Journal of Alloys and Compounds 581 (2013) 236–240

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Synthesis process investigation and electrochemical performance characterization of $SrLi_2Ti_6O_{14}$ by *ex situ* XRD

Jianhong Liu [a,b], Yanan Li [b], Xingqin Wang [b], Yun Gao [b], Ningning Wu [b], Borong Wu [a,*]

[a] School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China
[b] CITIC Guoan Mengguli Power Science and Technology Co., LTD, Beijing 102200, China

ARTICLE INFO

Article history:
Received 25 January 2013
Received in revised form 11 July 2013
Accepted 11 July 2013
Available online 20 July 2013

Keywords:
Solid state reaction
$SrLi_2Ti_6O_{14}$
Standard-less quantitative analysis
Capacity retention

ABSTRACT

The solid state reactions of $SrLi_2Ti_6O_{14}$ was investigated using thermo-gravimetric and differential thermal analysis (TG–DTA), *ex situ* X-ray diffraction (XRD), and scanning electron microscopy (SEM). The phase compositions of samples obtained at temperatures of 500–1000 °C were identified by their respective XRD patterns. The relative quantities of each phase were analyzed using standardless quantitative analysis. The changes in composition during the solid-state reaction were discussed and three reactions possibly involved in the formation of $SrLi_2Ti_6O_{14}$ were examined. The $SrLi_2Ti_6O_{14}$ obtained at 950 °C had minimal impurities, noticeable high rate performance, and achieved 90% capacity retention in a coin cell at room temperature after 1000 cycles at a 1C rate.

1. Introduction

As the global energy crisis and environmental problems unfold, environmental friendliness and energy efficiency have become increasingly important. Lithium-ion batteries have high energy density and have thus received intense attention as a power source in hybrid electric vehicles, plug-in hybrid electric vehicles, and fully electric vehicles [1,2]. As a key component in lithium-ion batteries, anode material has become a research hotspot in recent years, especially $Li_4Ti_5O_{12}$ material due to zero strains during charge–discharge and non-formation of solid-electrolyte interfaces [3,4]. However, when used at high rate conditions, it remains difficult for $Li_4Ti_5O_{12}$ to retain high capacity and cycling stability due to its low electronic conductivity [5]. In addition, the output voltage of lithium-ion batteries using $Li_4Ti_5O_{12}$ as the anode is lower than those of lithium-ion batteries that use carbonaceous anodes. This lower output voltage in batteries with a $Li_4Ti_5O_{12}$ anode decreases its energy density and leads to shorter endurance mileage when these batteries are used in electric vehicles [6]. Thus, it is necessary to investigate other anode materials with lower operating voltages (vs. Li^+/Li) in order to increase overall energy density of the cell while operating within the electrolyte stability region.

$SrLi_2Ti_6O_{14}$ has also received much attention for use as an anode in lithium-ion batteries, in part because of its lower voltage range for inserting lithium ions [7–9]. The theoretical capacity of $SrLi_2Ti_6O_{14}$ is 262 mA h/g if all six Ti^{4+} ions are reduced to Ti^{3+}. Additionally, $SrLi_2Ti_6O_{14}$ has higher tap density than does $Li_4Ti_5O_{12}$, and lithium-ion batteries built with it can more easily achieve a higher volume energy density [9]. Single crystals of $SrLi_2Ti_6O_{14}$ were first prepared using the flux method in 2002 [10], and the electrochemical performance of $SrLi_2Ti_6O_{14}$ powder was first investigated in 2003 [7]. $Na_2Li_2Ti_6O_{14}$ was subsequently synthesized and was demonstrated to have a crystal structure with Cmca space group, similar to $SrLi_2Ti_6O_{14}$ and $BaLi_2Ti_6O_{14}$ [11,12]. The Li insertion behavior and electrochemical properties of the isostructural materials $Na_2Li_2Ti_6O_{14}$ and $BaLi_2Ti_6O_{14}$ when used as anodes had also been studied [8]. $SrLi_2Ti_6O_{14}$ was shown to have better electrochemical properties, and it was thought to be a promising anode in high-power Li-ion batteries. However, it has been difficult to obtain pure $SrLi_2Ti_6O_{14}$, even when synthesized using the sol–gel method [8]. Thus, it is necessarily to investigate the details of $SrLi_2Ti_6O_{14}$ synthesis, clarify the mechanisms and means of impurity occurrence and removal, and provide basic information for future mass-production. To our knowledge, no studies have reported on the details of phase transitions of $SrLi_2Ti_6O_{14}$ during sintering.

In this work, we calcined $SrLi_2Ti_6O_{14}$ at temperatures of 500–1000 °C, and then used *ex situ* X-ray diffraction and standardless quantitative analysis to investigate the reactions and phase changes that occurred, as well as the impurities present. By comparing the products found at different reaction temperatures, we

* Corresponding authors. Address: School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China (B. Wu). Tel./fax: +86 010 89702984.
E-mail addresses: ljh2962@gmail.com (J. Liu), borongwu@gmail.com (B. Wu).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.07.070

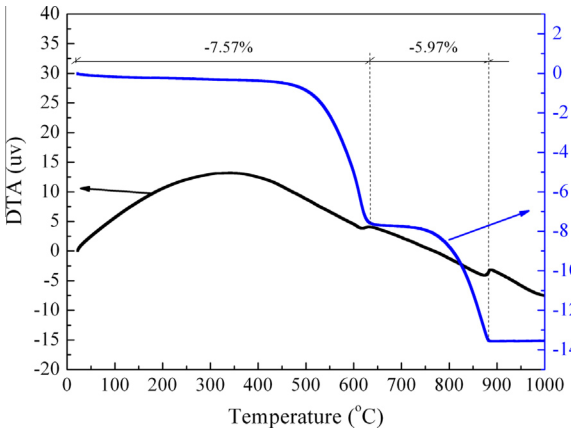

Fig. 1. Thermal analysis cures of the precursor in O_2 atmosphere.

found the $SrLi_2Ti_6O_{14}$ sintering condition that produced the least impurities to be 950 °C for 8 h. After synthesizing $SrLi_2Ti_6O_{14}$, we characterized its electrochemical performance.

2. Experimental

2.1. Materials preparation

The starting materials of $SrCO_3$ (Sinopharm, Beijing, China, AR), Li_2CO_3 (Tianqi, Sichuan, China, 99.95%), and anatase TiO_2 (99.5%, mean size = 50 nm, Hangzhou Wanjing Co. Ltd., China) were mixed in a planetary ball mill at a molar ratio of Sr/Li/Ti = 1:2.04:6 (0.04 unit of Li used to compensate for Li volatilization) using pure ethyl alcohol as a solvent. ZrO_2 balls with 5 mm diameter were used as media and the materials were milled for 60 min at a minimum rotation speed of 400 rpm. After mixing, the precursors were evaporated until completely dry. The precursors were then ground, placed in a box furnace, and calcined at temperatures varying from 500 °C to 1000 °C for 8 h under an air atmosphere. After sintering, the samples were ground and sieved through a 150 mesh sieve for subsequent characterization and testing.

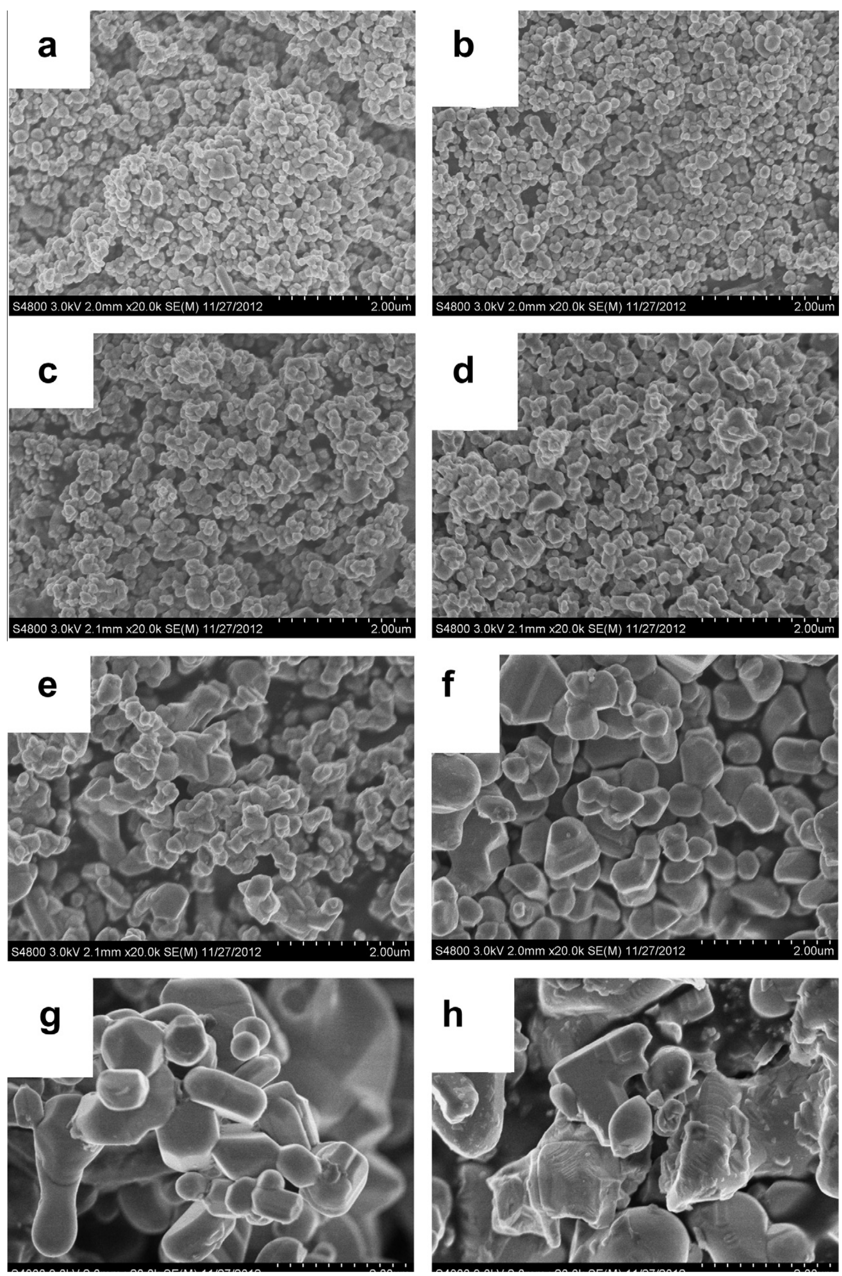

Fig. 2. SEM photographs of various samples, calcined for 8 h at different temperatures: (a) raw materials, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, (f) 900 °C, (g) 950 °C and (h) 1000 °C.