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**Title:** Improving High Rate Cycling Limitations of Thick Sintered Battery Electrodes by Mitigating Molecular Transport Limitations through Modifying Electrode Microstructure and Electrolyte Conductivity

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## Materials and methods

#### 1. Electrolyte preparation

Lithium bis(fluorosulfonyl)imide (LiFSI) was used as the primary salt in the electrolyte and dimethyl carbonate (DMC) was used as solvent. Three initial concentrations of electrolyte were selected. The target LiFSI concentration for three electrolytes were 1 mol L<sup>-1</sup>, 2 mol L<sup>-1</sup> and 3 mol L<sup>-1</sup>, respectively. To suppress possible corrosion caused by trace Cl<sup>-</sup> in LiFSI salt sample,<sup>1,2</sup> 0.5 mol L<sup>-1</sup> LiPF<sub>6</sub> was added to all electrolytes. Thus, the total target Li<sup>+</sup> concentrations were 1.5 mol L<sup>-1</sup>, 2.5 mol L<sup>-1</sup> and 3.5 mol L<sup>-1</sup> for three electrolytes, respectively. However, at high concentration regime, the volume increase caused by adding salts was no longer negligible. After volume measurements, the actual concentrations for three electrolytes were 1.3 mol L<sup>-1</sup>, 2.0 mol L<sup>-1</sup> and 2.5 mol L<sup>-1</sup>, in which the LiFSI:LiPF<sub>6</sub> molar ratios were 2:1, 4:1 and 6:1, respectively. The conductivity of different blend electrolytes at different concentration was measured with a Mettler Toledo<sup>@</sup> conductivity probe.

The commercial "GEN2" electrolyte (Gotion) was composed of 1.2 mol L<sup>-1</sup> LiPF<sub>6</sub> in 3:7 (w/w) ethylene carbonate (EC)/ ethyl methyl carbonate (EMC) solvent and was used as received.

- 2. Powder material preparation
- 2.1 Active material powder

LiCoO<sub>2</sub> (LCO) was used as the cathode material. LCO was synthesized via firing a mixture of  $Li_2CO_3$  powder and  $CoC_2O_4 \cdot 2H_2O$  precursor.<sup>3</sup> Coprecipitation was used to synthesize the precursor. First, 1800 mL of 62.8 mmol·L<sup>-1</sup> Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Fisher Reagent Grade ) solution (50 °C) was poured into 1800 mL of 87.9 mmol L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O (Fisher Certified ACS) solution (50 °C) all at once. After maintaining at 50 °C for 30 minutes with a stir bar stirring at 800 rpm, the solid precipitate was collected using vacuum filtration and rinsed with 4 L deionized (DI) water. The powder was then dried in an 80 °C oven for 24 h in air atmosphere. Then, the oxalate precursor powder was mixed with  $Li_2CO_3$  (Fisher Chemical) powder with a molar ratio of 1.02:1 for Li:Co using mortar and pestle. The powder mixture was fired at a ramp rate of 1 °C·min<sup>-1</sup> to 800 °C in air in a Carbolite CWF 1300 box furnace. The sample was cooled to room temperature without control of cooling rate after reaching 800 °C. The resulting LCO material was ground with mortar and pestle by hand and was further milled in a Fritsch Pulverisette 7 planetary ball mill using 57 zirconia beads (5 mm diameter) at 300 rpm for 5 hours. 5 g of LCO was used for each batch of the planetary ball milling.

 $Li_4Ti_5O_{12}$  (LTO) was used as anode material. It was purchased from a commercial supplier (NANOMYTE BE-10 from NEI Corporation) and was used without any additional treatment. The characterization and electrochemical properties of both LCO and LTO material used in this study can be found in previous publications.<sup>1,4</sup>

2.2 Polystyrene powder

Colloidal polystyrene (PS) particles (diameters 300 nm to 500 nm) were synthesized using procedures adapted from literature.<sup>5</sup> Styrene (Sigma-Aldrich, ReagentPlus, with 4-tert-butylcatechol as stabilizer,  $\geq$  99.0%) was pretreated using a prepacked column (Sigma-Aldrich, inhibitor, prepacked column for removing tert-butylcatechol) to remove the polymerization inhibitor. First, a three-neck 500 mL round bottom flask was filled with 290 mL DI water with 8.86 g styrene added. The flask was heated to 70 °C in an oil bath and thermally equilibrated for 30 minutes. Next, 0.204 g potassium persulfate (Sigma-Aldrich) was added as catalyst for the styrene polymerization reaction. During the reaction, the head space was purged with nitrogen flowed at 1 mL s<sup>-1</sup>. The two-phase system was stirred for 8.5 h with a stir bar, resulting in a final milky white suspension. After drying in the air at room temperature until all water was evaporated, the PS powder was collected.

3. Electrode preparation

# 3.1 Sintered LCO preparation

Sintered LCO electrodes were used as cathodes in this study. First, the LCO active material powder was mixed with 1 wt.% polyvinyl butyral (Pfaltz & Bauer) solution dissolved in ethanol (Acros). 1 g LCO powder was blended with 2 mL polymer binder solution with a mortar and pestle. After all the solvent was evaporated, the mixture was collected. Then, 0.2 g of the mixture was loaded into a 13 mm diameter Carver pellet die and pressed with 12,000 lbf for 2 minutes in a Carver hydraulic press. Next, the pellets were heated in a Carbolite CWF 1300 box furnace in an air atmosphere. The ramping rate was 1 °C min<sup>-1</sup> from 25 °C to 600 °C and was held at 600 °C for 1 hour. After that, the pellets were cooled to 25 °C at a rate of 1 °C min<sup>-1</sup>.

### 3.2 Sintered LTO preparation

The sintered LTO electrodes were prepared using a similar method for sintered LCO electrodes. However, if the identical processing was used, the resulting LTO pellets generally had a geometric pore/void volume of 40%. Thus, in order to match the geometric pore/void volume of the ice-templated LTO pellets (~55%), sacrificial PS particles were mixed with the LTO powder before the hydraulic pressing step. The mass ratio of LTO powder and PS powder was 5:1 for LTO:PS. Then, the powder mixture was blended with 1 wt.% polyvinyl butyral solution. 2 mL solution added to 1 g LTO powder in the mixture. After the solvent was evaporated, 0.24 g of the powder mixture was loaded in the 13 mm diameter pellet die and pressed with 12,000 lbf for 2 minutes. Then, the pellets were fired in a Carbolite CWF 1300 box furnace in air atmosphere at 600 °C for 1 h. The heating and cooling rate were set to be 1 °C min<sup>-1</sup>. The resulting LTO pellets had a porosity of ~55%.

## 3.3 Ice-templated LTO preparation

Ice-templated LTO materials were fabricated from aqueous suspensions containing 30% by volume LTO particles. To prepare an aqueous suspension, as-received LTO powder was mixed with DI water and yttria stabilized zirconia (ZrO<sub>2</sub>) spheres (5 mm diameter, Inframat Advanced

Materials LLC) in a Nalgene bottle, with ceramic powder to milling media mass ratio of 1:4. Then, cetyl trimethyl ammonium bromide (CTAB) cationic dispersant, at a concentration of 0.02 g cm<sup>-3</sup> of distilled water, was added to the aqueous LTO suspension. The addition of CTAB caused slight foaming in the suspension. To avoid foaming, an antifoaming agent Surfynol 104PG50 (0.003 g g<sup>-1</sup> of LTO powder) was added to LTO suspension. Then, the LTO suspension was milled for 24 h at 30 RPM. Next, a binder solution was prepared by dissolving poly(2-ethyl-2-oxazoline) in distilled water, and the binder solution was added to the LTO suspension such that the binder amount was 4% of the LTO powder mass. LTO suspension was further ball milled for another hour at 10 rpm to ensure proper mixing of binder solution and LTO suspension.

A custom-made ice-templating device was employed to fabricate LTO electrodes with aligned pores.<sup>6</sup> This setup contains an assembly of a polytetrafluoroethylene tube (mold) placed on a thin copper plate (referred to here as "cold-finger"), which is filled with an aqueous ceramic suspension. Next, to freeze the suspension under the influence of unidirectional temperature gradient, the mold assembly containing ceramic suspension was inserted inside a liquid nitrogen Dewar, where the cold-finger was placed above the liquid nitrogen. The distance between cold-finger and liquid N<sub>2</sub> determines the unidirectional temperature gradient, and hence the growth velocity of the freezing front. In this work, a 1 mm gap between the cold-finger and liquid nitrogen was used to achieve a relatively high freezing front velocity (FFV) of about 28  $\mu$ m s<sup>-1</sup>. As the temperature of the cold-finger reaches below 0 °C, ice crystals nucleate at the bottom of the suspension in contact with the cold-finger and grow upward under the influence of the applied thermal gradient.

Unidirectionally solidified samples were freeze dried in a freeze-dryer (2.5 L, Labconco, Kansas City, MI) for 96 h at a pressure of 0.014 mbar and temperature of -50 °C. Freeze dried LTO pellets were then sintered using a tube furnace (NBD, T-1700-60IT). Samples were first heated to 450 °C at a rate of 5 °C min<sup>-1</sup> and held for 4 hours to burn out binders. Next, samples were heated to 950 °C at a rate of 2 °C·min<sup>-1</sup> and sintered for 2 h. After that, samples were cooled down to room temperature using a cooling rate of 5 °C min<sup>-1</sup>. Dimensions of sintered LTO samples were approximately 13 mm in diameter and 10 mm in height. From each sintered LTO sample, an electrode disk of 1 mm thickness was extracted from a 2 mm height above the bottom of the sample and was denoted as LTO\_ICE in the following discussion.

### 4. Electrochemical cell fabrication

Electrochemical evaluation of sintered electrode LTO/LCO full cells was conducted using CR2032 coin cells. To fabricate the cell with Gen 2 electrolyte, the LCO pellets were pasted onto the bottom plate of the coin cell and LTO pellets were pasted on a stainless steel spacer (15.5 mm in diameter and 0.5 mm in thickness). To fabricate the cells with LiFSI-containing electrolytes, the LTO pellets were pasted onto the bottom plate and LCO pellets were pasted on an aluminum spacer (15.5 mm in diameter and 0.5 mm in thickness). The paste for attaching sintered electrodes to current collectors was composed of 1:1 weight ratio Super P carbon black (Alfa Aesar) to polyvinylidene difluoride (PVDF, Alfa Aesar) binder dissolved in N-methyl

pyrrolidone (NMP, Sigma-Aldrich). After drying in an 80 °C oven for 12 hours in air atmosphere, the pellets were transferred into an Ar atmosphere glove box with both  $O_2$  and  $H_2O$  content <1 ppm. Then, LTO and LCO electrodes were assembled into a coin cell with glass fiber separator (Fisherbrand, 09-804-24A) between the anode and cathode. In a coin cell, 18 total drops of electrolyte were added. Assembly of sintered electrode full cells was described in greater detail in previous publications.<sup>7,8</sup>

The rate capability of LTO/LCO sintered electrode coin cells was determined by galvanostatically cycling at different C rates using a MACCOR battery cycler. The C rate was based on the assumption that the capacity of LCO was 150 mAh g<sup>-1</sup>, and thus 1C was assumed to correspond to 150 mAh g<sup>-1</sup> and the current was adjusted based on the actual LCO mass in the cell and the desired C rate. For cells fabricated in this study with LCO loadings typical in sintered electrodes, 1C would also correspond to ~21.4 mA cm<sup>-2</sup> (28.4 mA). The voltage range used for all LTO/LCO cells was 1.0 V to 2.8 V (cell voltage, relative to LTO anode).



**Fig. S1.** LiPF<sub>6</sub> conductivity in 3:7 (w/w) EC/EMC electrolyte. (1.2 mol L<sup>-1</sup> was the initial concentration of commercial Gen 2 electrolyte). The plotted line resulted from the experimental test and numerical fitting from ref. 9. The fitted function is:  $\kappa$ =1.297c<sup>3</sup>-25.1c<sup>1.5</sup>+33.29c, where  $\kappa$  is the conductivity (mS cm<sup>-1</sup>), c is the concentration (mol L<sup>-1</sup>).



**Fig. S2.** Average discharge capacity at different discharge rates for each cell type reported in this manuscript. For C/50 discharge, the charge rate was C/50, and before all other discharge processes the charge rate was C/20. The last C/20\* was the C/20 discharge process performed after all the cycles at increasing rates, indicating minimal capacity loss during the test.



**Fig. S3.** Cycle life results for sintered LTO/LCO cells with GEN2 (blue circles) and PEAK (green circles) electrolyte, with the first cycle being the first cycle after the rate capability test (Fig. S2) was completed. The charge and discharge rate was C/20 for all of the cycle life test cycles.

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