



Study of Synthesis Mechanism and Electrochemical Performance of $\text{LiTi}_2(\text{PO}_4)_3$

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$\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ was synthesized by high-temperature solid-state method. The microstructure, morphology of the samples were characterized and investigated by X-ray diffraction and its electrochemical properties were characterized in an organic and aqueous electrolyte. Galvan static charge-discharge cycling of the resulting lithium titanium phosphate showed an initial discharge capacity of 142.7 mAh/g and quite good capacity retention during cycling, 97 % after 50 cycles and 90.17 % after 50 cycles at a 5 C cycling rate in an organic electrolyte. Choosing $\text{LiFePO}_4/2\text{M}$, $\text{Li}_2\text{SO}_4/\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ and $\text{LiCoO}_2/2$ mol/L, $\text{Li}_2\text{SO}_4/\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ as the aqueous solution battery system, test $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ /Galvan static charge-discharge performance. The result showed an initial discharge capacity of 69.4 mAh/g and 59.1 mAh/g respectively and their voltage platform is 0.9 V and 1.5 V at a 4 C cycling rate. All of those two aqueous battery systems have a good cycle performance.

Keywords: $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$, High-temperature solid-state method, Negative electrode, Organic system, Aqueous electrolyte.

INTRODUCTION

NASICON-type compound as the active material for lithium-ion batteries have been widely studied. Polyanion compound $\text{LiTi}_2(\text{PO}_4)_3$ is formed a lithium ion $\text{Ti}_2\text{P}_3\text{O}_{12}$ free embedding and extraction of the three-dimensional tunnel structure in which the PO_4 tetrahedron is $\text{Ti}_2\text{P}_3\text{O}_{12}$, TiO_6 octahedra connected through a vertex constituting $\text{Ti}_2\text{P}_3\text{O}_{12}$ and each four PO_4 body and with four TiO_6 octahedra are interconnected with each TiO_6 octahedron six PO_4 tetrahedra are connected only subtly constitute such a three-dimensional spatial structure¹. In the $\text{LiTi}_2(\text{PO}_4)_3$, there are two different positions lithium Li, Li (1) and Li (2), Li (1) is completely filled and Li (2) is the empty position. At a certain temperature, Li^+ in $[\text{Ti}_2(\text{PO}_4)_3]^-$ skeletal lattice of two different series of moving slit between nodes, therefore $\text{LiTi}_2(\text{PO}_4)_3$ has a high electrical conductivity^{2,3}. $\text{LiTi}_2(\text{PO}_4)_3$ may reversibly insert two lithium ions, operating on the $\text{Ti}^{4+}/\text{Ti}^{3+}$ at 2.48 V vs. Li^+/Li , relative to a standard hydrogen electrode potential of -0.5 V, just electrochemical stability window of water (1.5 - 0.5 V) within off line, which can be used for safe and efficient preparation of the aqueous lithium-ion battery cathode materials⁴. However $\text{LiTi}_2(\text{PO}_4)_3$ material itself there is a small rate of ion conductivity, electrical conductivity and low defects. For the first charge and discharge capacity of the irreversibility is the nature of the material, but low electrical conductivity by doping the carbon-coated and metal ions both to be improved, the slow diffusion of ions can be effectively controlled $\text{LiTi}_2(\text{PO}_4)_3$ particles size having a high

specific surface area and improved synthetic mesoporous materials⁵. Several methods for synthesis of lithium titanium phosphate [$\text{LiTi}_2(\text{PO}_4)_3$] such as the traditional high-temperature solid-phase method, Pechini method, hydrothermal, sol-gel-microwave heating and microbial synthesis method⁶ have been reported in the literature. Several researchers⁷⁻¹² had performed the appropriate research for $\text{LiTi}_2(\text{PO}_4)_3$ in the organic system as the electrochemical properties and modified. Recently, other researchers¹³⁻¹⁷ also reported the aqueous electrolyte electrochemical performance.

In this work, $\text{LiTi}_2(\text{PO}_4)_3$ was synthesized by high temperature solid conducting carbon-coated preparation $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composites. First there is a test of the electrochemical properties in the organic system and then being extremely appropriate aqueous lithium-ion battery cathode materials testing $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composites in aqueous electrochemical performance.

EXPERIMENTAL

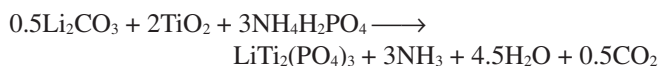
Experiments using the solid phase method in an oxidizing atmosphere warmed sub-step synthesis of 1 $\text{LiTi}_2(\text{PO}_4)_3$, grinding adding a certain percentage of carbon mixed in an inert atmosphere carbon-coated synthetic/C composites.

Synthesis of lithium titanium phosphate- $\text{LiTi}_2(\text{PO}_4)_3$

High-temperature solid-state method was carried out in the way: TiO_2 , $\text{NH}_4\text{H}_2\text{PO}_4$ and Li_2CO_3 as the starting materials, weighed according to the stoichiometric ratio, then ethanol

was added as a dispersing agent, put into a planetary ball mill at a rotational speed 400 rpm. According to the ball and material mass ratio of 5:2 the ball-mill mixing milled 8 h the mixture were dried at 70 °C in a oven, then with pestling and mortaring evenly into grille strongly in a muffle furnace to 10 °C/min heating to 350 °C and hold for 2 h and then heated to 950 °C and hold for 12 h. After that cooled it slowly to room-temperature in the furnace, then get a white solid of $\text{LiTi}_2(\text{PO}_4)_3$.

The $\text{LiTi}_2(\text{PO}_4)_3$ was coated with conductive carbon by mixing it with a polymer of glucose (according to the mass ratio $\text{LiTi}_2(\text{PO}_4)_3 : \text{C}_6\text{H}_{12}\text{O}_6 = 8:2$) uniformly mixing and grinding at 10 °C/min heating to different firing temperature in argon. After a certain time holding furnace cooled slowly to room temperature to get the product. The overall reaction is as follows:



X-ray diffraction (XRD) analysis was carried out to identify the samples on XRD-6000 (36 kV, 20 mA) with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm) in the 2θ range of 10-80° at the scan speed at 3°/min.

Electrode preparation and cell construction: A slurry containing the $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite material and acetylene black (as the conductive agent) a binder (LA-133) ratio of 85:10:5 by mass ratio was prepared, then the slurry was stirred at room temperature and was sonicated for 1 h immediately prior to electrode preparation. Electrodes containing $\text{LiTi}_2(\text{PO}_4)_3$ were prepared by dipping stainless steel mesh or foil into the slurry. The electrodes were then dried at room temperature for 2 h and roll pressed.

Then the cells were constructed by an aqueous electrolyte containing pH-neutral 2M Li_2SO_4 , the industrialization of LiFePO_4 , LiCoO_2 as the battery positive material and the $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ be used as negative materials. Electrochemical characterization of Pouch cells was carried out by assembling named the 2XZ-2B of battery testing system for galvanostatic charge/discharge and CV measurements with different current densities in the electrochemical performance in an organic electrolyte ranging from 0.5 V-1.8 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed at room temperature by using a CHI660B electrochemical workstation (CH Instruments, Shanghai, China), CV and EIS measurements were also performed on CHI660B, the scan rate of CV measurements is 10^{-4} mV/s ranging from 1.6 to 3.6V.

RESULTS AND DISCUSSION

The XRD patterns of the $\text{LiTi}_2\text{PO}_4/\text{C}$ composite samples are shown in Fig.1, for comparison, the products by solid-phase method at different temperatures (850, 950, 1000 °C), are also listed. The power X-ray diffraction spectrum of the $\text{LiTi}_2(\text{PO}_4)_3$ matched the previously reported spectrum for this material. The spectrum sharp diffraction peak intensity, which shows that the material with crystalline NASICON. However carbon coated on $\text{LiTi}_2(\text{PO}_4)_3$ of the crystal structure has no influence. The XRD of samples prepared at 850 °C peak intensity is relatively weak, incomplete crystallization, appeared

small amounts of other impurities, such as LiTiOPO_4 , LiTiPO_5 , $\text{LiTi}(\text{PO}_4)\text{O}$. However with increasing temperature, the impurity disappeared, the XRD peak intensity, the material is more complete crystal. But the XRD of samples synthesized at 950 °C peak height and width were similar with samples synthesized at 1000 °C, so the high temperature does not significantly affect for the structure crystal of the material.

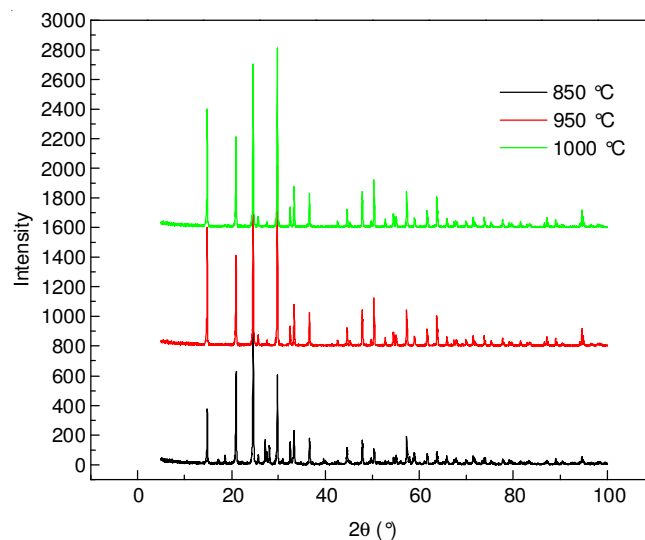


Fig. 1. XRD diffraction patterns of $\text{LiTi}_2(\text{PO}_4)_3$ synthesized at different temperature

Cyclic voltammetry and charge-discharge rate capability in organic system: It can be seen that the scan rate of CV measurements is 0.5 mV/s ranging from 1.8 to 3.2 V. As shown in Fig. 2, the redox peaks of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite are located at 2.45 V and the areas are basically the same. The peaks are characteristic of the insertion and removal of Li ion into/from the $\text{LiTi}_2(\text{PO}_4)_3/\text{Li}_3\text{Ti}_2(\text{PO}_4)_3$ structure. It is correspond to the discharge platform of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composites at 2.45 V. The $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ has shown good reversibility of the electrode. Moreover, the CV profile of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite exhibits the higher peak current, which facilitates the kinetic process of the electrochemical reactions, indicative of a higher specific capacity.

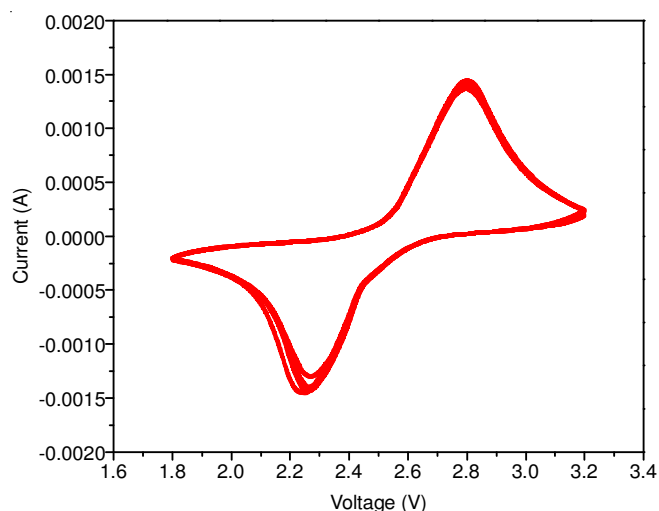


Fig. 2. Cyclic voltammetry for $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ synthesized with scanning rate of 0.5 mV/s

The electrochemical behaviour of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ in an organic electrolyte was shown in Figs. 3 and 4. The $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite has stable charge-discharge curves under various ratio (0.3 C-10 C), the discharge curves are characterized by a plateau at about 2.4 V, which corresponds to the cyclic voltammetry. As the current density increases, the specific capacity decreases, while the charge/discharge polarization becomes more pronounced. The trend of battery capacity is almost similar to the cycle at 0.3-5 C, as current continues to increase to 8 C, 10 C the capacity is suddenly reduced significantly and can be seen from the circulation loop 5 C capacity and the loop is stable, but at the 8 C, 10 C the initial capacity is low and the attenuation phenomenon is more serious. The capacity of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite is 126.9 mAh/g and is 113.4 mAh/g after 100 cycles at 1 C, approximately 89.36 % of the initial capacity. The data demonstrated the $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite has excellent cycling stability and a certain high-magnification rate discharge performance.

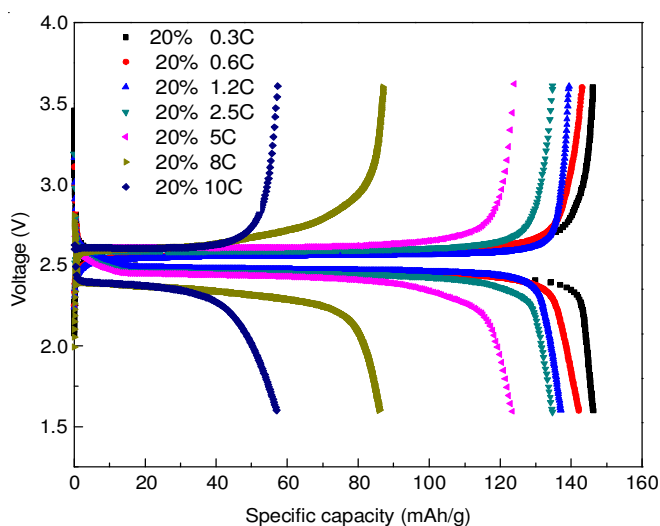


Fig. 3. Specific capacity of charge and discharge for $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ synthesized at different charge/discharge rate, at room temperature

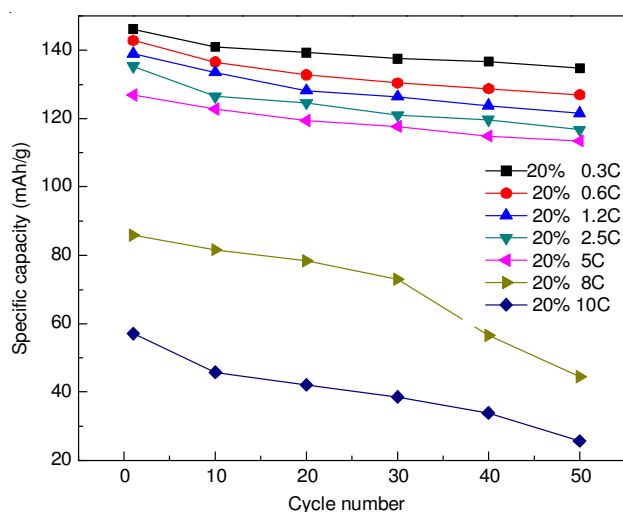


Fig. 4. Specific capacity vs. cycle number for $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ synthesized at different charge/discharge rate, at room temperature

It can be seen that the initial capacity is slightly higher than the theoretical of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ from the charge-discharge

curve at various rates. It is mainly due the $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ has different structure, rhombohedral crystal (NASICON) and monoclinic. During the process of charge-discharge, NASION (rhombohedral) of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ material can transfer two electrons, theoretical capacity is 138 mAh/g, but monoclinic crystal transferred more than two electrons during the process, material in the tube furnace and muffle furnace may be heated unevenly, so a few monoclinic crystal $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ were blended in NASION $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$.

Electrochemical properties of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ in an aqueous electrolyte: Industrial LiFePO_4/C (product of battery factory in Chong Qing) was used as the positive electrode material in aqueous system. Figs. 5 and 6 show charge-discharge curves and cycle performance of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}/\text{pH}$ -neutral 2M, $\text{Li}_2\text{SO}_4/\text{LiFePO}_4/\text{C}$. It can be seen this system has about 1 V charge-discharge plateau when testing its electrochemical performance at the rate of 0.5C, 2C and 4C the initial discharge capacity of the cells is 81, 70, 64 mAh/g respectively. The initial capacity of material is decreased during the process of discharge but it remained about 55 mAh/g though there is a process of capacity fluctuate related to the posterior 30-50 cycles.

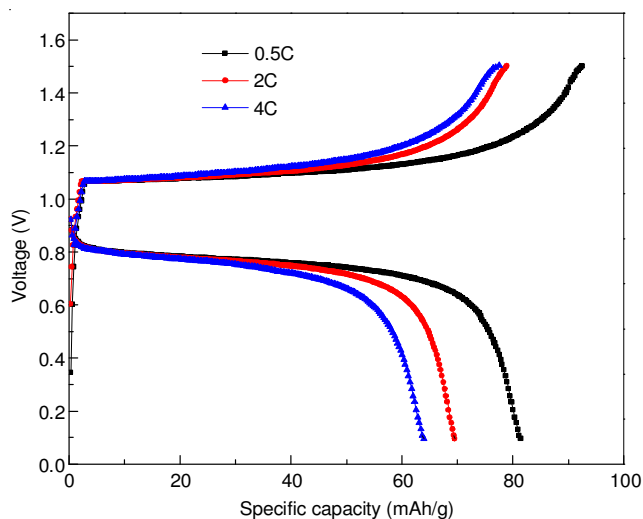


Fig. 5. Specific capacity of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}/2 \text{ mol}/\text{Li}_2\text{SO}_4/\text{LiFePO}_4/\text{C}$ at different charge/discharge rate, at room temperature

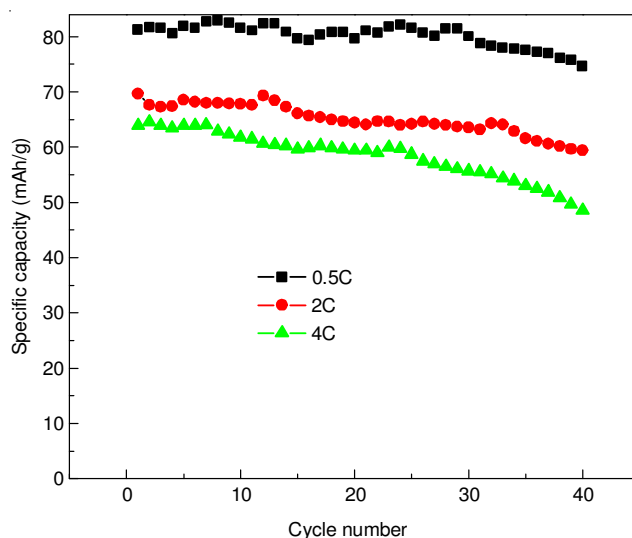


Fig. 6. Specific capacity vs. cycle number of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}/2 \text{ mol}/\text{Li}_2\text{SO}_4/\text{LiFePO}_4/\text{C}$, at different charge/discharge rate, at room temperature

Following the Figs. 7 and 8 have shown the aqueous lithium ion battery of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}/\text{pH} = 6$, 2 M $\text{Li}_2\text{SO}_4/\text{LiCoO}_2$ charge-discharge. LiCoO_2 was carried out in the way: Co_2O_3 and Li_2CO_3 (AR) as the starting materials, weighed according to the stoichiometric ratio, then ethanol was added as a dispersing agent, put into a planetary ball mill at a rotational speed 400 rpm, according to the ball and material mass ratio of 5:1 the ball-mill mixing milled for 4 h to be mixed uniformly the mixture were dried at 80°C , then with pestling and mortaring evenly into gridde strongly in a muffle furnace to $10^\circ\text{C}/\text{min}$ heating to 800°C and hold for 8 h and after that cooled it slowly to room-temperature in the furnace, then get the product.

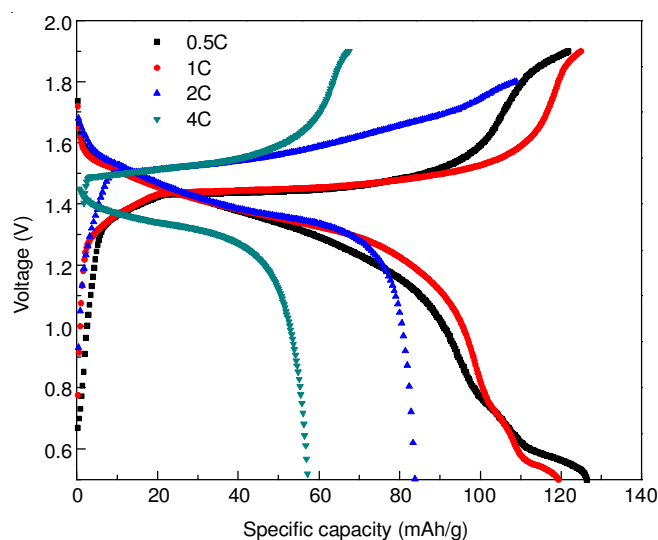


Fig. 7. Specific capacity of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}/2\text{mol}/\text{Li}_2\text{SO}_4$, $\text{pH} = 6/\text{LiCoO}_2$ at different charge/discharge rate, at room temperature

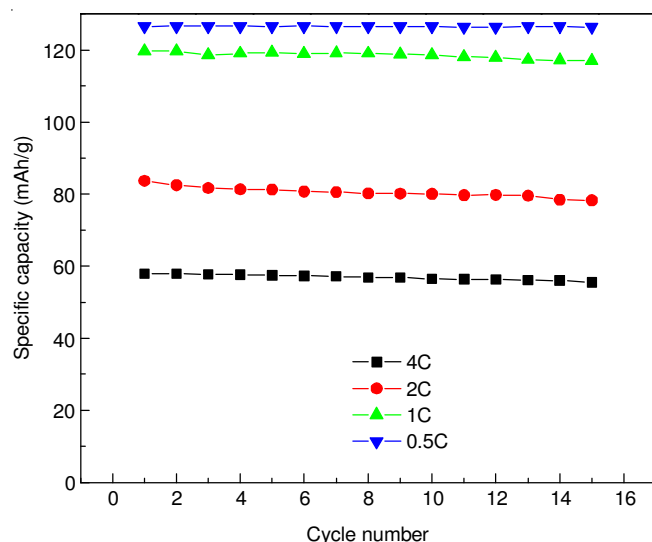


Fig. 8. Specific capacity vs. cycle number of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}/2\text{mol}/\text{Li}_2\text{SO}_4$, $\text{pH} = 6/\text{LiCoO}_2$ at different charge/discharge rate, at room temperature

There were the charge-discharge curves at various rates and cycle performance of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}/\text{pH} = 6$, 2M, $\text{Li}_2\text{SO}_4/\text{LiCoO}_2$ in the Figs. 7 and 8. From the figures, we can see there is a flat charge-discharge curve of $\text{LiTi}_2(\text{PO}_4)_3$ in aqueous

electrolyte. With increasing of current density, the initial capacity of charge-discharge has faded plenty.

As shown as the Figs. 7 and 8, the initial capacity of discharge at 0.5C, 1C, 2C, 4C are 126.7 mAh/g, 119.4, 86.5, 57.89 mAh/g, respectively. But general speaking, there is a excellent cycle performance. At various current densities, there is little attenuation capacity after 15 cycles. However, the battery capacity fading speed is quite fast in an aqueous lithium-ion electrolyte. There may be several reasons for the phenomenon as follows:

(1) The cathode materials of battery is unstable in aqueous electrolyte, being dissolved there may be generated side effects during the reaction process.

(2) Cathode materials may be embedded amount of protons during the process of insertion of Li^+ , resulting the capacity decreased.

(3) The sealing of the battery is not good, the electrolyte were deteriorated, the second, taking amount of air into the battery destroyed the system of neutral and anaerobic environment.

So far there has been a great breakthrough for the battery of aqueous, such as Yongyao Xia, a professor of Fudan University after years of research considers the main reason of the lithium ion battery capacity attenuation is oxygen. I believe in the future this system of aqueous lithium-ion battery is expected to a practical applicability.

Conclusion

The $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ has been synthesized by high-temperature solid-state. The microstructure, morphology of the samples were characterized and investigated by X-ray diffraction. It is shown that the preparation of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite has a good structure of NASICON and the electrochemical properties were characterized in an organic and aqueous electrolyte. According to the electrochemical studies, the $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite delivered high initial discharge capacity at different current rates. All of those two battery systems of an organic and aqueous electrolyte have a good cycle performance.

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