Synthesis and characterization of mesoporous titanium pyrophosphate as lithium intercalation electrode materials

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Received 15 July 2005; received in revised form 9 September 2005; accepted 18 September 2005

Available online 3 November 2005

Abstract

Mesoporous titanium pyrophosphates have been synthesized by a sol–gel template method with further calcinations at or below the temperature of 700 °C. When calcined at 800 °C, crystalline TiP_2O_7 will be formed accompanied with the break down of meso-structure in the precursor. Mesoporous TiP_2O_7 shows a similar lithium ion intercalation behavior to that of solid solution in the electrochemical tests. When cycled at high charge/discharge rate, mesoporous TiP_2O_7 calcined at 700 °C delivers a higher specific discharge capacity than that of crystalline TiP_2O_7, indicating that mesoporous structure is beneficial for improving the transportation and intercalation/deintercalation behavior of lithium ions in the materials, thus improving the charge/discharge performance of the materials at high charge/discharge rate.

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Keywords: Mesoporous materials; Titanium pyrophosphate; Cathode material; Lithium ion batteries

1. Introduction

Nanotechnology is playing a more and more important role in the development of advanced rechargeable lithium ion batteries [1–4]. In the past several years, many nano-structured transition-metal oxides and transition-metal phosphates have been reported to have good electrochemical performance as electrode materials for batteries [5–10]. For example, mesoporous materials, besides their traditional use in catalysis, ion exchange and separation [11], have also found their new applications in batteries [12–17], fuel cells [18] and electrochemical supercapacitors [19]. Moreover, micro-electro-mechanical systems (MEMS) and micro-electron chip (MEC) devices are making significant contributions in many areas including sensors and actuators [20], which cause urgent needs of batteries in micro-meter scale [21,22]. Long et al. [4] proposed a type of battery with three-dimensional configuration which can offer one means to keep lithium ion transport distance short, and can provide enough material so that the batteries can power MEMS devices for extended periods of time. Therefore, mesoporous materials will be appropriate candidates for 3D batteries because of the three advantages brought by their ordered 2D or 3D porous structure [11]. Firstly, the porous structure facilitates the fast transport of electrolyte containing lithium ions. Secondly, the large specific surface area of the materials can provide enough active sites for many lithium ions to simultaneously intercalate/deintercalate into/from them. Thirdly, the thin pore wall of the materials can reduce the lithium ion diffusion path and thus enhance the electrochemical performance of the materials, especially at high current density.

Many approaches for synthesis and characterization of mesoporous electrode materials have been made by researchers in recent years. For example, Peng et al. [10] firstly reported a mesoporous Sn–TiO_2 composite electrode for lithium batteries. Then, mesoporous tin oxides [12] and mesoporous tin phosphate/Sn_3P_2O_7 composites [13] with good performance were reported as anode materials in
lithium battery. In mesoporous tin phosphate/Sn$_2$P$_2$O$_7$ composites, the mesoporous structure acted as a buffer layer to alleviate the volume expansion of the tin phosphate anode during lithiation/delithiation, which brought higher specific capacity and improved cycling performance. Zhou et al. [14] also found ordered mesoporous carbon had an extra higher reversible capacity (Lix: C$_x$ = 2.3–3.0) than graphitic carbon (Lix: C$_x$ = 1). But the exact mechanism of lithium ion intercalation into mesoporous carbon still remains unclear up to now. They also reported a mesoporous Li$_3$Fe$_2$(PO$_4$)$_3$ as cathode material with enhanced discharge behavior at the first cycle [15]. Liu et al. [16] demonstrated that mesoporous VO$_x$ could deliver a capacity of 125 mA h g$^{-1}$ at 50 C rate approaching the typical discharge rate for electrochemical capacitors. In our recent work [17], mesoporous FePO$_4$ showed enhanced specific capacity than that of reported ones. To get reversible lithium ion intercalation/deintercalation performance of the electrodes, nano-structured material should have a stable crystal structure during intercalation/deintercalation process (i.e. charge/discharge process) [23]. It is well known that poly-anion type compounds, such as LiFePO$_4$ [24] and TiP$_2$O$_7$ [25], can keep their crystal structures during lithium ion intercalation/deintercalation process [26], which brings excellent thermal stability and cyclic performance.

Here we report some results about synthesis, characterization and electrochemical performance of mesoporous TiP$_2$O$_7$ materials. The mesoporous TiP$_2$O$_7$ were synthesized by using tri-block copolymer as a structure-directing agent. It is demonstrated that mesoporous TiP$_2$O$_7$ materials are able to deliver higher reversible capacity than that of crystalline ones at high charge/discharge rate as lithium ion insertion materials. In our knowledge, there are not any reports about such kind of study in the literatures.

2. Experimental

2.1. Materials synthesis

For the synthesis of TiP$_2$O$_7$, 5 g of P123 HO(CH$_2$-CH$_2$O)$_{20}$(CH(CH$_3$)CH$_2$O)$_{70}$(CH$_2$CH$_2$O)$_{20}$H, Aldrich) was ultrasonically dissolved in 100 g of ethanol. Subsequently, 0.01 mol of Ti(OC$_4$H$_9$)$_4$ and 0.02 mol of 85% H$_3$PO$_4$ were added step by step and each stirred for 10 min after addition. Then the mixture was further stirred for 10 h in 40$^\circ$C oil bath. The resulting sol solution was gelled in an open petri dish for 5 days at 30$^\circ$C. The resulting gel was then dried at 130$^\circ$C for 5 days. Then TiP$_2$O$_7$ sample was obtained by calcinations of the dried gel for 24 h at 600, 700 or 800$^\circ$C at a heating rate of 1$^\circ$C min$^{-1}$ under the flow of pure N$_2$ (100 ml min$^{-1}$) in a tube stove. Calcination temperatures were chosen based on TG-DTA experiments which were performed by a STA 409 PC analyzer (Netzsch, Germany) at a heating rate of 10$^\circ$C min$^{-1}$ under the flow of N$_2$ (40 ml min$^{-1}$).

2.2. Materials characterizations

The residual carbon in the samples was detected by an elemental analysis on an EA 1110 element analyzer (ThermQuest Italia S.p.A., Italy). XRD measurements were performed with a Panalytical XPert diffractometer with Cu K$_\alpha$ radiation ($\lambda$ = 1.5406 Å). FTIR spectra were recorded on an Avatar 360 spectrophotometer ( Nicolet, USA). XPS was conducted on a Multilab 2000 X-ray photoelectron spectrometer (Thermo Electron Corporation, USA) with Mg K$_\alpha$ radiation at 300 W. The observed spectra were corrected by a C1s binding energy at 284.0 eV [25]. N$_2$ adsorption–desorption at –196$^\circ$C were carried out on a TriStar 3000 surface area and porosimetry analyzer (Micromeritics, USA) after degassing of the samples at 300$^\circ$C for 3 h. The pore diameter distributions were calculated from desorption branches of isotherms based on a BJH method. Transmission electron microscopy (TEM) experiments were performed by using a Philips-FEI Tecnai 30 microscope operated at 300 kV. Sample particles were suspended in alcohol and the suspension was deposited on a copper grid coated with a polymer supported film and carbon.

2.3. Electrochemical tests

Electrochemical performance of TiP$_2$O$_7$ samples was evaluated by using of CR2025 coin cells [27]. The cathodes were prepared by mixing 75% of the active material with 20% carbon black and 5% PVDF. The cells were assembled with the cathode as prepared, lithium metal as anode, and Celgard 2300 film as separator in an argon-filled glove box (Model 100G, MBraun, Germany, C$_{H_2O}$ < 2 ppm, C$_{O2}$ < 2 ppm). Charge–discharge experiments were performed between 1.5 and 4.0 V at 0.1 C and then 1 C rate (current density: 12 and 120 mA g$^{-1}$) by using a LAND CT2001A Battery Cycler (Wuhan, China).

3. Results and discussion

3.1. Materials synthesis

In order to get mesoporous TiP$_2$O$_7$, we used TG/DTA techniques to make sure of the appropriate calcination temperatures of the precursors. Fig. 1A shows a set of TG/DTG/DTA curves of the dried gel. The main weight loss (40%) occurs over the temperature range from 150 to 400$^\circ$C, which corresponded to the decomposition and combustion of P123 and other derived organic compounds. This main weight loss, containing two different processes centered at 234 and 257$^\circ$C shown in the DTG curve (Fig. 1A inset), brings a strong endothermic peak at 240$^\circ$C and a weak exothermic peak at 300$^\circ$C in the DTA curve. No significant weight loss is observed at higher temperature. Exothermic peak at 859$^\circ$C in the DTA curve, with no weight loss, is caused by the crystallization process of TiP$_2$O$_7$. 
According to the above results, a series of samples were synthesized at 500, 600, 700, 800 and 900 °C. XRD results show that the crystal TiP$_2$O$_7$ phase can be found in the samples synthesized at 800 and 900 °C, which do not agree well with the previous thermal analysis results, i.e. the crystallization temperature of TiP$_2$O$_7$. This might be due to the burning of the organic components in the precursor and the higher heating rate in the thermal analysis experiments than that during samples preparation. Then, P123 was extracted by ethanol from the precursor before thermal analysis experiments. Fig. 1 B shows the TG/DTG/DTA curves of the treated precursor. At this time, the main loss (20%) centers at 120 °C, while only 10% weight loss centering at 298 °C is generated from 200 to 400 °C, caused by the decomposition of organic–inorganic hybrid network which was formed by Ti(OC$_4$H$_9$)$_4$ and other reactants. The significant change is that the crystallization temperature of TiP$_2$O$_7$ decreased to 792 °C. Therefore, we conclude that the faster heating rate (10 °C min$^{-1}$) must have caused the severe decomposition of P123 leaving many non-uniform pores in the samples, then resulting in the decrease of the thermal conductivity of the materials, and finally increasing the crystallization temperature of TiP$_2$O$_7$. In this work, only representative samples prepared at 600, 700 and 800 °C under the flow of pure N$_2$ were studied here. It is measured that the residual carbon in above three samples were 2.76, 0.90 and 0.29 wt.%, respectively. The specific capacities of the materials were corrected by considering the residual carbon.

3.2. Materials characterizations

3.2.1. XRD

As shown in Fig. 2, several diffracting peaks of crystalline phase can only be observed in the LA-XRD (large angle X-ray diffraction) pattern of the sample prepared at 800 °C. This crystalline phase was identified as cubic TiP$_2$O$_7$ with a Pa3 (205) space group (ICDD#38-1468) by using an X'pert HighScore software [25]. No crystalline phase can be found in the samples prepared at 600 and 700 °C. In the SA-XRD (small angle X-ray diffraction) diagram (Fig. 2 inset), only sample prepared at 600 °C shows one shoulder peak at around 2θ = 0.78°, which indicates the relatively ordered mesoporous structure in it. But it is quite hard and not accurate to decide the d-spacing value and then the pore size only based on this shoulder peak. However, no clear peak can be observed in the SA-XRD pattern of the other two samples. The microstructure of these three samples will be further characterized by N$_2$ adsorption and TEM experiments.

3.2.2. XPS and FTIR

All samples were further characterized by XPS and FTIR techniques. Fig. 3A shows high-resolution XPS spectra of the Ti(2p3/2) peaks. In crystalline TiP$_2$O$_7$, Ti$^{4+}$ lies in octahedral site with Ti(2p3/2) at a binding energy of 459.8 eV, similar to that reported in Ref. [25], and other two amorphous samples at 459.7 eV. No much difference for Ti(2p3/2) peaks was found in these crystalline and amorphous samples.

Fig. 1. TG (△), DTA (△) and DTG (inset) curves of gel precursor with surfactant (P123) (A) and P123-free gel precursor (B). The arrows show the exothermic direction of the curves.

Fig. 2. Large angle XRD (LA-XRD) and small angle XRD (SA-XRD, inset) patterns of TiP$_2$O$_7$ calcined at 600 °C (a), 700 °C (b) and 800 °C (c).
The FTIR spectra of crystalline and amorphous TiP$_2$O$_7$ are mainly caused by the vibrations of (P$_2$O$_7$)$_4$ group, which has been demonstrated by Marcu et al. [28]. The FTIR spectra of our three samples in the range of 500–1500 cm$^{-1}$ are presented in Fig. 3B. The spectrum of the crystalline TiP$_2$O$_7$ (Fig. 3B, curve c) exhibits a broad maximum between 1000 cm$^{-1}$ and 1200 cm$^{-1}$, which should be assigned to P–O vibrations of pyrophosphates. The two bands at 961 and 745 cm$^{-1}$ should be attributed to P–O–P vibrations and two weak bands at 623 and 566 cm$^{-1}$ assigned to O–P–O vibrations. In the case of amorphous mesoporous TiP$_2$O$_7$ (Fig. 3B, curves a and b), similar bands but broader absorption were observed. The band between 1000 and 1200 cm$^{-1}$ is largely broaden, which causes the peak at 961 cm$^{-1}$ to appear as a shoulder peak. Moreover, the maximum of this broad band shifts from 1095 cm$^{-1}$ to 1088 and then 1062 cm$^{-1}$, indicating an increase of the P–O bond distances in an amorphous state [28]. We also observed another two broad peaks, one located at 745 cm$^{-1}$ and the other located between 623 and 566 cm$^{-1}$. That all of the three samples show two peaks at 961 and 745 cm$^{-1}$ indicates the existence of pyrophosphate groups.

### 3.2.3. N$_2$ adsorption and TEM

Normally, excessive P precursor does not cross-link effectively with each other to form inorganic framework [29]. Therefore, the reported mesoporous titanium phosphates, such as TiPO$_x$ (Ti:P = 1:1) and TiO$_2$–P$_2$O$_5$ (Ti:P = 3:2) [30–32], are both low P content. Here we reports a high P content mesoporous material–TiP$_2$O$_7$ (Ti:P = 1:2). In the following paragraphs, it can be seen that quite good mesoporous structure of TiP$_2$O$_7$ can be synthesized under suitable conditions. Fig. 4 shows the N$_2$ adsorption/desorption isotherm plots and pore diameter distribution plots of the three samples. Typical type-IV isotherm plots of samples prepared at 600 and 700 °C indicate the club-shaped mesoporous structure. Besides, overlapped lamellar mesoporous materials can be observed in the sample prepared at 600 °C (Fig. 5A). But the crystalline sample calcined at 800 °C does not show any mesoporous structure in pore diameter distribution plot (Fig. 4 inset), which can be further supported by TEM image (Fig. 5C). The microstructure of this crystalline TiP$_2$O$_7$ sample can be seen in the HR-TEM image (Fig. 5C inset). As the calcination temperature increased from 600 to 700 and 800 °C, the pore diameter distributions are broaden, but the specific surface areas (BET) of the three samples decrease significantly from 185 to 119 and then 8.6 m$^2$ g$^{-1}$, and the pore volumes from 0.51 to 0.44 and 0.07 cm$^3$ g$^{-1}$. In addition, the center of pore diameter distributions of the samples changed from 8.0 nm for 600 °C sample and 11.2 nm for the 700 °C sample. No mesoporous information for the 800 °C sample.

### 3.3. Electrochemical performance of mesoporous TiP$_2$O$_7$

Electrochemical performances of mesoporous TiPO$_x$ electrode material were preliminarily reported for the first time in this lab in the previous study [30]. It was shown that mesoporous TiPO$_x$ showed an average discharge potential of 2.4 V and delivered a specific capacity of 95 mA h g$^{-1}$ at the first cycle at 1 C. Fig. 6 shows three discharge curves at the first cycle (rate: 0.1 C) and related differential capacity–potential curves of three TiP$_2$O$_7$ samples. It is found that the voltage profile of TiP$_2$O$_7$ calcined at 800 °C displays a plateau at about 2.6 V vs Li$^+$/Li, similar to that of reported crystalline TiP$_2$O$_7$ [25]. According to the corresponding differential capacity–potential curve (Fig. 6 inset
c), this lithium ion insertion behavior can be divided into two distinguished processes at 2.63 and 2.55 V, which have been proved to represent two different two-phase domains by Patoux et al. [33]. As for the other two mesoporous TiP$_2$O$_7$ samples calcined at 600 and 700 °C, the lithium ion insertion behavior are quite different from the crystalline one (i.e. the sample calcined at 800 °C), both of them show a slope curve from 3.0 to 2.3 V in the discharge experiments and one broad peak on the differential capacity–potential curves (Fig. 6 inset a and b), which indicate a consecutive lithium insertion process similar to that of solid solution. The onset lithium ion intercalation potential in the first discharge curve increases from 2.7 V in crystalline TiP$_2$O$_7$ to 3.0 V in mesoporous TiP$_2$O$_7$ (Fig. 6). The higher discharge voltage of meso-TiP$_2$O$_7$ means the more energy needed in the lithium ion intercalation process because Ti$^{4+}$ locates at a lower energy level in the mesoporous TiP$_2$O$_7$ than in the crystalline TiP$_2$O$_7$ which might be caused by the effects of P$_2$O$_7^{4-}$ with longer P–O bond length in meso-TiP$_2$O$_7$ as measured by FTIR experiments (Fig. 3B). In addition, mesoporous TiP$_2$O$_7$ shows an average discharge potential at 2.6 V, higher than that of mesoporous TiPO$_x$ [30] (about 2.4 V) and nano-TiO$_2$ [34] (about 1.6 V). Therefore, we can conclude that our mesoporous samples are not just mechanically mixed by titanium oxides and phosphorous oxides, but really composed of TiP$_2$O$_7$.

The electrochemical performance of the three samples was also investigated by charge/discharge measurements at the various rates (as shown in Fig. 7). It is known that the theoretical capacity of TiP$_2$O$_7$ is 121 mA h g$^{-1}$. At a low charge/discharge rate of 0.1 C, the discharge capacities at first cycle are 90, 98 and 99 mA h g$^{-1}$ for the samples prepared at 600, 700, and 800 °C, respectively. All of the three samples show that the first irreversible capacities are about 10 mA h g$^{-1}$. If these samples are further cycled at high rate of 1 C, the TiP$_2$O$_7$ sample prepared at 700 °C
delivers the highest capacity of 57 mA h g⁻¹, but the crystalline one only gets a capacity of 49 mA h g⁻¹ and the one prepared at 600 °C below 40 mA h g⁻¹. The low capacities at high rate of the crystalline TiP₂O₇ sample might be caused by the poor lithium intercalation kinetics in the crystal structure. For the other sample prepared at 600 °C, the effects might be due to its smaller pore size (Fig. 4 inset) and existence of other un-reacted impurity. These results also imply the role of mesoporous structure in facilitating the fast transport and intercalation kinetics of lithium ion in the materials. In this respect, the improved behavior is quite similar to our previous study of mesoporous FePO₄ material [17]. Therefore, this work presents a new example for improving the performance of poly-anion type materials with mesoporous structure at high rate for batteries and other energy storage devices such as high power batteries and electrochemical supercapacitors.

4. Conclusions

In summary, mesoporous TiP₂O₇ can be easily prepared by a sol–gel template method with further calcinations at 600 or 700 °C. The mesoporous TiP₂O₇ becomes crystalline at higher temperature accompanied with the break down of mesoporous structure. Mesoporous TiP₂O₇ shows a lithium ion insertion behavior similar to that of solid solution. At high current density, mesoporous TiP₂O₇ shows a higher specific capacity than that of the crystalline one, which should be due to its mesoporous structure which improve the transport and intercalation kinetics of lithium ions. These results will also help us to understand the role of meso-structure and their applications in electrode materials for lithium batteries and electrochemical supercapacitors.

Acknowledgement

The financial supports from the National Natural Science Foundation of China (No: 20433060, 20473068, 29925310, 20021002) and the Ministry of Science and Technology of China (2001CB610506) are acknowledged.

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