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Electrochemical and diffusional insights of combustion synthesized $SrLi_2Ti_6O_{14}$ negative insertion material for Li-ion Batteries

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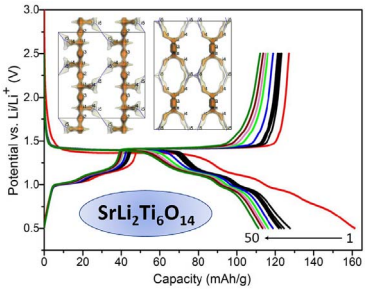
HIGHLIGHTS

- Rapid combustion synthesis of $SrLi_2Ti_6O_{14}$ by annealing for only 2 h.
- Homogeneous nanoparticles having reversible Ti^{4+}/Ti^{3+} activity at 1.38 V.
- Reversible capacity exceeding 135 mAh g^{-1} with rapid Li (de)insertion.
- Bond valence site energy (BVSE) analysis showing diffusional pathways.

GRAPHICAL ABSTRACT



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ABSTRACT

Solvothermal synthetic routes can provide energy-savvy platforms to fabricate battery anode materials involving relatively milder annealing steps vis-à-vis the conventional solid-state synthesis. These energy efficient routes in turn restrict aggressive grain growth to form nanoscale particles favouring efficient Li^+ diffusion. Here, we report an economic solution combustion synthesis of $SrLi_2Ti_6O_{14}$ anode involving nitrate-urea complexation with a short annealing duration of only 2 h (900 °C). Rietveld refinement confirms the phase purity of target product assuming an orthorhombic framework (*Cmca* symmetry). It delivers reversible capacity of ~125 mAh.g^{-1} at a rate of C/20 involving a 1.38 V Ti^{4+}/Ti^{3+} redox activity with excellent rate kinetics and cycling stability. Bond valence site energy (BVSE) calculations gauge $SrLi_2Ti_6O_{14}$ to be an anisotropic 3D Li^+ ion conductor with the highest ionic conductivity along the *c* direction. The electrochemical and diffusional pathways have been elucidated for combustion prepared $SrLi_2Ti_6O_{14}$ as an efficient and safe negative electrode candidate for Li-ion batteries.

1. Introduction

The ever-burgeoning trepidation of global warming ensuing from the greenhouse gas emissions and diminution of fossil fuel reserves has kindled research efforts on sustainable energy storage and delivery. Since their commercialization by SONY® (1991), Li-ion batteries have become ubiquitous in the ambit of energy storage devices vying for applications in electric vehicles, renewable energy storage and grid power storage systems [1–5]. The steady urge for improved batteries has paved way for developing efficient electrodes for high energy density Li-ion batteries. In this pursuit, anodes play crucial role in realizing operationally safe and robust batteries.

Graphitic compounds with low cost, adequate capacity (ca. 372 mAh.g^{-1}), robust cycling and acceptable operational safety for

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common C-rates have remained the front-runner anodes for Li-ion batteries. Nonetheless, the need to further improve the capacity and to avoid irreversible Li-losses by the formation of a solid-electrolyte interphase as well as the desire to increase the charging rates beyond the safety limits of graphite-based systems has triggered the development of alternate safe anodes for Li-ion batteries. Amongst them, Ti-based anodes such as lithium titanate $Li_4Ti_5O_{12}$ spinel (density = 3.43 g cm^{-3}) has been commercialised having a good combination of capacity, thermodynamic stability, cyclability, zero strain operation and high operating potential window (ca. 1.5–1.8 V) within the electrolyte stability window [6–9]. However, it is limited by moderate theoretical capacity (175 mAh.g^{-1}), the reduced cell voltage by a higher than necessary operating potential to suppress Li plating on fast charging and electronically insulating nature.

Aspiring for superior Ti-based anodes, Belharouak et al. reported a new class of compounds with the general formula $MLi_2Ti_6O_{14}$ (M = Ba and Sr) [10], which was structurally characterized by Kosova et al. [11]. Following, several reports on $MLi_2Ti_6O_{14}$ (M = Sr, Ba, 2Na) as Li-battery anodes revealed that all these were isostructural (or for the case of M = 2 Na isomorphous) capable of inserting Li^+ reversibly at a slightly lower but still safe voltage (1.25–1.4 V vs. Li/Li^+) and having potential to supersede the electrochemical performance of spinel titanate [12–17]. In this family, $SrLi_2Ti_6O_{14}$ (density = 3.85 g cm^{-3}) is the frontrunner candidate having a three-dimensional orthorhombic structure (s.g. *Cmca*) with a potential uptake of 6.0 Li^+ ions (per formula unit) leading to a theoretical capacity of 262 mAh/g. While the heavier Sr can lower the gravimetric capacity, the possible occurrence of multiple electron reaction can compensate the gravimetric capacity in addition to enhancing the volumetric capacity.

Cost and safety are major overriding factors that hinder practical implementation of Li-ion batteries. Constraints related to cost are primarily due to the materials cost (precursors) and processing cost (energy input in heat treatment) during the electrode synthesis. So far, there are few reports on the synthesis of $SrLi_2Ti_6O_{14}$ anode, such as flux method (for single crystals) [11], conventional solid-state synthesis [18,19], sol-gel method [20], template-assisted synthesis [21] and electro-spinning routes [22]. All these routes involve (i) high temperature annealing (800-1000 °C), (ii) long annealing duration (6-24 h), (iii) expensive precursors and (iv) tedious pre-annealing synthetic procedures. In an effort to realize an economic and energy-savvy synthesis, here we present solution combustion synthesis of $SrLi_2Ti_6O_{14}$ anode starting with less expensive precursors (like metal nitrates and urea) followed by annealing at 900 °C for just 2h. The resulting anode microstructure delivers high capacity, excellent reversibility and rate kinetics corroborating predictions from bond valence site energy analysis showing the existence of 3-dimensional Li^+ insertion mechanism. We present the synthesis, physical and electrochemical characterizations of $SrLi_2Ti_6O_{14}$ as a case-study to show the versatility of combustion synthesis to produce variety of Ti-based negative insertion materials.

2. Experimental section

2.1. Preparation of $SrLi_2Ti_6O_{14}$ anode

$SrLi_2Ti_6O_{14}$ (SLT) microstructure with pomegranate seed type assembly was prepared via energy and time efficient single-step solution combustion synthesis followed by annealing at 900 °C for 2 h (in air). In a typical synthesis, stoichiometric amounts of metal nitrates (considered as oxidants) such as strontium nitrate [$Sr(NO_3)_2$, Sigma Aldrich, 99%], lithium nitrate ($LiNO_3$, Merck, 99%) and $TiO(NO_3)_2$ were mixed with urea (acting as fuel) in aqueous medium as per equation (1). $TiO(NO_3)_2$ was prepared in-house by acid hydrolysis of Ti(IV) iso-propoxide (Sigma Aldrich, 97%) with 1:1 HNO_3 (SD fine chemicals, 99%). Though slightly expensive, Ti(IV) iso-propoxide precursor is widely used for solvothermal (soft chemical) synthesis of various Ti-based inorganic compounds as an efficient complexing agent [23–25]. The resulting solution was preheated with steady magnetic stirring at 130 °C leading to dehydration, gelation and formation of a dry intermediate complex. This complex, upon annealing at 350 °C, underwent self-combustion to yield a yellowish product. It quickly transformed to the final product upon annealing at 900 °C for just 2 h [26,27]. The overall combustion reaction can be expressed as:

$$Sr(NO_3)_2\ (s) + 2\ LiNO_3\ (s) + 6\ TiO(NO_3)_2\ (s) + 13.33\ CH_4N_2O\ (s)$$

$$SrLi_2Ti_6O_{14}\ (s) + NO_x\ (g) + CO_2\ (g) + H_2O\ (g) \quad (1)$$

2.2. Structural and physical characterization

X-ray powder diffraction patterns of SLT anode were collected with a PANanalytical X'Pert Pro instrument using a Cu-Kα target (λ_1 = 1.5408 Å) operating at 40 kV/30 mA. Typical diffraction patterns were recorded in the 2θ range of 10–90° (step size = 0.026°/s). Rietveld refinement was performed using FullProf Suite program and the structural features were illustrated using the VESTA software [28,29]. Morphological studies were performed by using an FEI Inspect F50 scanning electron microscope operating at 10 kV and an FEI Tecnai F 30 STwin transmission electron microscope operating at 200 kV.

2.3. Computational methods

The distribution of additional Li^+ inserted into $SrLi_2Ti_6O_{14}$ and the corresponding migration barriers were analyzed by the bond valence site energy method, as discussed in our earlier work [30–32]. Pathways for mobile Li^+ ions are identified as regions of low bond valence site energy E_{BVSE}(Li), which has been demonstrated to be a simple and reliable way of identifying transport pathways in reliable local structure models. Since the mismatch $|\Delta V|$ of the bond valences $s_{Li\text{-}X} = exp[(R_{0,Li\text{-}X} - R_{Li\text{-}X})/b_{Li\text{-}X}]$ can, as demonstrated by our group [33–35], be expressed on an absolute energy scale by rewriting bond valence into a Morse-type interaction potential between the reference cation Li^+ and anion X.

$$E_{BVSE}(Li) = \sum_x D\left[\sum_{i=1}^{N}\left(\left(\frac{s_{Li-X}}{s_{\min,Li-X}}\right)^2 - 2\frac{s_{Li-X}}{s_{\min,Li-X}}\right)\right] + E_{repulsion} \quad (2)$$

The required bond valence parameters are taken from our *softBV* database as published in ref. 33. Migration pathways for Li^+ are analyzed as regions of low bond valence site energy E_{BVSE}(Li) in grids covering the structure model with a resolution of ca. (0.1 Å)^3. It has been demonstrated for a wide range of materials that the pathways found from this computationally cheap method are closely approximating pathways observed by *ab initio* approaches [36,37]. Using the same bond-valence based interaction potentials, structure models for the phases $SrLi_{2+x}Ti_6O_{14}$ with x > 0 are derived from an iterative series of adding a Li to a site identified above as a Li interstitial in $SrLi_2Ti_6O_{14}$, energy minimizing and relaxing the structures by short NPT simulations until the composition $Sr_8Li_{16}Ti_{48}O_{112}$ was reached. As the immobile host matrix in the resulting structure models and the Li occupancies (for even values of x) assumed values compatible with the host symmetry, the resulting relaxed structure models were geometry optimized imposing *Cmca* space group symmetry to facilitate a comparison with the delithiated parent phase. While this appeared to be a natural choice due to the proximity of the relaxed structures to this orthorhombic symmetry, it may be noted that for the highest Li content (x = 6) a slight monoclinic distortion cannot be ruled out.

2.4. Electrochemical characterization

To test the SLT anode in Li-half cell architecture, working electrode