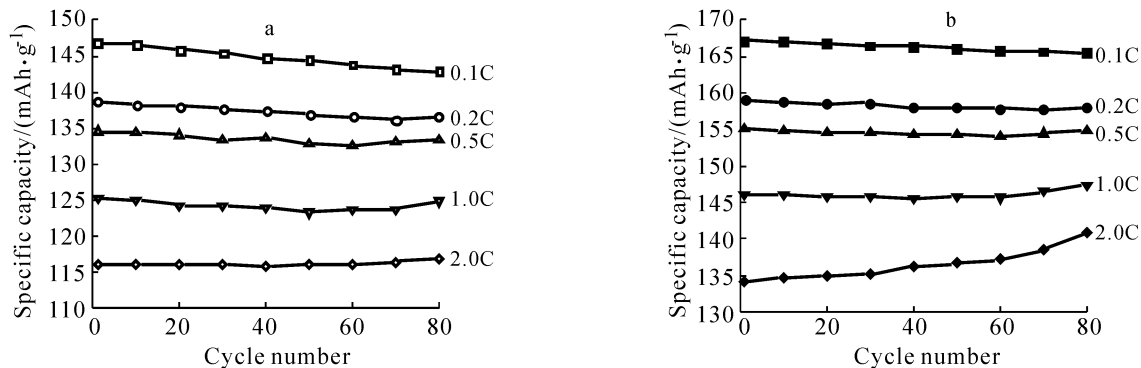


Fig. 6 Rate Performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Graphite Composite}$ (b) Powders

3 Conclusions

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ precursor was prepared by sol-gel method using ethyl alcohol as solvent, lithium acetate and tetrabutyl titanate as raw materials, and graphite as carbon source. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ with 5% carbon containing can be obtained by calcinating the precursor at 600 °C for 6h in Ar atmosphere. The composites can deliver a specific capacity of 167.1 mAh/g, 99.0% and 105.1% of the capacity can be retained after being discharged for 80 times at 0.1 C and 2.0 C, respectively. Compared with pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ shares larger discharge capacity, better cyclability and rate performance, suggesting $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{graphite composite}$ is a promising anode material for lithium-ion batteries.

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References:

- [1] FU L J, LIU H, WU Y P, et al. Electrode Materials for Lithium Secondary Batteries Prepared by Sol-Gel Methods [J]. Prog. Mater. Sci., 2005, 50: 881- 887.
- [2] WU Y P, DAI X B, MA J Q. Lithium ion Batteries—Practice and Application [M]. Beijing: Chemical Industry Press, 2004.
- [3] AMATUCCI G, BADWAY F, PASQUIER A D, et al. An Asymmetric Hybrid Nonaqueous Energy Storage Cell [J]. J. Electrochem. Soc., 2001, 148(8): A930- 939.
- [4] SINGHAL A, SKANDAN G, AMATUCCI G, et al. Nanostructured Electrodes for Next Generation Rechargeable Electrochemical Devices [J]. J. Power Sources, 2004, 129(1): 38- 44.
- [5] OHZUKU T, UEDA A, YAMAMOTO N. Zero-Strain Insertion Material of $\text{Li}[\text{Li}_{1/3}\text{T}_5/3]\text{O}_4$ for Rechargeable Lithium Cells [J]. J. Electrochem. Soc., 1995, 142(5): 1431- 1435.
- [6] PROSINI P P, MANCINI R, PETRUCCI L, et al. $\text{Li}_4\text{T}_5\text{O}_{12}$ as Anode in All-Solid-State, Plastic, Lithium-Ion Batteries for Low-Power Applications [J]. Solid State Ionics, 2001, 144(1/2): 185- 192.
- [7] KAVAN L, PROCHAZKA J, SPITLER T M, et al. Li Insertion into $\text{Li}_4\text{T}_5\text{O}_{12}$ (Spinel) [J]. J. Electrochem. Soc., 2003, 150(7): A1 000- 1 005.
- [8] HUANG S H, WEN Z Y, ZHU X J, et al. Preparation and Electrochemical Performance of Ag Doped $\text{Li}_4\text{T}_5\text{O}_{12}$ [J]. Electrochem. Commun., 2004, 6(11): 1 093- 1 097.
- [9] GUERFI A, CHAREST PA, KINOSHITA K, et al. Nano Electronically Conductive Titanium-Spinel as Lithium ion Storage Negative Electrode [J]. Journal of Power Sources, 2004, 126: 163- 168.
- [10] GUERFI A, SÉVIGNY S, LAGACÉ M, et al. Nano-Particle $\text{Li}_4\text{T}_5\text{O}_{12}$ Spinel as Electrode for Electrochemical Generators [J]. Journal of Power Sources, 2003, (119/ 121): 88 - 94.
- [11] LIU Dong-qiang, LAI Qiong-yu, HAO Yan-ying, et al. Study on Synthesis and Mechanism of $\text{Li}_4\text{T}_5\text{O}_{12}$ by Sol-Gel Method [J]. Wujihuaxue Xuebao (Chinese Journal of Inorganic Chemistry), 2004, 24(7): 829- 832.
- [12] WANG G X, BRADHURST D H, DOU S X, et al. Spinel $\text{Li}[\text{Li}_{1/3}\text{T}_5/3]\text{O}_4$ as an Anode Material for Lithium ion Batteries [J]. J. Power Sources, 1999, 83(1/2): 156- 160.

$\text{Li}_4\text{T}_5\text{O}_{12}$ / 石墨负极材料的湿法制备与电化学表征

何则强^{1,2}, 熊利芝^{1,2}, 梁 凯¹

(1. 吉首大学化学化工学院, 湖南 吉首 416000; 2. 中南大学化学化工学院, 湖南 长沙 410083)

摘 要:以无水乙醇为溶剂, 醋酸锂、钛酸酯和石墨为原料, 采用湿法制备了 $\text{Li}_4\text{T}_5\text{O}_{12}$ / 石墨复合材料. 采用 X-射线衍射、红外光谱、扫描电镜和电化学测试等对合成产物进行了表征. 结果表明: 600 °C 氩气气氛中煅烧 6 h 可制得碳质量分数 5% 左右的 $\text{Li}_4\text{T}_5\text{O}_{12}$ / 石墨复合材料, 其可逆容量达到 $167.1 \text{ mAh} \cdot \text{g}^{-1}$; 经 80 次循环后, 0.1C 放电时, 容量保持率为 99.0%, 2.0 C 放电时容量保持率达到 105.1%. 与纯 $\text{Li}_4\text{T}_5\text{O}_{12}$ 相比, $\text{Li}_4\text{T}_5\text{O}_{12}$ / 石墨复合材料具有更好的循环性能和倍率性能, 是一种优良的锂离子电池负极材料.

关键词: 锂离子电池; $\text{Li}_4\text{T}_5\text{O}_{12}$; 负极; 湿法

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