

Short communication

Synthesis and electrochemical performance of $\text{Li}_2\text{CoSiO}_4$ as cathode material for lithium ion batteries

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Abstract

$\text{Li}_2\text{CoSiO}_4$ has been prepared successfully by a solution route or hydrothermal reaction for the first time, and its electrochemical performance has been investigated primarily. Reversible extraction and insertion of lithium from and into $\text{Li}_2\text{CoSiO}_4$ at 4.1 V versus lithium have shown that this material is a potential candidate for the cathode in lithium ion batteries. At this stage reversible electrochemical extraction was limited to 0.46 lithium per formula unit for the $\text{Li}_2\text{CoSiO}_4/\text{C}$ composite materials, with a charge capacity of 234 mAh g^{-1} and a discharge capacity of 75 mAh g^{-1} . © 2007 Published by Elsevier B.V.

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1. Introduction

Since the demonstration of reversible lithium intercalation between the layers of TiS_2 [1], considerable effort has been devoted to the identification of other lithium-insertion compounds that can be used as the cathode for a secondary lithium battery. During recent decades, intensive research on transition metal oxides with a framework structure suitable for rapid insertion/extraction of lithium ions has led to the development of a variety of positive active materials for secondary lithium batteries, including LiCoO_2 , LiNiO_2 with a layered structure [2,3], and LiMn_2O_4 [4] with a spinel structure. More recently, polyanionic cathodes such as olivine type LiMPO_4 [5–7] have attracted considerable attention as next-generation cathodes due to their better safety characteristics compared with metal oxide materials, which act as strong oxidizers at charged state in direct contact with an organic electrolyte [8]. Compared with phosphate materials which only one lithium ion can be reversibly cycled, silicate materials (Li_2MSiO_4) would allow reversible extraction of two lithium ions in principle thus it should deliver higher capacity (e.g., $\text{Li}_2\text{MnSiO}_4$: 333 mAh g^{-1} and $\text{Li}_2\text{CoSiO}_4$: 325 mAh g^{-1}) than phosphates. This makes it a very attractive new cathode material for lithium ion batteries. Nyten et al. first reported $\text{Li}_2\text{FeSiO}_4$ as a new cathode material [9]. A first testing of $\text{Li}_2\text{FeSiO}_4$ has shown reversible capacity around 130 mAh g^{-1}

cycled at 60°C at a $C/16$ rate. Jamnik et al. have recently reported 0.6 Li was reversibly exchanged in $\text{Li}_2\text{MnSiO}_4$ in the first cycle [10]. Our group has successfully synthesized $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite materials which delivered a discharge capacity as high as 209 mAh g^{-1} (about 1.25 lithium ions) in the first cycle [11–13], and Fe-doped $\text{Li}_2\text{MnSiO}_4$ such as $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$ [12–14] which delivered a large reversible capacity of 214 mAh g^{-1} with an average discharge voltage of 2.76 V at Mn content as high as $x=0.5$. These indicate that silicates might act as promising cathode materials in lithium ion batteries. As $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$ operate on a lower voltage (discharge plateau at about 2.8 V), it will be very interesting to synthesize $\text{Li}_2\text{CoSiO}_4$ which may operate on a higher voltage.

We have developed a new synthesis route for $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$ by adding sucrose to the synthetic precursor with ball-milling techniques followed by sintering in nitrogen atmosphere.

In this paper, we report the redox behavior of $\text{Li}_2\text{CoSiO}_4$ synthesized by this new method by the ball milling process in the present of carbon to coat the particles with carbon and, alternatively, by hydrothermal reaction. The results demonstrate that this material is a potential candidate for the cathode in lithium ion batteries.

2. Experimental

$\text{Li}_2\text{CoSiO}_4$ was prepared by a solution route [8]. In briefly, 0.04 mol $\text{LiOH}\cdot\text{H}_2\text{O}$, 0.02 mol CoCO_3 and 0.02 mol tetraethyl

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orthosilicate were dispersed in 50 ml ethanol, and were stirred and refluxed at 348 K for 24 h. Then the ethanol was evaporated. The resulting powder was mixed acetone then ground by ball milling. After evaporating the acetone, the mixture was pressed into pellets. The pellets were heated in a horizontal quartz tube oven and calcinated at 873 K for 10 h with a fixed nitrogen flux (50 sccm min^{-1}).

In order to improve the conductivity of the $\text{Li}_2\text{CoSiO}_4$ prepared by a solution route, it was coated with carbon by ball milling process in the present of carbon. Typically, for such experiments, about 0.8 g of $\text{Li}_2\text{CoSiO}_4$ power and 20 wt% carbon is mixed and then milled at a rotation rate of 450 rpm for 20 h; the result carbon-coated $\text{Li}_2\text{CoSiO}_4$ material was used for electrochemical test.

Alternatively, $\text{Li}_2\text{CoSiO}_4$ was prepared by hydrothermal reaction. The starting precursors, 0.02 mol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and nanosized SiO_2 —Cabosil M5 (Cabot Co., USA) were mixed together in 40 mL of deionized water and sonificated in an ultrasonic bath. Graphite was also added to increase the conductivity of the product formed, graphite and $\text{Li}_2\text{CoSiO}_4$ formed in weigh ratio 1: 9 was used. Separately 0.08 mol of $\text{LiOH} \cdot \text{H}_2\text{O}$ was dissolved in 20 mL of deionized water. The prepared dispersion and solution were mixed together and transferred into a Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 180°C for 20 h. Precipitates were collected by suction filtration and dried at 120°C for 20 h in the vacuum oven.

The XRD patterns of $\text{Li}_2\text{CoSiO}_4$ samples were obtained using a Panalytical X-pert diffractometer (PANalytical, Netherlands) with a $\text{Cu K}\alpha$ radiation operated at 40 kV and 30 mA.

The morphology of $\text{Li}_2\text{CoSiO}_4$ particles were observed with a scanning electron microscopy (SEM) (LEO1530 Field Emission Scanning Electron Microscope, Oxford Instrument) operated at 15 kV.

The electrochemical properties of the $\text{Li}_2\text{CoSiO}_4$ samples were assessed using CR2025 coin cells as described in our previous publications [15]. That is, the cathode was prepared by mixing 80% of the active material with 10% carbon black and 10% poly (vinylidene fluoride) (PVDF). The mixture was made into slurry by ball milling using *N*-methyl-2-pyrrolidone (NMP) (water content was below 0.01 wt%) as the solvent. The electrodes were formed by coating the slurry onto Al foils and pressing at 16 MPa after drying overnight at 393 K in a vacuum. The typical cathode loading was $4\text{--}5 \text{ mg cm}^{-2}$. The cells were assembled with the cathode as prepared, with lithium metal as the anode, and with Celgard 2400 film as a separator. The electrolytes were 1 M LiPF_6 dissolved in EC + DMC (1:1 volume ratio). Cell assembly was carried out in an argon-filled glove box (Master 100 Lab, Braun, Germany), where water and oxygen concentrations were kept less than 3 ppm. Cyclic voltammogram (CV) experiment was performed using a CHI 608A potentiostat/galvanostat system (Shanghai, China) in the potential range 3.0–4.6 V at a scanning rate of 0.2 mV s^{-1} . Charge–discharge testing was performed galvanostatically at a 5 mA g^{-1} rate between 3.0 and 4.6 V at 30°C by an Arbin BT-2043 battery test system.

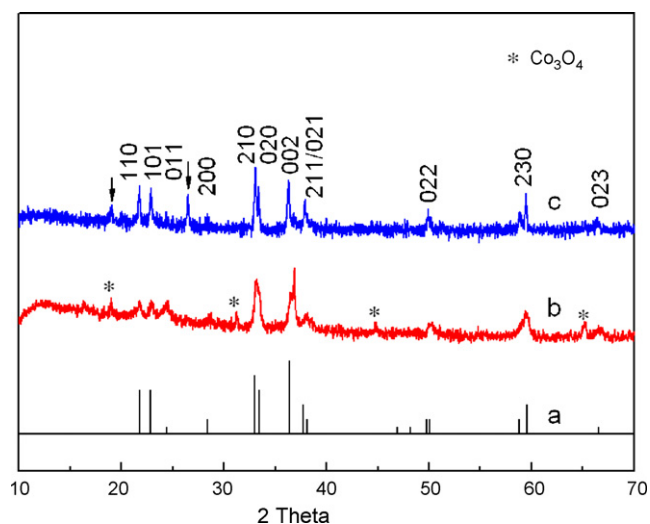


Fig. 1. XRD patterns of (a) $\text{Li}_2\text{CoSiO}_4$ (JCPDS card no. 00-024-0608); (b) $\text{Li}_2\text{CoSiO}_4$ prepared by solution route; (c) $\text{Li}_2\text{CoSiO}_4$ prepared by hydrothermal reaction. The Co_3O_4 impurity for (b) are marked with asterisks (*) and two unidentified peaks for (c) are marked with arrow (↓).

3. Results and discussion

The X-ray diffraction patterns of $\text{Li}_2\text{CoSiO}_4$ samples prepared by solution routine and hydrothermal reaction are shown in Fig. 1. An impurity of Co_3O_4 was detected for the sample prepared by solution routine and two unidentified impurity peaks were observed for the sample prepared by hydrothermal reaction. The crystal system for both two samples could be shown to be orthorhombic and space-group $\text{Pmn}2_1$. The lattice parameters (a , b and c) calculated for $\text{Li}_2\text{CoSiO}_4$ samples prepared by solution routine and hydrothermal reaction were: $a = 6.287(6)$, $b = 5.353(1)$, $c = 4.937(1) \text{ \AA}$, and $a = 6.267(9)$, $b = 5.370(8)$, $c = 4.939(4) \text{ \AA}$, respectively.

Scanning electron microscopy pictures of $\text{Li}_2\text{CoSiO}_4$ powder materials prepared by solution routine and hydrothermal reaction are shown in Fig. 2. SEM analysis indicate that the average size of the $\text{Li}_2\text{CoSiO}_4$ particles prepared by solution routine and hydrothermal reaction is about 0.5–1 and 2–4 μm , respectively.

The cyclic voltammogram for $\text{Li}_2\text{CoSiO}_4$ sample prepared by the hydrothermal reaction is shown in Fig. 3. The material exhibited one oxidation peak at 4.47 V and one distinct reduction peak at 4.10 V, indicating a reversible process of extracting and intercalating lithium from and into $\text{Li}_2\text{CoSiO}_4$. The voltage profiles of $\text{Li}_2\text{CoSiO}_4$ samples prepared by solution routine and hydrothermal reaction with a current rate of 5 mA g^{-1} in a voltage range of 3.0–4.6 V were shown in Figs. 4 and 5, respectively. For the sample prepared by solution routine, we tested the electrochemical performance of both the pristine and carbon coated samples for comparison. The cell potential for both $\text{Li}_2\text{CoSiO}_4$ samples prepared by solution routine and hydrothermal reaction shows a plateau at 4.3 V during charge and a plateau at 4.1 V during the sequent discharge process. As expected, charging/discharging of $\text{Li}_2\text{CoSiO}_4$ proceeds at significantly higher potentials if compared to $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$. A large irreversible capacity was found during the first cycle for both

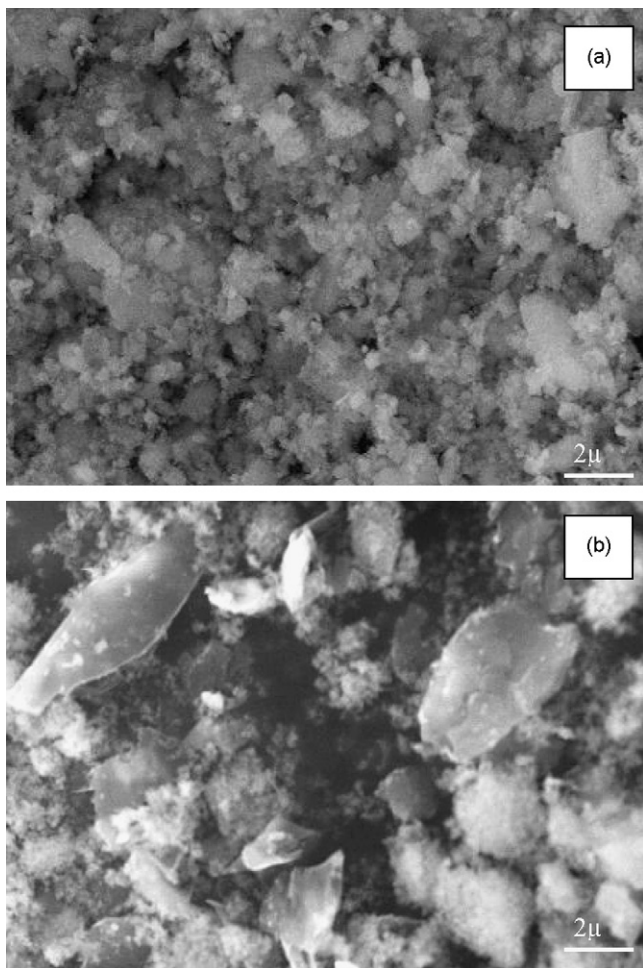


Fig. 2. SEM image of $\text{Li}_2\text{CoSiO}_4$ powder prepared by (a) solution routine and (b) hydrothermal reaction.

$\text{Li}_2\text{CoSiO}_4$ samples. For samples prepared by solution routine, during the 1st charge about 1.0 Li^+ per unit formula can be extracted from the pristine sample, however, only 0.26 Li^+ per unit formula can be inserted back over the following discharge.

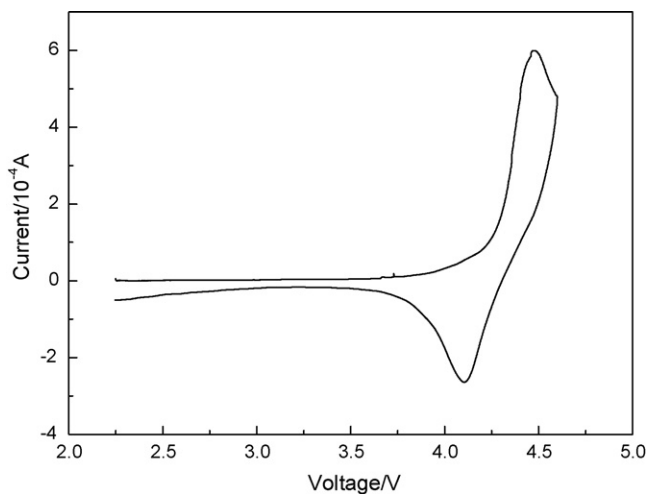


Fig. 3. Cyclic voltammogram for $\text{Li}_2\text{CoSiO}_4$ sample prepared by hydrothermal reaction at 0.2 mV s^{-1} between 3.0 and 4.6 V vs. Li/Li^+ in 1 $\text{MLiPF}_6/\text{EC} + \text{DMC}$ (1:1).

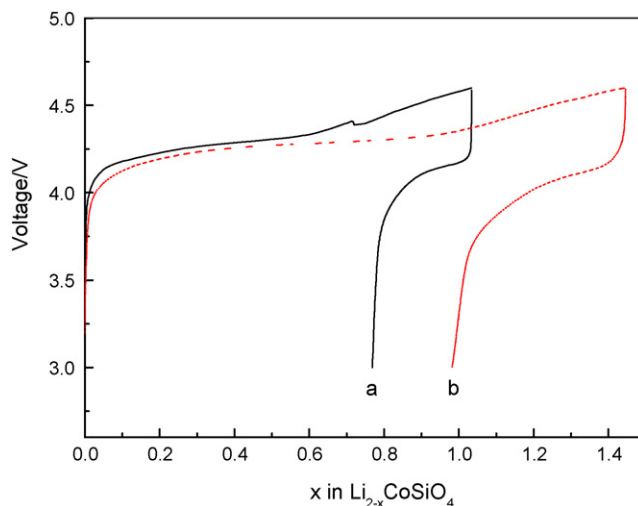


Fig. 4. Voltage profiles of $\text{Li}_2\text{CoSiO}_4$ samples prepared by solution routine (a) pristine sample and (b) carbon coated sample cycled at a rate of 5 mA g^{-1} .

After coated with carbon, its electrochemical performance was partly improved. However, there was still a large irreversible capacity during the first cycle, about 1.4 Li^+ per unit formula was extracted during the 1st charge and only 0.46 Li^+ per unit formula can be inserted back over the following discharge. For sample prepared by hydrothermal reaction, during the 1st charge about 1.2 Li^+ per unit formula can be extracted, however, only 0.41 Li^+ per unit formula can be inserted back over the following discharge. The cause of the large irreversible capacity during the first cycle, are being investigated in the lab. The differential capacity (dx/dV) plot for $\text{Li}_2\text{CoSiO}_4$ samples prepared by solution routine and hydrothermal reaction is shown in Fig. 6. It providing information similar to that in a CV—shows an oxidation peak at about 4.3 V and a reduction peak at 4.1 V for both $\text{Li}_2\text{CoSiO}_4$ samples.

Due to limited stability of the electrolyte used, just one lithium ion per unit formula can be extracted in our experiment

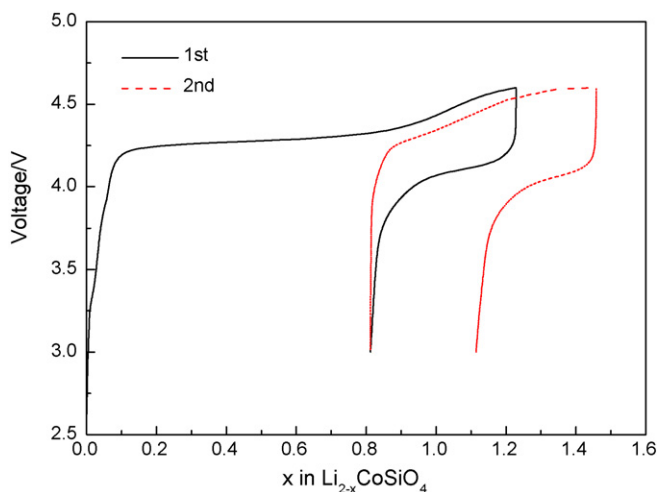


Fig. 5. Voltage profiles of $\text{Li}_2\text{CoSiO}_4$ sample prepared by hydrothermal reaction cycled at a rate of 5 mA g^{-1} .

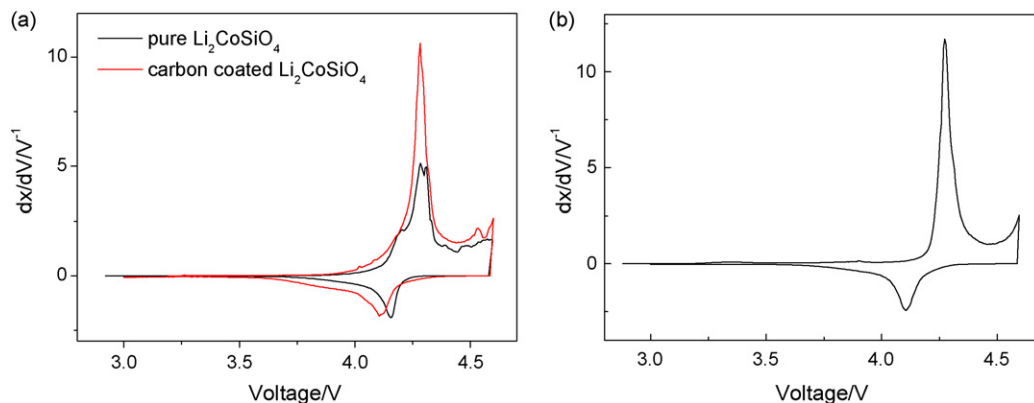


Fig. 6. Differential capacity (dx/dV) plots for $\text{Li}_2\text{CoSiO}_4$ samples prepared by (a) solution routine and (b) hydrothermal reaction.

(about 1.4 Li^+ per unit formula, the excess of lithium extracted maybe cause by the side reaction). As extraction of the second lithium ion will occur at a high voltages (about 5.0 V) [16], an electrolyte that is stable well above 5.0 V is necessary in order to apply the second lithium of this compound.

4. Conclusion

The compounds lithium cobalt orthosilicate ($\text{Li}_2\text{CoSiO}_4$) has been prepared successfully by a solution route and hydrothermal reaction. The electrochemical performance of both $\text{Li}_2\text{CoSiO}_4$ samples as cathode material in lithium ion batteries was investigated. Reversible extraction and insertion of lithium from and into $\text{Li}_2\text{CoSiO}_4$ at 4.1 V *versus* lithium was achieved. The pristine $\text{Li}_2\text{CoSiO}_4$ prepared by solution route shows poor electrochemical performance. After coated with carbon by ball milling, its electrochemical performance was partly improved and shows a reversible capacity of 0.46 Li per unit formula at an average voltage of 4.1 V.

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