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Lithium Titanate Aerogel for Advanced Lithium-Ion Batteries

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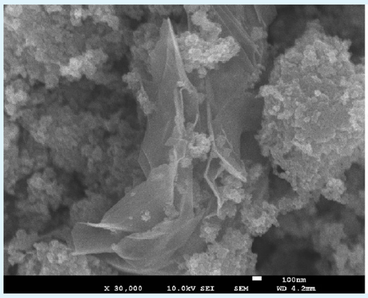
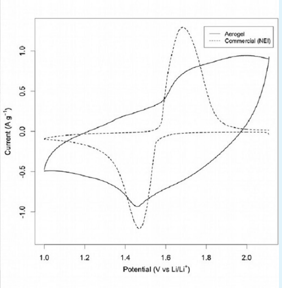
ABSTRACT: This work details the synthesis and characterization of a novel lithium titanate aerogel as an anode material for lithium ion batteries. Excessive loss of lithium during supercritical drying can be overcome by increasing the lithium precursor concentration during synthesis. Chronopotentiometry shows the aerogel to have a capacity about 80 % of theoretical at a symmetric C/3 rate, which is comparable to a commercial product. Cyclic voltammetry reveals a batt-cap behavior for the high-surface area aerogel, implying the potential for improved rate capability if electrical conductivity can be maintained.





KEYWORDS: *aerogel, lithium titanate, lithium-ion batteries, sol−gel*

INTRODUCTION

As society transitions to a carbon neutral energy future, it is becoming increasingly apparent that advances in energy storage technology are necessary. For automotive applications in particular, battery technology needs to be more powerful, store more energy, and cost less to manufacture, while improving both safety and cycle life.[1,2]

Densification via sintering,[3] atomic layer deposition,[4] and nanostructuring[5] of the electrode have all been successful in improving cathode stability and performance. However, limited progress has been made on the anode. Metal alloy electrodes are attractive because of an extremely large capacity, but the excessive volume change associated with that capacity limits their cycle life.[6]

Lithium titanate spinel ($Li_4Ti_5O_{12}$, LTO) is another candidate material that holds promise as an anode material for advanced lithium ion batteries. Known as a zero-strain insertion oxide, it can undergo of thousands of cycles with little capacity loss.[7−9] Additionally, its insertion potential (1.55 V vs. Li/Li$^+$) remains above the onset of Solid Electrolyte Interphase (SEI) formation, allowing one to take advantage of nanoscale features not normally feasible with carbon electrodes due to excessive SEI buildup. The most basic method of making LTO is through a solid-state reaction, where suitable precursors (usually lithium carbonate and titanium dioxide) are combined via ball milling, then calcined at elevated temperatures (800−1000°C) in air to form the correct phase. Many groups have made progress in increasing the active surface area through high-energy ball milling[7] of the final LTO powder, or through sol-gel processing methods.[10−13] However, the sol−gel processing generally utilized ambient drying techniques, which lead to more dense structures and increased particle sizes after calcination.

Aerogels, formed via the supercritical drying of sol−gels, have shown much promise as advanced energy storage materials.[14−16] The high surface area of the aerogel increases reaction kinetics, decreases solid-state ion diffusion distances, and can even enhance capacity by increasing the number of surface defects in certain oxides.[17] To date, no lithium titanate aerogel has been reported in literature. This work details the fabrication of such an aerogel, and characterizes the electrochemical properties of the high-surface-area electrode.

EXPERIMENTAL SECTION

Sample Preparation. Lithium acetate dihydrate (SigmaAldrich, L6883), titanium isopropoxide (Alfa Aesar, 77115), triethanolamine (TEA) (Sigma-Aldrich, T58300), chloroform (Mallinckrodt Chemicals, 4440-08), methanol (SigmaAldrich, 34860), and water (reverse osmosis purified) were used as received. Styrene-butadine rubber (SBR) and carboxymethyl cellulose (CMC), both from MTI Corp., were used as aqueous binding agents for electrode fabrication. Commercial LTO was obtained from NEI Inc. (BE-10). Graphite nanoPlatlets (GnP) were used as a high-aspect-ratio conductive additive, for which the fabrication procedure is described elsewhere.[18]

The molar ratio of titanium isopropoxide:TEA:water:methanol:-chloroform was kept constant at 5:1.4:15:60:60, with the amount of lithium acetate varying from 5 to 20 mols. In one vial, the TEA and chloroform were combined with stirring for 10 min, to which the titanium isopropoxide was added and stirred for another 30 min. In a second vial, the water and methanol were combined with stirring for 10 min, to which the lithium acetate was added and stirred for another 30 min until dissolved. The lithium acetate solution was then added to the titanium isopropoxide solution dropwise with vigorous stirring. After stirring for 5 min, the solution was separated into 14 mL glass molds, sealed, and allowed to gel. The wet gels were aged for 3 days, and then supercritically dried with carbon dioxide in a 12 L critical point dryer (Accudyne Systems Inc.) without any intermediate solvent exchanges. The dried gels were calcined at 800°C for 3 h under flowing argon.

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For samples intended for electrochemical testing, 5 wt % GnP (with respect to the final $Li_4Ti_5O_{12}$ mass) was added to the bulk solution and bath sonicated for 2 min before separating into the smaller molds. Calcining under flowing argon prevents oxidation of the graphite. After calcination, an aqueous electrode slurry was prepared by ball-milling a mass ratio of 75:15:5:5:540 LTO:GnP:SBR:CMC:water, taking into account the GnP already included in the LTO gel. This was spread onto an aluminum current collector with a doctor blade at approximately 150 um thick. The final electrode was calendared down to 27 um, with a total areal loading of 0.8 mg cm^{-2}. Electrodes were also made using a commercial LTO product from NEI Inc., with an areal loading of 2.48 mg cm^{-2} at the same thickness.

Characterization. X-ray diffraction (XRD) spectra were collected with a Bruker D8 ADVANCE diffractometer on powder samples roughly ground with an alumina mortar and pestle. Surface areas were measured by nitrogen adsorption with a Micromeretics ASAP 2020. Both XRD and nitrogen adsorption used samples without GnP – all other characterization was performed on samples with a Li:Ti precursor molar ratio of 10:5, with the 5 wt % GnP additive. Scanning electron micrographs were obtained using a JEOL 7500F SEM without the use of a conductive coating. For electrochemical testing, 1/4 in. diameter electrodes were punched out, dried under vacuum at 110 °C for 4 h, and assembled in a three-electrode swagelok cell inside an argon-filled glovebox with an electrolyte composed of 1M $LiPF_6$ in a 1:1:1 volumetric mixture of ethylene carbonate, diethyl carbonate, and dimethyl carbonate (MTI Corp.), using metallic lithium as both reference and counter electrodes. Whatman glass filter paper (GF/F) was used as a porous separator.

■ RESULTS

Solid-state methods of producing lithium titanate spinel utilize a Li:Ti precursor ratio that is typically 10% higher than stoichiometric (4.4:5) in order to compensate for the loss of lithium during calcination. Figure 1 shows the composition of the LTO aerogel as a function of the Li:Ti precursor ratio. It is immediately apparent that even a 25% increase in the Li:Ti ratio (5:5) is insufficient to obtain phase purity, and that a mixture of LTO spinel and lithium-poor titanates are instead formed.

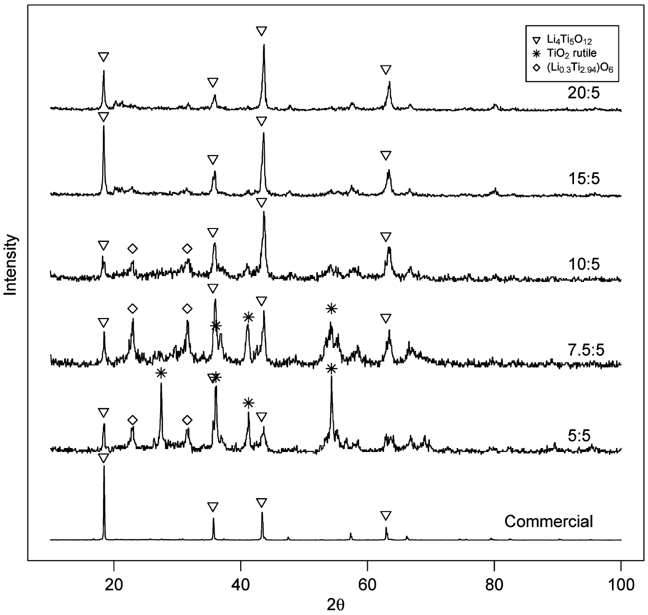

Figure 1. Increasing the lithium:titanium precursor ratio increases the phase purity of the spinel.

There are two possible mechanisms for such extensive loss of lithium. First, the high surface area of the aerogel may increase the rate of lithium loss during calcination. Alternatively, it is possible that the wet gel that forms may only be an amorphous titanium oxide gel, with a high concentration of lithium in the pore fluid. Solvent exchanges would wash away the lithium-rich pore fluid, leaving behind an insufficient amount of lithium to form the spinel phase. It was found that placing a wet gel in a solution of methanol and chloroform caused the gel to dissolve, indicating that the gel components are at best tenuously bound. By increasing the Li:Ti ratio and drying without preliminary solvent exchanges, it was possible to increase the phase purity of the calcined gel. Unfortunately, this came at the expense of the calcined gel's surface area, as shown in Figure 2. This is in contrast to the findings of Mohammadi et al., who found an increase in surface area with increasing lithium precursor content of thin-film LTO.[19] Although the mechanism for the effect of lithium content on the surface area is not given, it is likely the difference between the two results can be attributed to the gelation process. In the acid-catalyzed thin film, an increase in the lithium precursor content reduced the overall HCl molarity, adjusting the isoelectric point of the forming particles and changing the degree to which they cross-link to form the gel. In the base-catalyzed gel of this work, the increase in lithium precursor (lithium acetate dihydrate) carried with it an increase in water content, increasing the rate of hydrolysis and shortening the gelation time. This shorter gelation time yields larger particles with fewer crosslinks, reducing the overall surface area. It was decided that a Li:Ti ratio of 10:5 gave the best balance between phase purity and surface area, and this ratio was used for all subsequent characterization.

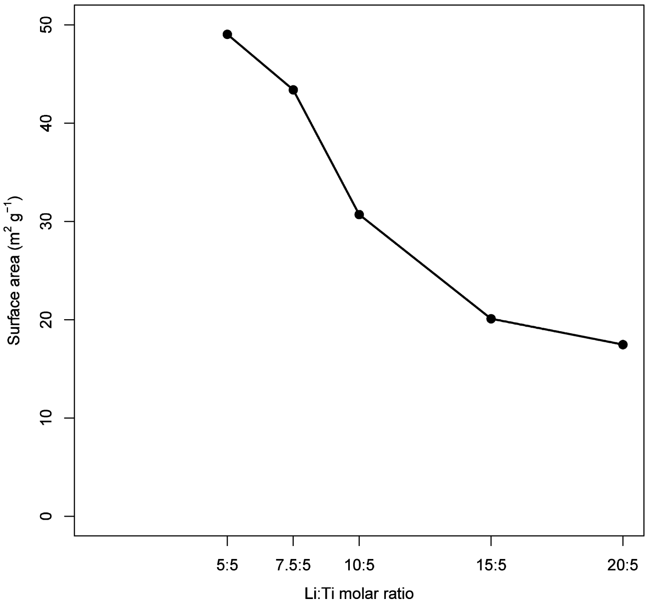

Figure 2. Increasing the lithium:titanium precursor ratio decreases the surface area of the calcined aerogel.

Figure 3 shows the morphology of the calcined aerogel clustered around the conductive GnP additive. The primary particle sizes are around 10–50 nm, forming aggregates up to a few micrometers in diameter and showing good dispersion of the GnP. GnP was chosen as conductive additive for two reasons; to demonstrate that novel high-aspect-ratio additives can be easily incorporated into the sol–gel and maintained

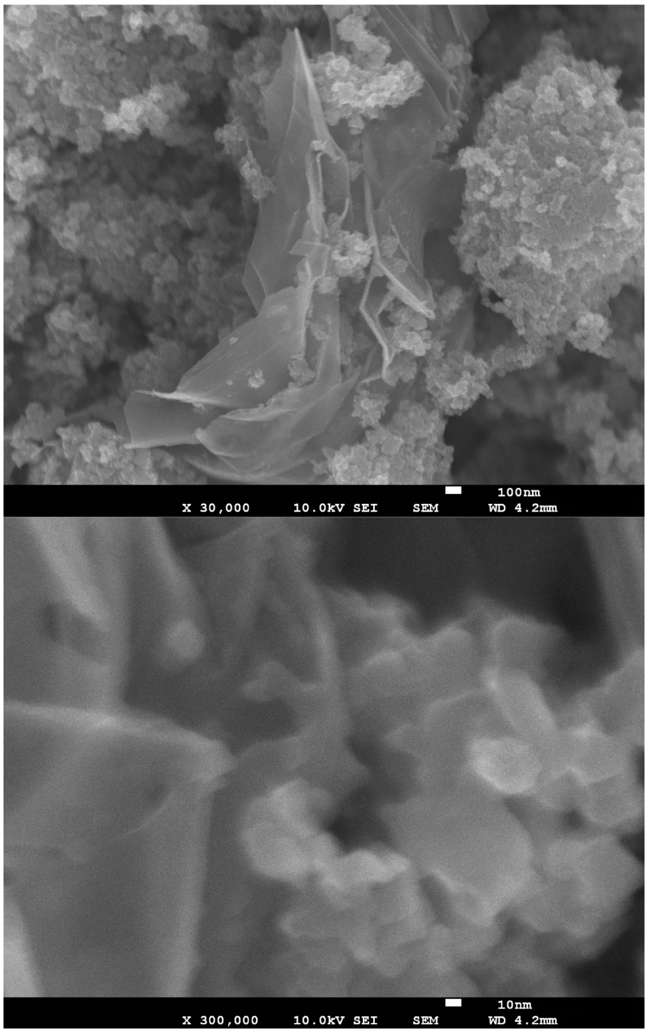

Figure 3. Calcined powder shows nanoscale crystallites (bottom) in good contact with the conductive additive (top).

during calcination, and to enable future work on intrinsically wired high-power electrodes that can take advantage of the nanoscale LTO aerogel morphology.

Figure 4 shows the cyclic voltammetry curves of an LTO aerogel electrode, with a similar commercial LTO electrode for comparison. The low surface area commercial LTO (5−7 m^2 g^{-1}) exhibits a pair of redox peaks centered at 1.55 V, typical of an LTO battery. The high-surface-area aerogel (30 m^2 g^{-1}) also has a redox behavior at 1.55 V, but it is superimposed onto a large pseudo-capacitive box profile. This "batt-cap" behavior is typical of high surface-area electrodes,[16] and is advantageous in that it increases the power density of the electrode material without sacrificing capacity. Galvanostatic charge-discharge curves (Figure 5) show that the aerogel has a capacity comparable to the commercial product (137 vs. 147 mA h g^{-1}). The sloping potential profile of the aerogel is typical of high surface area aerogel electrodes with a distribution of particle sizes, as the surface energies of the nanoparticles affect the insertion potential.[20,21] This is in contrast with the ambiently dried sol−gel LTO reported in literature,[10−13] which exhibit a potential plateau similar to the commercial product shown here.

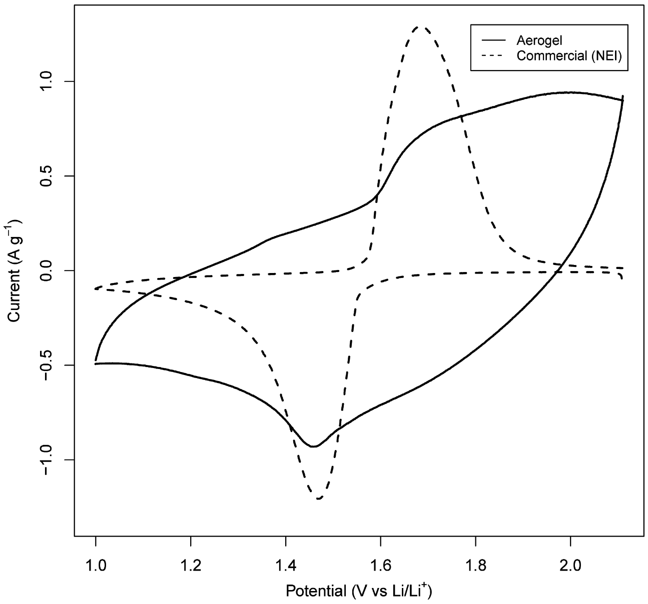

Figure 4. Cyclic voltammetry shows a batt-cap behavior for the aerogel. Testing was done at 0.5 mV/s.

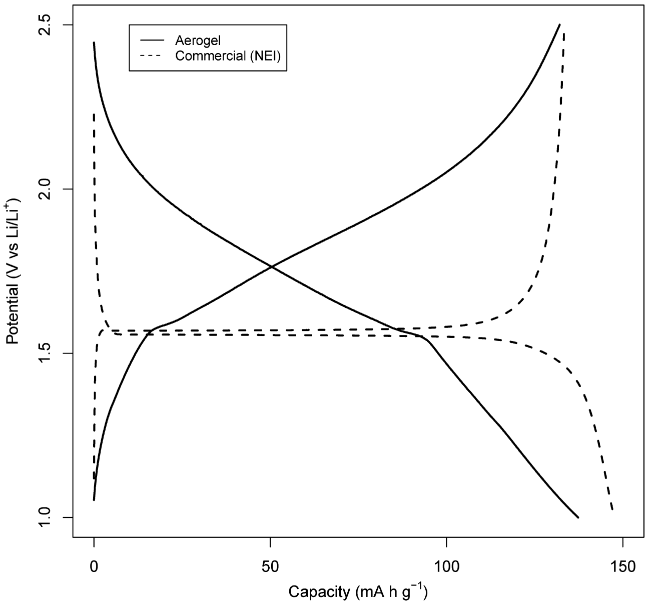

Figure 5. At a C/3 rate, the aerogel has a capacity comparable to the commercial product.

CONCLUSIONS

This work represents the first report of producing a lithium titanate spinel aerogel for lithium ion batteries. Sol−gel-derived LTO gels are more susceptible to lithium loss than solid-state processed compounds, and a higher lithium:titanium precursor ratio is necessary to maintain phase purity. This purity comes at the expense of surface area, and a ratio of 10:5 appears to be a sufficient compromise between the two. The high surface area of the aerogel yields a pseudocapacitive behavior, which should allow for high pulse-power performance. The capacity of the aerogel was 137 mA h g^{-1}, which is comparable to a commercial LTO electrode tested under the same conditions. Incorporation of conductive additives in the sol−gel, and calcination of the gels in an argon atmosphere, allow for intrinsic wiring of the oxide. This should enable the use of nanoscale LTO aerogels at high rates, and will be the subject of future work.

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Notes

The authors declare no competing financial interest.

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