

Spray-Pyrolysis Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Si}$ Composites for Lithium-Ion Batteries

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Abstract

This paper introduces the novel anode material which is $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Si}$ prepared by gas-stated method, mainly spray-pyrolysis technique. The literature review performed in this paper revealed two main components which can be potentially mixed into the efficient anode material. Silicon (Si) has the highest possible capacity of 4200 mAh g^{-1} among all commonly used anodes. Due to its ‘zero-strain’ (<1% volume change) properties and stable cycling, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is considered as a promising anode for lithium ion batteries. Combination of these two anode materials is considered as a promising approach to prepare a high performance composite anode. The precursor solution consisted of homogeneous mixture of lithium nitrate and titanium tetraisopropoxide dissolved in deionized water with equimolar concentration of 0.5 M. The aerosol formation was performed at nitrogen environment and the droplets were carried into the quartz tube reactor at the flowrate of 4 L min^{-1} . The reactor temperature was held at 800 °C. The spray-pyrolysis synthesis was performed as one-step operation, excluding the need of calcination of as-prepared powders, and continuous process by the mean of peristaltic pump. The as-prepared powders had wide size distribution from nanometers to microns. The materials obtained had well-crystallized structure with insignificant amount of impurities. The powders were analyzed by the following analytical equipment: 1) the presence of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Si in the obtained composite was confirmed by X-ray diffraction technique (XRD); 2) The structure and morphology of LTO and Si molecules were observed and studied with Scanning Electron Microscopy (SEM).

1. Introduction

Increasing concern of energy crisis and environment pollution has been recognized as an issue warranting consideration. The current challenges in energy and environment demand an emerging renewable energy. Thereby, lithium-ion batteries (LIBs) have been recognized as a part of pollution-free renewable energy sources because they present modern efficient energy storage system. LIBs are widely used by the society because of their small volume, slow discharging rate, reusability (they can be used over many cycles), high power density and energy. However, LIBs with graphite-based anode, which is the most used

anode material for LIBs, are not suitable for modern electric vehicles of different type (hybrid, plug-in or pure) and other modern communication systems, because they require two to five times more energy density than LIBs with graphite-based anode can offer [1–3]. Thus, there is an extreme need for introduction of novel materials for anode replacement in LIBs. Despite that lithium metal has one the highest capacities of 3860 mAh g^{-1} , it is unsafe to use this material as anode in LIBs, because it can cause a short circuit between the electrodes [4].

Titanium oxides have several remarkable features which are minimum safety issues, low cost, low toxicity, volume stability (1–3% change) and long life duration [5, 6]. On the other hand, titanium oxides have low theoretical capacity (175–350 mAh g^{-1}) and low electronic conductivity [7].

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Therefore, they are mainly used as an additive to the other active materials to improve capacity, cycling and rate capability [8]. The most efficient combination of titanium dioxide is the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), because of superior Li-ion reversibility at relatively high operating potential of 1.55 V vs Li/Li⁺. One of the advantages of this compound is the stability of the structure during the insertion of Li-ions [5, 9], and because of that the solid electrolyte interface (SEI) does not appear and dendrites, which is of the most concern in carbon-containing anodes, can be avoided. However, despite of the safety conditions which bring the usage of LTO and its suitability as anode in LIBs, there are some drawbacks of this compound. It has very low theoretical capacity (175 mAh g⁻¹) and low electronic conductivity (10–13 S cm⁻¹) leading to the reduction of the diffusion rate of Li-ions into the structure and charge-discharge rate [10]. Thus, there is a need for treatment techniques to overcome these problems, which will be discussed further. The first method is bringing the compound to nanoscale. Prakash et al. reported the way of synthesis of nano-crystalline LTO with the size range of 20–50 nm by solution combustion [11]. The result of his experiment is achievement of 170 mAh g⁻¹ of discharge capacity at 0.5C current rate (cycling).

Silicon is the component, which in chemical compound with lithium ($\text{Li}_{12}\text{Si}_5$) has the highest theoretical capacity of 4200 mAh g⁻¹ among the materials which have been discussed [12]. It has low discharge potential of 0.4V which is comparable with graphite. In addition, silicon is abundant on the earth, which makes it inexpensive and environmentally friendly material. However, the increase in volume almost by 360–400% during the charging and discharging damages the structure of the battery and causes short cycling life, irreversibility of lithium extraction and capacity damping [13]. Consequently, to overcome the above presented problems many efforts have been made: for instance, Park et al. achieved high specific capacity of 865 mAh g⁻¹ at 0.5C, significant improvement of volume change (increase by 42% after 200 cycles), and superior cycle and rate stabilities by producing Si nano-sheets using natural clays and molten salt-induced exfoliation [14]. Also, transcendent results were obtained by Chan et al. when the direct growth of Si nano-wires on the metallic collectors was performed [15]. Due to the direct electronic contact of Si nano-wires with the current collector, all the nano-wires took place in the alloy process,

good charge transport mechanism become possible, and volume increase was easily fitted because of the small diameter of Si nano-wires. The results of this experiment were 3500 mAh g⁻¹ of the specific capacity at 0.2C rate (for 20 cycles) and 2100 mAh g⁻¹ at 1C rate. However, despite the superior effectiveness of the methods described above and other methods developed by the researches to improve suitability of the Si in anode of LIBs, these techniques are not commercially reasonable which makes them not applicable for the industrial scale. Consequently, the alternative methods for materials fabrication are developed such as formation of matrices of active and inactive materials mentioned above. There are many techniques to fabricate these matrices such as spray-drying methods (e.g. spray pyrolysis), dry ball milling, wet ball milling, hydrothermal and solvothermal methods. However, the composites obtained by the solid-states method are widely used and described in details in literature, meanwhile, gas-state reactions are not well-investigated.

In this work, spray-pyrolysis method is used to prepare LTO/Si composite as anode material for LIB.

2. Experimental section

2.1. Materials synthesis

The precursor solutions were prepared by dissolving lithium nitrate (LiNO_3) and titanium tetraisopropoxide (TTIP, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) in distilled water. The concentration of the precursor solutions was 0.5M for both of them. Then, the solution was mixed with Si nanopowder (30–50 nm, Guangzhou Jiechuang Trading Co.) at ratio 95:5 respectively.

The spray-pyrolysis system, illustrated in Fig. 1 below, consists of the droplet generator, nebulizer, quartz-tube furnace and filter introduced at the exit of the reactor. The nebulizer was used to generate aerosol flow which was directed into the high-temperature quartz tube by the carrier gas (N_2). The precursor solution is fed into the nebulizer by peristaltic pump at the rate of 1 rpm. The droplets evaporated and decomposed in the reactor; the reaction proceeded in nitrogen gas environment. The powder is deposited on Teflon filter, which is then put into vacuum oven at 120 °C for 2 h. The dimensions of tubular reactor are 120 cm in length and 6 cm in diameter. The reactor temperature was maintained at 800 °C. The flow rate of nitrogen gas was set 4L/min.

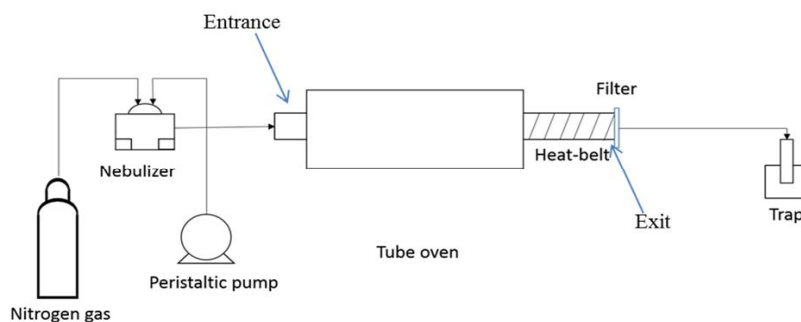


Fig. 1. Spray-pyrolysis apparatus setup.

2.2. Characterization

LTO, Si and LTO/Si composites were characterized by the X-ray diffraction (XRD, Rigaku SmartLab) using Cu-K α radiation ($\lambda = 0.15406$ nm) within a 2θ range of $10\text{--}80^\circ$. Morphology and microstructure of the samples were characterized by scanning electron microscopy (FE-SEM, JEOL JSM-7500F).

3. Results and discussion

Figure 2 shows the XRD patterns for the samples of different content. Figure 2a shows the sample containing sucrose, which was used as carbon source. As it can be seen, the powder collected is composed of primarily LTO and Si with small amount of carbon. Figure 2b-2c illustrate the spectra of the composite LTO/Si at the inlet and outlet of the tubular reactor respectively. Both spectrums exhibit the diffraction patterns of LTO and Si. As it can be seen from all the samples, rutile and anatase TiO₂ are formed as the by-products of the reaction.

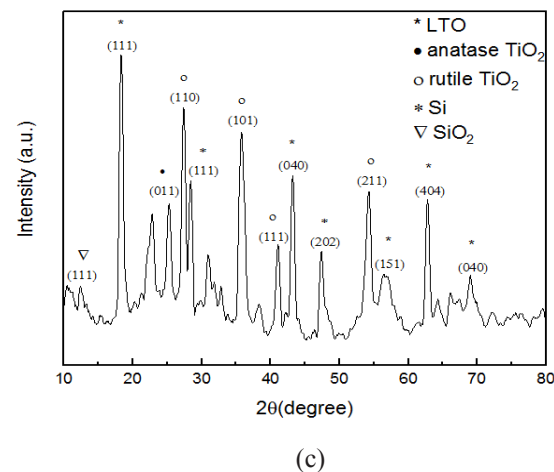
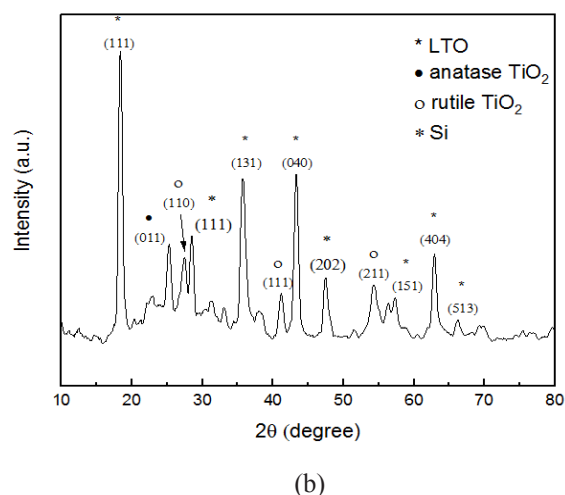
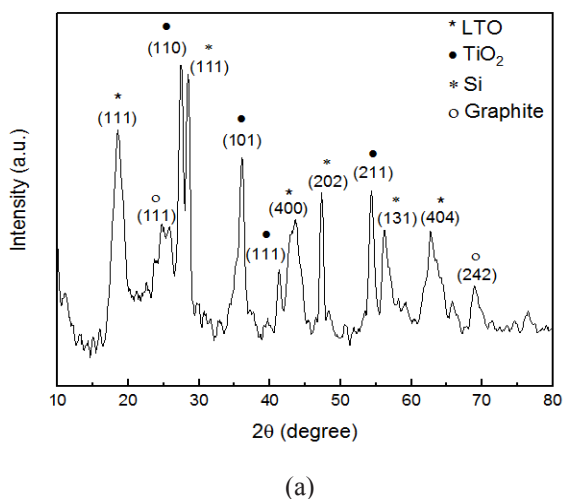


Fig. 2. XRD pattern: (a) – LTO/Si/C at operating conditions of 800°C , 4L/min, 0.5M, 40:3:57; (b) – LTO/Si at the entrance of the reactor at operating conditions of 800°C , 4L/min, 0.5M, 5% of Si; (c) – LTO/Si at the exit of the reactor at operating conditions of 800°C , 4L/min, 0.5M, 5% of Si.

SEM images in Figure 3 show the morphologies of the above described samples. As it can be seen, the silicon powders present a spherical morphology with size range from 30 to 90 nm (Fig. 3a). The LTO shows the same structure but with a size range of 100 to 900 nm (Fig. 3b).

Figure 3c and 3d illustrates the structure of LTO/Si sample at the entrance and the exit of the reactor. Some aggregation can be observed. As it can be seen, the LTO spheres are surrounded by the bulky structure of Si nanospheres. It can be said that the spray-pyrolysis technique is capable

to provide nanosize spheres of the desired product, LTO and Si nanomatrix in this particular case. SEM images demonstrate very dense coating of LTO spheres by Si spheres, which can enhance the electrochemical properties of the material.

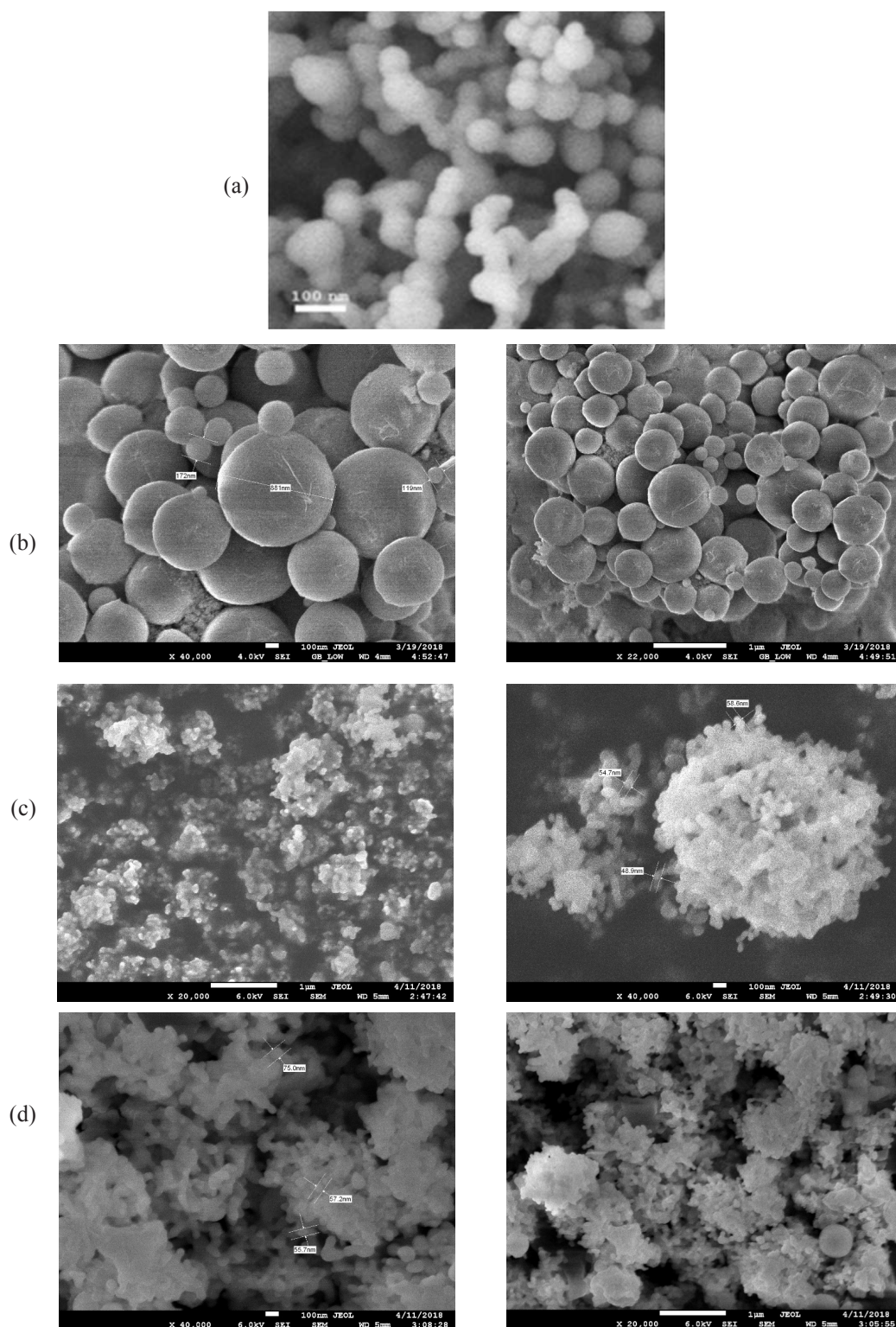


Fig. 3. SEM images of the Si nanopowder and collected powder: (a) – Si nanopowder; (b) – LTO at operating conditions of 800 °C, 4L/min, 0.5M; (c) – LTO/Si at the entrance of the reactor at operating conditions of 800 °C, 4L/min, 0.5M, 5% of Si; (d) – LTO/Si at the exit of the reactor at operating conditions of 800 °C, 4L/min, 0.5M, 5% of Si.

4. Conclusions

Spray-pyrolysis method has been successfully used to synthesize LTO/Si composites. The material produced is distinguished by spherical shape and nanosize. The obtained powder has spherical morphology and contains significant amount of LTO. The nanospheres showed very large size distribution, from 90 to 900 nm. The optimum operating conditions were set according to the literature review; it was concluded that changing the synthesis conditions, the sizes of spheres and content of the product can be adjusted. The electrochemical characterization and investigation of other carbon sources is in progress.

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References

- [1]. A. Manthiram, *J. Phys. Chem. Lett.* 2(3) (2011) 176–184. DOI: 10.1021/jz1015422
- [2]. L. Yanga, B. Ravdelb and B.L. Lucht, *Electrochem, Solid-State Lett.* 13 (2010) A95–A97. DOI: 10.1149/1.3428515
- [3]. R. Marom, S.F. Amalraj, N. Leifer, D. Jacob and D. Aurbach, *J. Mater. Chem.* 21 (2011) 9938–9954. DOI: 10.1039/C0JM04225K
- [4]. F. Orsini, A. du Pasquier, B. Beaudouin, J.M. Tarascon, M. Trentin, N. Langenhuizen, E. de Beer and P. Notten, *J. Power Sources* 76 (1998) 19–29. DOI: 10.1016/S0378-7753(98)00128-1
- [5]. M. Wagemaker and F.M. Mulder, *Acc. Chem. Res.* 46 (2013) 1206–1215. DOI: 10.1021/ar2001793
- [6]. P. Li, S.S. Qian, H.X. Yu, L. Yan, X.T. Lin, K. Yang, N.B. Long, M. Shui and J. Shu, *J. Power Sources* 330 (2016) 45–54. DOI: 10.1016/j.jpowsour.2016.08.138
- [7]. K. Yang, H. Lan, P. Li, H. Yu, S. Qian, L. Yan, N. Long, M. Shui and J. Shu, *Ceram. Int.* 43 (2017) 10515–10520. DOI: 10.1016/j.ceramint.2017.05.105
- [8]. A. Moretti, G.T. Kim, D. Bresser, K. Renger, E. Paillard, R. Marassi, M. Winter and S. Passerini, *J. Power Sources* 221 (2013) 419–426. DOI: 10.1016/j.jpowsour.2012.07.142
- [9]. S.K. Martha, O. Haik, V. Borgel, E. Zinigrad, I. Exnar, T. Drezen, J.H. Miners, and D. Aurbach, *J. Electrochem. Soc.* 158 (2011) A790–A797. DOI: 10.1149/1.3585837
- [10]. G.N. Zhu, L. Chen, Y.G. Wang, C.X. Wang, R.C. Che and Y.Y. Xia, *Adv. Funct. Mater.* 23 (2013) 640–647. DOI: 10.1002/adfm.201201741
- [11]. A.S. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J.M. Tarascon and A.K. Shukla, *Chem. Mater.* 22 (2010) 2857–2863. DOI: 10.1021/cm100071z
- [12]. X. Zuoa, J. Zhua, P. Müller-Buschbaum and Y.-J. Cheng, *Nano Energy* 31 (2017) 113–143. DOI: 10.1016/j.nanoen.2016.11.013
- [13]. M. Rahman, G. Song, A.I. Bhatt, Y.C. Wong and C. Wen, *Adv. Funct. Mater.* 26 (2016) 647–678. DOI: 10.1002/adfm.201502959
- [14]. T. Song, J. Xia, J.-H. Lee, D.H. Lee, M.-S. Kwon, J.-M. Choi, J. Wu, S.K. Doo, H. Chang, W.I. Park, D.S. Zang, H. Kim, Y. Huang, K.-C. Hwang, J.A. Rogers and U. Paik, *Nano Lett.* 10 (2010) 1710–1716. DOI: 10.1021/nl100086e
- [15]. C.K. Chan, R.N. Patel, M.J. O’Connell, B.A. Korgel, Y. Cui, *ACS Nano* 4 (2010) 1443–1450. DOI: 10.1021/nn901409q