ADVANCED ENERGY MATERIALS

Supporting Information

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Semi-Solid Lithium Rechargeable Flow Battery

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Design of Electrochemical Flow Cell

Figure S1 shows the design and components of the electrochemical flow cell used in this work.

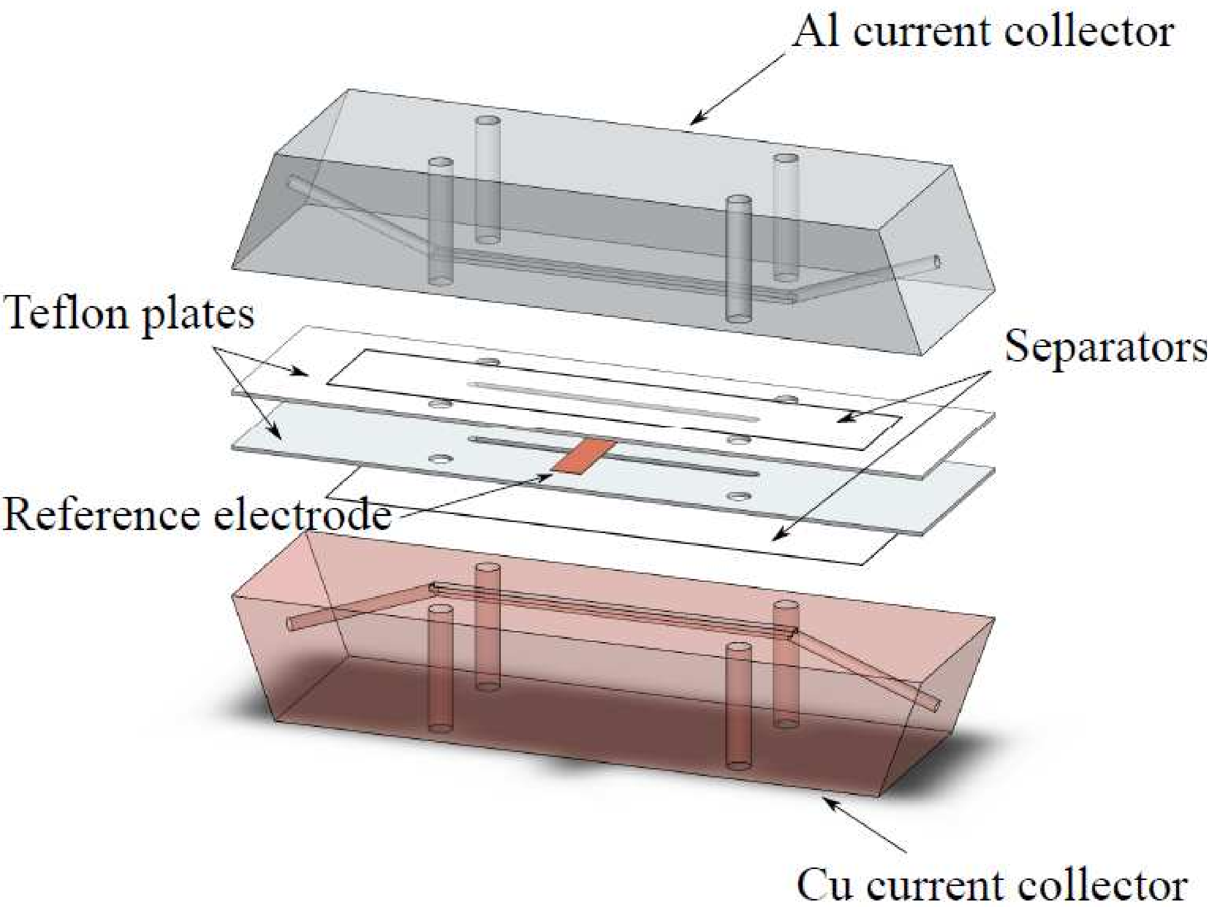

Figure S1. Schematic flow cell configuration for electrochemical testing.

Conductivity of Flowing Semi-Solid Suspensions

For each suspension formulation, the conductivity under flow was characterized using an apparatus shown schematically in **Figure S2** (1.6 mm cylindrical bore), to confirm that the electronic conductivity remains in an acceptable range for charge and discharge. For example, the conductivity of a 22.4 vol% LCO and 0.6 vol% Ketjen suspension at flow rates of 0 ml min^{-1}, 1 ml min^{-1}, and 10 ml min^{-1} are shown in the plot in Figure S2. The ionic conductivity is given by the high frequency intercept and does not change measurably as a function of flow rate. The electronic conductivity is obtained from the low frequency regime and decreases by less than a factor of 2 from 0 to 10 ml min^{-1} flow rates.

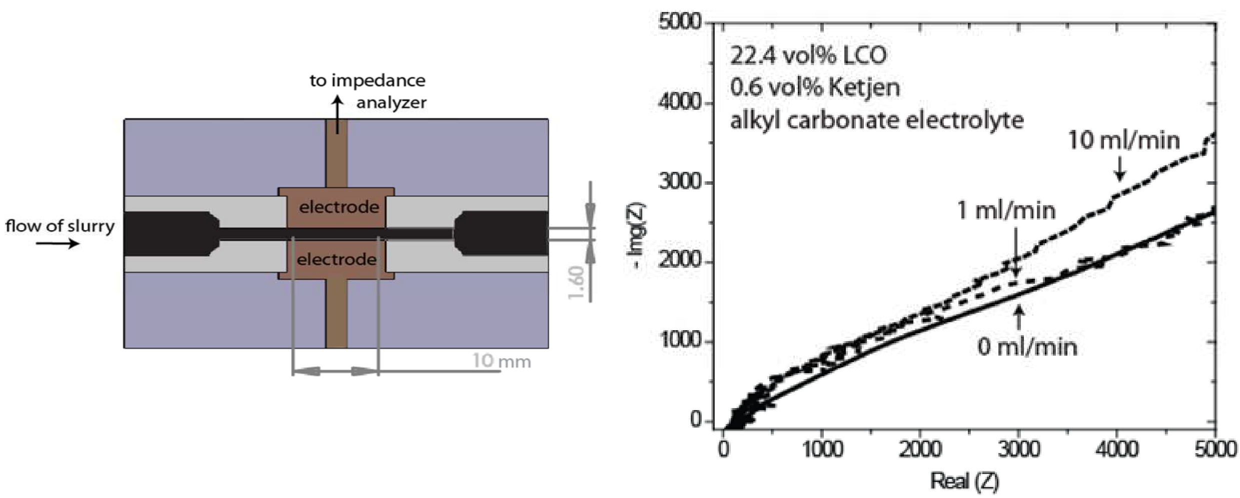

Figure S2. Apparatus for measuring conductivity during flow (left) and Nyquist plot for an $LiCoO_2$ + Ketjen suspension measured in a conductivity cell at various flow rates (right).

Electrochemical Test of Non-Flowing Full Lithium-Ion Semi-Solid Cell

A full lithium-ion was made using stable semi-solid suspensions at both cathode and anode, and tested in a non-flowing configuration. This cell used two different electrolytes in the cathode and anode suspensions, separated by Tonen separator. The cathode composition consisted of 20 vol% of a proprietary iron-containing olivine powder (A123 Systems, Watertown, MA) with 1 vol% Ketjen, in electrolyte consisting of 1.3M $LiPF_6$ in alkyl carbonate blend. The anode contained 6 vol% $Li_4Ti_5O_{12}$ (AltairNano, Reno, Nevada) and 1 vol% Ketjen in a 70:30 mixture by mass of 1,3-dioxolane and LiBETI (lithium bis (pentafluorosulfonyl) imide. Since the cell is anode-limited, the cell capacities are normalized to show the reversible capacity of the anode, **Figure S3**. The 2nd through 4th charge/discharge cycles are shown, conducted at C/4, C/2, and C/4 rates, respectively. Note the low polarization; the corresponding coulombic and energy efficiencies are 97-98% and 87-88%.

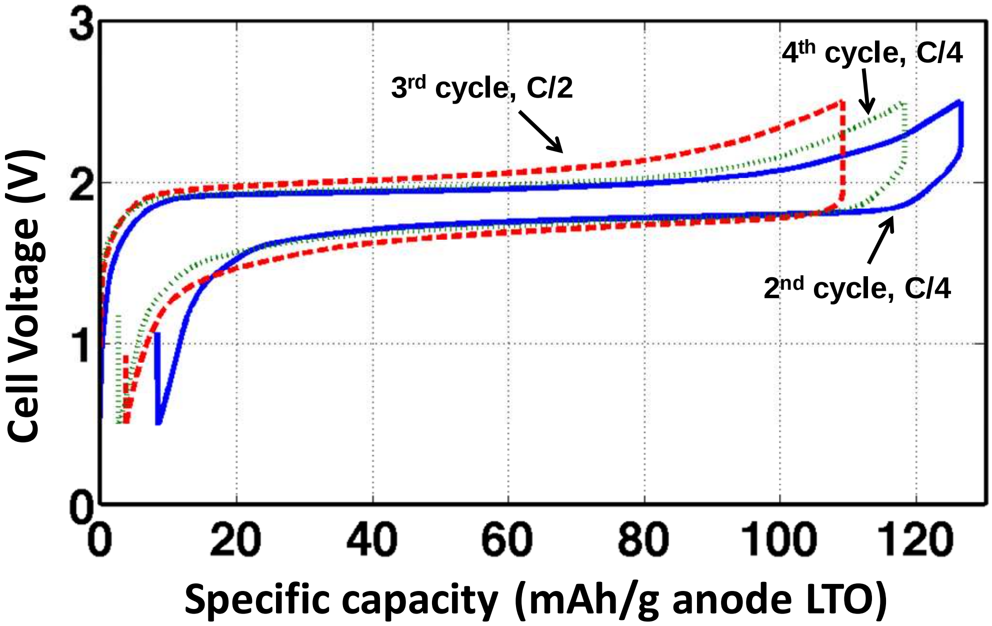

Figure S3. Galvanostatic cycling of a full lithium-ion using non-flowing suspensions at both cathode and anode.

Non-Newtonian Suspension Flow and Mechanical Energy Dissipation

In order to characterize the flow of the slurries through the cell and develop a quantitative estimate of the mechanical energy dissipation through pumping, computational fluid dynamics (CFD) calculations were performed. Star-CCM+ v4.06.011 software was used to solve steady state flows with non-Newtonian power law viscosities through the standard channel geometry at several representative flow rates. The power law takes the form of **Equation S1**, where η is the viscosity, $\dot{\gamma}$ the shear rate, and K and n are fitting parameters.

$$\eta = K\dot{\gamma}^{n-1} \qquad \text{(S1)}$$

Experimental viscosity vs shear rate data in Figure 2a were used to obtain the fitting parameters. All of the data presented below was calculated using K=7.41505 Pa s, and n =

0.130188, corresponding to the suspension containing 22.4% LCO and 0.6% Ketjen in Figure 2a.

Figure S4 shows the calculated velocity profile across a 1.4mm flow channel for a 15 mL min^{-1} flow rate. Due to the strong shear thinning characteristics, the suspension exhibits plug flow with little to no velocity gradient near the channel center and regions of high shear rate near the channel walls. This plug flow behavior is important for preventing mixing of regions of varying states of charge during flow, and also reduces the power required for pumping compared to a Newtonian fluid with the same average viscosity.

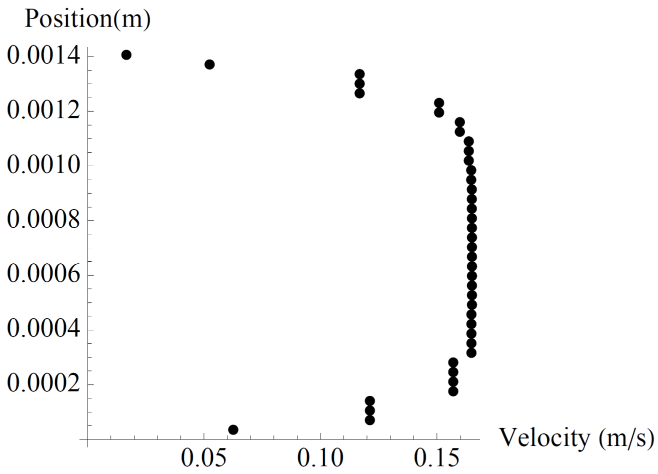

Figure S4. Calculated velocity vs. position across a 1.4mm flow channel, for a 22.4% LCO, 0.6% Ketjen suspension flowing at 15 mL min^{-1}.

The pressure gradient needed to sustain the flow at each flow rate was extracted from the CFD data based on a linear fit to the pressure as a function of position along the channel length. The power required to continuously flow the slurry through 20 cm of tubing (a length representative of the experimental setup) was calculated using **Equation S2**, where dP/dx is the pressure gradient and Q is the flow rate.

$$P_{continuous} = \frac{dP}{dx} \cdot 20cm \cdot Q \qquad \text{(S2)}$$

In addition the total energy required to circulate the suspension through 20 cm of tubing once was computed using **Equation S3**, where V_{20} is the volume of fluid in 20 cm of tubing.

$$E_{circulate} = \frac{dP}{dx} \cdot 20cm \cdot V_{20} \tag{S3}$$

Parasitic energy losses are calculated for each mode based on 21.4 mW discharge power for continuous flow operation and 2.52 J of energy stored in 20 cm of tubing (these values are taken from experimental data for a 22.4% LCO and 0.6% Ketjen suspension). For intermittent flow, it is assumed that each suspension is charged or discharged in a single pass during which the energy dissipated is $E_{circulate}$. Since there are two suspensions, and each needs to be pumped once to charge and once to discharge, the loss is $4E_{circulate}$ divided by the stored energy of 2.52 J. In continuous flow, the loss is taken as 4 times the pumping power divided by the electrical discharge power. The results, tabulated in **Table S1** for five different flow rates, show the great reduction in loss that is possible when cells and suspensions are designed to allow single-pass charging and discharging.

Flow Rate (mL min^{-1})	$P_{continuous}$ (mW)	$E_{circulate}$ (mJ)	Continuous flow loss (%)	Intermittent flow loss (%)
15	2.36	3.78	44.12	0.60
10	1.41	3.38	26.36	0.54
5	0.63	3.01	11.78	0.48
1	0.10	2.39	1.86	0.38
0.1	0.008	1.86	0.14	0.30

Table S1. Calculated parasitic energy loss percentages as a function of flow rate for two modes of pumping: continuous and intermittent.