Title: A Carbon-Free Lithium-Ion Solid Dispersion Redox Couple with Low Viscosity for Redox Flow Batteries

Authors names and affiliations:

Zhaoxiang Qi^a, Gary M. Koenig Jr.^a

^aDepartment of Chemical Engineering, University of Virginia, 102 Engineers Way, Charlottesville, VA, USA 22904-4741.

Email address:

Zhaoxiang Qi, zq6qb@virginia.edu; Gary M. Koenig Jr., gkoenig@virginia.edu.

Corresponding author: Gary M. Koenig Jr.

Department of Chemical Engineering, University of Virginia, 102 Engineers Way, Charlottesville, VA, USA 22904-4741

1-434-982-2714 phone

1-434-982-2658 fax

gkoenig@virginia.edu

Abstract

A new type of non-aqueous redox couple without carbon additives for flow batteries is proposed and the target anolyte chemistry is demonstrated. The so-called "Solid Dispersion Redox Couple" incorporates solid electroactive materials dispersed in organic lithium-ion battery electrolyte as its flowing suspension. In this work, a unique and systematic characterization approach has been used to study the flow battery redox couple in half cell demonstrations relative to a lithium electrode. An electrolyte laden with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been characterized in multiple specially designed lithium half cell configurations. The flow battery redox couple described in this report has relatively low viscosity, especially in comparison to other flow batteries with solid active materials. The lack of carbon additive allows characterization of the electrochemical properties of the electroactive material in flow without the complication of conductive additives and unambiguous observation of the electrorheological coupling in these dispersed particle systems.

Keywords

Flow battery; energy storage; lithium-ion battery; carbon-free; lithium titanium
oxide; suspension

1. Introduction

Redox flow batteries are ideal for large scale energy storage because of the decoupling of the power and the energy in the system, which provides the flexibility to independently adjust and design the power and energy requirements for an application [1]. The electrochemical energy is stored in electrolyte tanks, which in principle results in total energy only being limited by tank size.

Conventional flow batteries are typically comprised of transition metal redox couples dissolved in highly acidic aqueous electrolytes [2, 3]. Different approaches have been pursued in the literature to improve flow battery performance, including investigating new redox couples [4], designing more efficient current collectors [1, 5-7], incorporating electrolyte additives [8], and modifying the ion-transferring membrane [9]. The energy density in conventional flow batteries is highly limited by the solubility of the active species, because beyond the solubility limit inactive precipitates form in the electrolyte [2, 3]. The long-term performance or cycle life of these systems is also limited by the significant loss of stored energy (i.e., capacity loss) in the electrolytes over time due to transport of the active species across the separator [9].

Alternative flow battery systems beyond the conventional dissolved transition metal electrolytes have also been reported in the literature, including lead-based flow batteries with soluble lead [10] and polymer suspensions [11]. Another modified flow battery that has been developed is a convection battery with the electroactive materials fixed and electrolyte flowing to improve the mass

transport of ionic species in the electrolyte [12, 13]. These reported systems, however, have performance limitations due to maximum practical electrode thicknesses or the inefficient pumping due to high pressure drop. More recently, the possibility of combining lithium-ion battery chemistries with flow batteries has been proposed due to the high energy density and high operating voltages of lithium-ion battery active electrode materials [14]. While energy density is not necessarily a major concern for some stationary applications, higher energy density flow battery chemistries will be needed for flow batteries to be implemented in electric vehicles or stationary applications in urban areas where space is limited and energy demand is high. In some cases the active electrolyte materials are still soluble compounds, for example in the report of a membrane-free semiliquid flow battery composed of a ferrocene-based catholyte and a passivated metallic Li anode [15]. Other groups have moved to solid electroactive material flow battery designs, and recently the concept of semi-solid flow cells (SSFC) was demonstrated by Chiang's group for both organic and inorganic systems [16, 17]. In these reports, electrochemically active particles were suspended in the electrolytes together with conductive carbon, forming an interconnected network structure with relatively high conductivity. Other research groups have expanded on this concept and incorporated different chemistries into SSFC-type systems, including LiFePO_4 [18]. These SSFC-type systems have also explored improvements by incorporation of surfactants within the electrolyte and by developing electrochemical models [19, 20]. A high energy storage density ($> 130 \text{ Wh kg}^{-1}$) compared to conventional flow batteries was

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4 achieved in these SSFC-type systems as a result of the high energy density solid
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6 electroactive materials [16]. However, the operating cost of SSFC-type systems
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8 will likely be extremely high due to high viscosities ($> 1 \text{ Pa}\cdot\text{s}$ at the shear rate of
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10 35 s^{-1}) of the viscous electrolyte suspensions [16, 21]. Inactive carbon conductive
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12 additives in these systems also reduce the total electrolyte energy density.
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18 Herein, we first demonstrate a redox couple for a new type of flow battery without
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20 carbon additives and hence with a relatively low viscosity. The functional design
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22 of the system is similar to a SSFC, but the flowing suspension is comprised of
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24 only electroactive material particles dispersed in an organic lithium-ion battery
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26 electrolyte. In contrast to previous SSFC reports, electrochemical
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28 charge/discharge of our redox couple does not rely on an interconnected particle
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30 network throughout the electrolyte, but instead relies on the collisions of particles
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32 directly with the current collector (or through interparticle contacts to the current
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34 collector). For this initial experimental work, we took advantage of a lithium half
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36 cell configuration to characterize an electrolyte laden with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO). LTO
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38 was chosen because of its high capacity and good electrochemical performance
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40 at a variety of charge/discharge rates [22-24]. The details of LTO's material
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42 properties and electrochemical mechanisms have also been well described in the
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44 literature [25-28]. The flat charge/discharge profile for LTO should be
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46 advantageous at providing a consistent voltage during charge/discharge,
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48 regardless of the state of lithiation of the active material in contact with the
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50 current collector at any given time. LTO is also a zero-strain lithium insertion
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4 material [25, 29], which prevents fractures of the particles during electrochemical
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6 cycling. In addition, the charge/discharge potential of LTO (~ 1.55 V vs. Li/Li^+) is
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8 within the stability window of the electrolyte, which removes the complication of
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10 significant electrolyte decomposition and solid-electrolyte interphase formation
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12 [30]. We note that at this voltage the long term goal is to use LTO as an anolyte
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14 paired with a catholyte that contains a lithium-ion battery solid cathode active
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16 material. Thus, although for initial half cell characterization studies reported here
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18 relative to lithium metal LTO is a cathode, the eventual goal is to use the LTO as
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20 an anolyte in a full cell flow battery.
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29 Since this system was derived from conventional lithium-ion battery electrode
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31 materials, we adopted a distinct approach to demonstrate the as-proposed flow
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33 battery redox couple step-by-step. A conventional lithium-ion battery coin cell
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35 with LTO was prepared as a benchmark, and then a particle coin cell was
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37 constructed free of binders and conductive additives to show that the LTO active
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39 material could be successfully charged and discharged through direct contact
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41 with the current collector. After that, a vial cell was prepared to electrochemically
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43 characterize the LTO suspension during electrochemical cycling in a turbid
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45 flowing environment, and finally a flow cell was assembled to demonstrate the
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47 as-proposed flow battery redox couple. Rheological tests were conducted to
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49 demonstrate the viscosity of our particle-laden electrolyte as a function of particle
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51 loading and relative to other flow battery systems.
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2. Experimental

2.1. Preparation and Characterization of Materials

LTO (NEI Corporation) powders were obtained from the U.S. Department of Energy's (DOE) CAMP (Cell Analysis, Modeling, and Prototyping) Facility, Argonne National Laboratory. Detailed materials characterization of LTO powder from NEI can be found in other reports in the literature [31, 32]. The electrolyte (BASF Corporation) was 1.2 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with EC/EMC = 3:7 by volume ratio. The LTO suspensions of different loadings (5 vol%, 10 vol%, 20 vol%) were prepared by mixing the LTO powders with electrolyte under stirring overnight within an argon-filled glove box (with concentrations of $\text{O}_2 < 1$ ppm and $\text{H}_2\text{O} < 1$ ppm) at room temperature.

To characterize the LTO powder morphologies, scanning electron microscope (SEM) images were taken with a Quanta 650 SEM. X-ray diffraction (XRD) patterns were obtained with a Panalytical X'pert diffractometer using Cu $\text{K}\alpha$ radiation. Rheology testing of the LTO suspensions was performed with an Anton Paar rheometer (Physica MCR 301, with a 5 cm plate-plate geometry).

2.2. Electrochemical Characterization

A conventional LTO electrode was fabricated from a slurry comprised of 80 wt % LTO powder, 10 wt % carbon black as conductive additive, and 10 wt %

polyvinylidene fluoride binder (PVDF) dissolved in N-methylpyrrolidone (NMP, Sigma-Aldrich®). The slurry was agitated in a slurry mixer for 5 minutes and pasted (with a doctor blade with a gap height of 200 μm) onto aluminum foil. The pasted slurry was dried in an oven at 70 °C overnight and further dried in a vacuum oven at 70 °C for 3 hrs. Electrodes composed of only LTO particles as the electrode material without binders or conductive additives on the aluminum foil were also prepared. LTO particles were suspended in acetone (Fisher Scientific) with a concentration of $\sim 50 \text{ mg mL}^{-1}$, dropped on pre-punched aluminum foil discs (1.6 cm^2), and dried in a vacuum oven at 70 °C for 2 hrs. A coin cell using the as-prepared electrode was referred to as a “particle coin cell”. All coin cells were assembled in the glove box. LTO half cells were assembled with the LTO electrode as the cathode and lithium foil as the anode. The electrodes were separated by a polypropylene/polyethylene/polypropylene trilayer membrane. The galvanostatic charge-discharge cycling of coin cells was performed on a Maccor battery cycler. For all cycling tests where C rates are given, 1C was assumed to be 174.55 mA g^{-1} (the theoretical capacity of LTO) and the current adjusted by the amount of LTO active material.

2.3. Vial Cell and Flow Cell Testing

A customized cell was set up in the glove box as illustrated in Figure 1a, which we refer to as a “vial cell”. An aluminum wire (99.999%, Alfa Aesar) of 1.5 mm in diameter and 20 cm in length was immersed in an LTO suspension of desired particle loading. Lithium foil, which was attached to a copper foil extended to the

external circuit, was immersed into the electrolyte within a glass tube and separated from the LTO suspension by a trilayer membrane separator. Typically, particles would remain dispersed in the suspension for ~30 minutes if agitation was stopped, however, particles were kept suspended via agitation continuously during all electrochemical experiments. Addition of surfactant would have been one approach to further stabilize the suspension [33-35], however, the surfactant components would have introduced additional complications and sources for electrochemical currents within our system, and for this initial demonstration we focus on the electrochemical activity of just the active LTO particles free of conductive or stabilizing additives [33, 36].

A customized flow cell was set up as illustrated in Figure 1b. The flow channels were formed by cutting compact stacks of laboratory films (Parafilm®) to provide the desired spacing and trilayer membrane separators were used. Aluminum wire was used as the cathode current collector. A piece of lithium foil was attached on a stainless steel foil (McMaster-Carr) as the anode and connected to a potentiostat (Bio-Logic, SP-150) to perform electrochemical tests. The whole cell was sealed with two polypropylene plates (McMaster-Carr). Electrochemical tests for both the vial cell and flow cell were performed within the glove box.

3. Results and Discussions

3.1. Materials Characterization

Figure 2 shows XRD patterns for the LTO powder (Figure 2a), as well as reference patterns for spinel phase LTO material (Figure 2b, obtained from PDF 00-049-0207 [37]) and rutile TiO_2 (Figure 2c, obtained from PDF 00-001-1292 [38]). The peaks for the LTO powder are consistent with the majority of the powder being spinel phase LTO. There are two small but distinguishable peaks in the XRD pattern at 27.49° and 54.36° , which are consistent with an impurity rutile TiO_2 phase also being present in the LTO powder. Rutile TiO_2 impurity is a common impurity observed for LTO materials, and has been reported as an intermediate compound during solid-state synthesis of LTO using anatase TiO_2 and Li_2CO_3 [26, 39]. The morphology of the LTO powder is shown in the SEM image in Figure 3. The LTO powder consisted of irregularly shaped particulates with average particle lengths of 340 ± 200 nm (based on the measured lengths of 35 particles). The XRD and SEM results for this NEI LTO material was consistent with previous reports on LTO materials from NEI [31].

3.2. Conventional Coin Cell Electrochemical Characterization

Before using the LTO powder in our custom electrochemical cell geometries, we evaluated its electrochemical performance in conventional composite electrode architectures within coin cells. The first discharge and charge cycle of a conventional Li/LTO half cell is shown in Figure 4a. This cell was cycled at a rate

of 0.1C and had a first cycle discharge capacity of 131 mAh g⁻¹ and charge capacity of 132 mAh g⁻¹. While the first cycle had ~1% irreversible capacity loss, the columbic efficiency of subsequent cycles at 0.1C was ~100%. The LTO electrode had a flat charge/discharge plateau at approximately 1.55 V (vs. Li), consistent with literature reports [22, 23, 40-42]. Interestingly, even though the XRD patterns provided evidence of rutile TiO₂ (Figure 2), we did not observe associated discharge plateaus at 1.4 and 1.1 V [43]. The lack of capacity in these voltage regions was attributed to the small amount of the rutile TiO₂ impurities and the location of rutile TiO₂ phase possibly being segregated within the particle cores, making the rutile phase more difficult for lithium ions to access [26, 44].

3.3. Particle Coin Cell Electrochemical Characterization

To confirm that our LTO active material could maintain electrochemical activity in the absence of binders and conductive additives, a static particle coin cell battery was assembled where the electrode was comprised of only the LTO powder. The first charge/discharge cycle at a constant rate of 0.1C is shown in Figure 4b. This was the same rate (adjusted for active LTO mass) used for the conventional coin cells. The initial discharge capacity was 134 mAh g⁻¹, while the charge capacity was 127 mAh g⁻¹. Although the first cycle had 5.50% irreversible capacity loss, the columbic efficiency of subsequent cycles at 0.1C was ~99%. The particle coin cell had approximately equivalent gravimetric capacity within the same potential regions as the conventional coin cell, suggesting that electrochemical capacity was delivered from the entire thickness of the LTO electrode layer. The particle

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4 coin cell electrodes prepared for the tests had a thickness of greater than 70 μm ,
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6 which was far greater than the length scale of the particles ($340 \pm 200 \text{ nm}$).
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8 These results indicate LTO particles separated from the current collector by
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10 multiple layers of other LTO particles were participating in electrochemical
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12 lithiation/delithiation reactions. Thus, LTO-to-LTO particle contacts provided
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14 sufficient electronic conductivity for particles far from the current collector to
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16 contribute electrochemical capacity. Electrodes of different LTO loadings (and
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18 hence different thicknesses) were also prepared and tested (see Supplementary
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20 Data, Figure S1). The total capacity of the particle coin cells with increased LTO
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22 loading increased almost proportionally to the total LTO loading, further
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24 confirming that electrochemical capacity was contributed by LTO particles far
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26 from the current collector. An inverse relationship was observed between particle
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28 loading and rate capability of the particle coin cells. Thus, there are limits to the
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30 electrochemical capacity that can be extracted from particles far from the current
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32 collector, particularly at higher rates of charge/discharge. This was likely due to
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34 the increased resistance experienced by the electrons that had to traverse the
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36 extra distance via particle-to-particle LTO contact, as well as the lower lithium-ion
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38 accessibility to LTO close to the current collector for the thicker films. These
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40 results above, when combined, indicate that the LTO particles should be able to
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42 cycle when in contact with the current collector in the flow cell, and that capacity
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44 can also be contributed by particles far from the current collector if particle
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46 loadings are high enough to allow interconnected aggregated particle flocculation.
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The charge/discharge voltages for the particle coin cells were very flat with plateaus near 1.55 V, indicating minimal electrode polarization. This low polarization confirmed LTO as a good candidate active material for the flow cell. While the flow cell will have polarization due to other factors, including the low contact and loose packing of the suspended particles and larger electrolyte distance, the low polarization in the particle coin cell demonstrated the intrinsic capabilities of the LTO for the electrochemical flow cell. Interestingly, the particle coin cell had an even lower difference between the average charge and discharge potentials, even though the particle cell does not contain conductive additives or binders. We attribute this observation to the excellent electronic and ionic conductivity of LTO material [45]. Although the initial electrical conductivity of LTO has been reported to be $10^{-6} \sim 10^{-13} \text{ S cm}^{-1}$ [46], the conductivity has been demonstrated to rise sharply to 10^0 S cm^{-1} after very low levels of lithiation [45]. The electrochemical performance of the particle coin cells demonstrated that conductive additives were not necessary to effectively charge and discharge the LTO material when in contact with the current collector. These results provided additional motivation that a flow battery redox couple with LTO dispersed in electrolyte could be effectively charged and discharged through the contact of LTO particles with the current collector.

3.4. Rheological Characterization

Before evaluating the LTO material in custom flow geometries, we determined the rheological properties of LTO powder dispersed into the electrolyte. The

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4 rheological properties of a dispersed flow battery system are important both from
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6 an energy efficiency perspective and from a performance perspective. With
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8 regards to energy efficiency, the higher the viscosity of the particle-laden
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10 suspensions, the greater the energy demands of the pumps to move the particle
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12 dispersion through the flow battery system. Assuming the energy to drive the
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14 pumps is also provided by the flow battery, this parasitic energy loss will need to
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16 be considered in optimization of the overall energy efficiency of the battery [21].
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18 Some SSFC-type batteries have extremely high viscosities, for example a
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20 recently reported value of more than 2 Pa·s for the mixture of LCO and carbon
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22 additive, and thus high pumping energy demands are necessary to flow such a
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24 slurry [16]. The rheological properties of the suspension will impact the
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26 distribution of particles in the suspension, the access of material to the current
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28 collector, and the collision frequency and residence time for the particles in
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30 contact with the current collector. Various factors contribute to the rheological
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32 behavior, such as particle size and morphology, salt concentration, temperature
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34 and pressure, and particle loading [47, 48]. Considering the critical influence of
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36 particle loading on both rheological properties and energy density, we measured
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38 the viscosity of our LTO particle suspensions as a function of applied shear at a
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40 variety of particle loadings.
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51 Figure 5 displays the viscosity as a function of shear rate for the particle-free
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53 electrolyte (1.2 M LiPF₆ in EC/EMC = 3:7) and the electrolyte laden with 5, 10,
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55 and 20 vol% LTO. The viscosity for all samples changed multiple orders of
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57 magnitude over the shear range investigated. The electrolyte both with and
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without particles displayed shear-thinning behavior, with the viscosity decreasing with increasing shear rate [47]. The particle-free electrolyte had Newtonian behavior with a flat plateau at shear rates higher than 10 s^{-1} [47]. The viscosity increased with a higher LTO loading. For the lowest particle concentration of 5 vol%, the measured viscosity was close to that of the particle-free electrolyte at low shear rates. The drag force provided by the LTO particles in the electrolyte became more pronounced at higher shear rates. This behavior indicates that at the lowest concentration (5 vol%), the LTO particles had a minor influence on the viscosity of the fluid dispersion. However, at 10 and 20 vol% LTO concentration, the viscosities were significantly higher than particle-free electrolyte and 5 vol% LTO within the full range of applied shear. Also, the Newtonian plateau at higher shear rate disappeared, and instead an extended shear-thinning behavior was observed. This behavior is consistent with the extreme shear-thinning behavior of flocculated metal oxide suspensions [49, 50] and previous research on LTO suspensions, which have reported that the flocculated network breaks up into smaller flocculates after sufficient shear, resulting in the steep decrease in viscosity [48].

The relation between the viscosity and shear rate in the shear thinning region can be described by a power law or Ostwald–de Waele relationship [51], taking the form of Equation 1, where η is the viscosity, $\dot{\gamma}$ is the shear rate, and K and n are fitting parameters. K is known as the flow consistency index, giving the viscosity at a shear rate of 1 s^{-1} . The dimensionless power law index describes

the fluid behavior compared with a Newtonian fluid. For a Newtonian fluid, $n = 1$; for a shear-thinning fluid, $n < 1$ and for a shear-thickening fluid n is greater than 1.

$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

Experimental data from the LTO suspensions in Figure 5 were used to obtain the fitting parameters K and n . The fits of the 5 vol% LTO suspension was $K = 0.18$ and $n = 0.44$ ($R^2 = 0.98$); the 10 vol% LTO suspension was $K = 0.96$ and $n = 0.39$ ($R^2 = 0.99$); and the 20 vol% LTO suspension was $K = 7.80$ and $n = 0.38$ ($R^2 = 0.97$). These results and the quality of the fitting parameters further confirmed the shear-thinning behavior of the LTO suspensions [47]. The increasing K values with increased particle loadings indicated that suspensions with higher loadings generally have greater viscosities as would be expected; however, the decreasing n values with increased particle loading indicated that suspensions with higher loadings have more extensive shear-thinning behavior. The increased shear thinning with increasing particle loading is consistent with the higher loading suspensions being more flocculated, and with the flocculates becoming less stable and breaking up with sufficient applied shear. We also note that the n values are very close for 10 vol% and 20 vol% LTO, indicating that the transition to a more flocculated suspension occurs between 5 vol% and 10 vol% LTO. The observed shear-thinning is important to the operation of a carbon-free solid dispersion flow battery, because the rheological data indicate that there will be advantages from the perspective of reducing the suspension viscosity to operating at higher shear rates. A higher shear rate of the suspension means a higher flow rate in the tubing and the electrochemical channels of the flow cell.

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4 While the flow battery cannot be operated at an arbitrarily high flow rate,
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6 operation beyond the limit where flocculates break up would be desirable from
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8 the standpoint of reducing suspension viscosity. Also, the increases in viscosity
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10 for higher LTO concentration means that there is a trade off in the flow cell
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12 between energy density and energy efficiency. Future studies will be conducted
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14 to understand the structure of the particle aggregates and the conditions that
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16 control the onset of the flocculation.
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23 *3.5. Vial Cell Electrochemical Characterization*

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25 In advance of constructing a full flow cell to characterize the dispersed particle
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27 electrolyte suspensions, the vial cell was used to characterize our particle
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29 suspensions electrochemically. For vial cell Chronoamperometry (CA)
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31 experiments, a fixed discharge potential of 1.2 V was used and the current was
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33 measured for 120 seconds. This voltage was chosen because it was below the
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35 1.55 V discharge plateau of LTO, but above the potential where electrolyte
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37 decomposition and lithium aluminum alloy formation would be expected to
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39 compete with lithium intercalation for the currents measured [52-54]. The short
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41 measuring time of 120 s was chosen because it was enough to observe a stable
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43 current output and time-efficient to perform the tests. The results of CA using the
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45 vial cell for increasing particle loadings in the electrolyte dispersions can be
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47 found in Figure 6a. The electrolyte without particles dispersed was used as a
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49 control, and as expected the measured current was very low, with the steady-
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51 state value approaching 0 mA. Compared with the electrolyte baseline, all the
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other samples achieved a measureable current output (the currents were negative because the cell was discharging). Therefore, the LTO particles in the suspension were the source of the observed electrochemical activity. To further understand if the reactions were caused by lithium insertion into the LTO particles, cyclic voltammetry (CV) testing was performed for these suspensions in the vial cell at 5 mV s^{-1} and the results are shown in Figure 6b. The reduction and oxidation peaks were around 1.55 V. No other peaks were observed, indicating no other major redox reactions were occurring in the vial cell system except for the desired oxidation/reduction of LTO. The electrochemical responses that were observed could have been caused either by LTO particles attached on the aluminum wire or by the particles in the suspension colliding with the aluminum wire. To provide insights into whether electrochemical activity originated from attached or colliding LTO particles, a CA test was performed in the vial cell where the suspension stirring was halted during the test. If the electrochemical activity was from adsorbed particles, the current signal would be expected to remain approximately constant, while if the current was due to colliding particles we expected the measured current to drop to approximately zero due to the absence of stirring initiating particle collisions with the current collector. This CA experiment was conducted at 1.2 V with the 10 vol% LTO suspension. As shown in Figure 7a, when the stirring was stopped at ~160 s, the current response quickly dropped to the background level. The measured current increased back to ~0.2 mA (0.02 mA cm^{-2}) as the stirring was resumed at ~360 s. The results in Figure 7a demonstrate that the discharge current from the LTO suspension is

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4 dependent on the agitation of the solution provided by stirring. The results above
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6 lead us to conclude that the electrochemical reactions observed were due to
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8 lithium insertion and extraction into/out of LTO particles as they collided with the
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10 aluminum wire current collector.
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16 As shown in the insert of Figure 6a, the discharge current linearly increased with
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18 the LTO concentration. This dependence of the measured CA current on LTO
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20 loading could be caused by the change in the collision frequencies of LTO
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22 particles on the aluminum wire. In the simplest case where the LTO particles
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24 were discrete units, a higher LTO concentration would provide more LTO
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26 particles within the range of the electron transfer distance from the aluminum
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28 wire, and hence more LTO particles would be able to collide on the aluminum
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30 wire and subsequently were discharged, resulting in the increased observed
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32 output currents. In addition, as discussed previously, rheological data suggested
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34 a more flocculated particle structure formed as the suspended particle
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36 concentration was increased. The flocculated aggregates would promote inter-
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38 particle charge transfer, further increasing the discharge current. The
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40 electrochemical plateaus had surprisingly little noise in the measured current for
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42 the first ~20 s of each CA curve, especially when compared to the steady-state
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44 current. This behavior was attributed to the electrochemical activity of a small
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46 amount of LTO powder attached on the aluminum wire. These attached particles
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48 were discharged as soon as the test started and were fully discharged quickly
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50 due to their small total capacity in the system. The steady-state current plateau;
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4 however, was attributed to the electrochemical discharge of LTO particles from
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6 the suspension colliding with the aluminum surface. We note that the CA curves
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8 were not flat but had fluctuations in the measured current. We attribute the
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10 fluctuations of the CA curves to the LTO particles not being perfectly
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12 homogeneously dispersed within the electrolyte. Thus, the concentration of LTO
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14 particles near the current collector, as well as number of particles/aggregates in
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16 direct contact, varies at any given instant. This local inhomogeneity in the
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18 dispersion results in the fluctuation in the observed current because when more
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20 total particles/aggregates were in contact with the current collector, greater
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22 electrochemical current was produced.
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31 The CV curves in Figure 6b were also influenced by the LTO concentration in the
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33 suspension. The CV results were consistent with the CA measurements from the
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35 perspective that there was an increase in the measured current as the LTO
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37 loading was increased. During electrochemical reduction of the LTO in the CV
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39 scan, a typical CV peak is not observed. These CV scans were not taken in
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41 quiescent solution, but instead were in a highly turbid constantly stirred
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43 suspension. We attribute the lack of a reduction peak and the increased noise in
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45 the measured current at lower voltages on reduction to the electrochemical
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47 reactions in this regime being limited by the collision rate of particles in the
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49 suspension with the current collector wire. An interesting phenomenon observed
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51 in the CV curves was that there were significant oxidation peaks, even though
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53 only a very small fraction of the LTO particles (which initially should all be in the
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oxidized state) have been reduced. We estimate the fraction of the LTO material in the suspension that has been reduced before the oxidation half cycle to be only < 0.01% of the total electrochemical capacity within the dispersion. Thus, the significant LTO oxidation peaks in the CV scans indicate that the same LTO particles that participated in electrochemical reduction were still available to participate in electrochemical oxidation reactions on the aluminum wire current collector. The polarization of the CV curves was observed to be independent of loading of LTO particles. Great care was taken to use the same aluminum wire, lithium foil, and the wire-foil separation for all measurements at the different loadings and hence the IR drop associated with these components would be expected to be equivalent for all the measurements [55].

To further characterize the discharging behavior of the vial cell system, chronopotentiometry (CP) testing was performed for the 10 vol% sample. For currents of -0.02, -0.05, and -0.10 mA (-0.002, -0.005, and -0.010 mA cm⁻², respectively), the potentials measured for the vial cell are shown in Figure 7b. Decreasing steady-state potentials were observed as the current was increased, consistent with previous reports [23, 42, 56-58]. The observed behavior was attributed to the increased IR drop in the vial cell with increasing current. The open cell voltage (OCV) was measured to be 1.57 V, and the steady-state potentials for 0.02, 0.05 and 0.10 mA discharge currents were 1.54, 1.49 and 1.40 V, respectively. These results were consistent with an almost linear relationship of the IR drop with increasing current. We note that the CP curve for

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4 the 0.10 mA test was relatively unstable compared to the 0.02 mA and 0.05 mA
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6 currents. We speculate that at 0.10 mA we are starting to reach the limits of the
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8 stable current that we can draw for the stochastic particle collision process, at
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10 least for the level of agitation and amount of exposed surface area on the current
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12 collector in the vial cell.
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19 Constant current discharging and charging was performed with the vial cell to
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21 demonstrate the viability of charging and discharging the vial cell as a battery.
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23 The constant current charge/discharge tests were performed using the 10 vol%
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25 dispersion. As shown in Figure 7c, the cell was first discharged at 0.05 mA
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27 (0.005 mA cm^{-2}) for 10 minutes and was then switched over to charge at the
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29 same current, with the cell being successfully charged for ~3 minutes before
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31 hitting the upper voltage cut-off of 2.1 V, resulting a coulombic efficiency of 38%.
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34 The charge and discharge plateaus were both at ~1.55 V, consistent with lithium
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36 insertion and extraction into/out of LTO particles with low polarization [22, 23, 40-
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38 42]. While the total capacities charged/discharged were relatively low (the total
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40 discharge capacity was $8.33 \times 10^{-3} \text{ mAh}$ and the total charge capacity was $3.18 \times$
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42 10^{-3} mAh , corresponding to < 0.01% of the capacity of the LTO particles in the
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44 suspension), full discharge and charge of the cell would have been impractical
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46 because of the relatively low current densities and large amount of LTO active
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48 particles in the vial cell. The columbic efficiency also appears artificially low
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50 because most of the discharged material was exchanged into the solution laden
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52 with LTO particles in the oxidized state, limiting the total capacity available. The
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primary purpose of the test was to demonstrate 1) that the vial cell was capable of charge and discharge with colliding LTO particles, and 2) that the polarization during charge and discharge was low. Both of these principles were demonstrated in the vial cell, and thus we moved to finally demonstrating electrochemical capacity of the LTO suspension within a custom flow cell geometry.

3.6. Flow Cell Electrochemical Characterization

We assembled a custom flow cell (Figure 1b) using the 10 vol% LTO suspension. The flow rate used for the LTO suspension through the flow channel and tubing was 120 mL min^{-1} . A CA test was performed for the flow cell at a fixed potential of 1.2 V and the results are shown in Figure 8a. The CA curve displayed similar behavior to that observed for the vial cell. The significant current measured in excess of the baseline confirmed that the LTO particles were discharged in the flow cell. CV was used to further confirm that there was electrochemical capacity from the LTO within the flow cell (Figure 8b). The redox peaks at $\sim 1.55 \text{ V}$ were consistent with the lithiation and delithiation of LTO particles [22, 23, 40-42]. Similar to the vial cell, the current output fluctuated due to the local inhomogeneity of the LTO suspension. The CV profile in the flow cell was similar to the vial cell, although the oxidation peak was much smaller. This was because the amount of LTO material in the flow cell experiment was larger than the amount used in the vial cell, while the surface area available from the current collector was less, resulting in a decrease in the relative amount of LTO particles

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4 discharged. In the flow cell, the oxidation current was smaller relative to the vial
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6 cell because a much smaller portion of LTO particles were discharged; and the
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8 “peak” was broadened because the residence time was short and the reaction
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10 was not limited by lithium-ion diffusion but rather by the available discharged LTO
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12 particle concentration.
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18 A constant current discharge and charge was also performed for the same 10
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20 vol% sample (Figure 8c). The profile used was similar to the vial cell described
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22 previously. A constant current discharge was performed at 0.02 mA (0.0064 mA
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24 cm⁻²) for 10 minutes, followed by a constant current charge at the same current
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26 that reached the upper voltage cut-off after ~4 minutes. The discharge plateau
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28 was at ~1.55 V, and the charge cycle starts at a plateau at ~1.55 V before quickly
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30 increasing in potential. The capacities were of 3.33×10^{-3} mAh for discharge and
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32 1.49×10^{-3} mAh on charge, resulting a coulombic efficiency of 45%. It is not
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34 surprising that only a fraction of the discharge capacity is recovered on charge,
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36 as a very small portion of LTO particles were discharged. We note that the
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38 charging curve has more noticeable fluctuations and a greater polarization
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40 relative to the vial cell. This is because the vial cell had constant access to the
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42 discharged particles during testing while the flow cell was only able to charge the
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44 small portion of the discharged particles that was in the flow chamber at any
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46 given time. While the capacities obtained in this cell are relatively modest, they
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48 successfully demonstrate the galvanic cycling of a solid dispersion LTO flow
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50 battery redox couple that relies on collision of LTO particles with the current
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collector to store and deliver electrochemical energy. Future efforts will be taken to increase the power of the cell to achieve full discharge and charge cycles within practical time limits.

We will note here that both the vial cell and flow cell experiments were limited in their discharge and charge times due to practical constraints of our system and its low current and power densities in this initial demonstration, and this limitation was not due to limited capacity of the LTO in the suspension. The mass of LTO in the vial cell with a 10 vol% suspension was 2.98 g. Based on the total cycling current in the cell of 0.02 mA, the time to fully discharge the cell would be ~348 days (2.98 g LTO at ~140 mAh g⁻¹ is ~417 mAh). The ~12 months to discharge our vial cell made complete cycles impractical. These factors highlight the need for current collector designs to increase the current density in our system. We also note our Li/LTO flow cell has a power density of ~0.01 mW cm⁻², in this initial half cell demonstration flow system. The particle size of the LTO particles is also expected to have a major impact on the power density measured in the flow and vial cells. The resistance from the LTO particles will be dependent on the ionic and electronic conductivity of the particles and their diameters [59, 60]. Minimizing active material particle sizes has been a typical approach to enhance conventional battery performance by increasing active surface areas, decreasing lithium ion diffusion distance and compensating the electronic conductivity [24, 59, 61-65]. Previous reports have established that the electrode resistance per unit mass of active material follows a general power law relationship with the

particle diameter [59]. In the case of our uncoated LTO particles with no carbon in the slurry, we expect the particle collisions result in active particles with effectively a point-contacted conductor. Considering the relatively low ionic conductivity of LTO particles compared to their electronic conductivity (in particular after partial lithiation), we expect the resistance per unit mass of particles undergoing electrochemical reactions in our system to scale with the square of the particle diameters [59]. A smaller particle size is also generally preferable in the solid dispersion redox couple because with smaller particles lithium ions need a shorter diffusion distance from the surface to the center of the particles to fully discharge/charge the particle, and there is a finite residence time during collision with the current collector. Future experiments will be conducted to understand the detailed impacts of particle size and polydispersity on the power density in our dispersed particle electrochemical system.

It is instructive to discuss the carbon-free solid dispersion flow system relative to existing flow battery systems. Assuming that we can achieve capacities for the LTO in our LTO dispersions comparable what was reversibly measured for our LTO particle coin cells, the anolyte within our flow cell setup would be able to achieve a capacity of 55.6 mAh g⁻¹ (total anolyte mass basis) with a viscosity of ~0.17 Pa·s at 20 vol% LTO loading. Some of the highest reported vanadium anolyte concentrations for vanadium redox flow batteries have theoretical capacities and viscosities within a similar range [66], however, the dispersion flow battery has the advantages of the ability to pair our anolyte with higher

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4 voltage lithium-ion catholyte materials and we are exploring the possibility of
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6 increasing LTO particle loading which would result in an even higher capacity
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8 dispersion. Also, relative to the semi-solid flow battery systems reported in the
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10 literature [16], for similar particle volume loadings of particles the solid dispersion
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12 flow battery redox couple reported here operates without carbon additives and
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14 has a lower viscosity. The maximum packing volume fraction is the upper limit for
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16 the active material loading. Depending on the particle size and morphology, this
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18 limit will range from 52.4 vol% [67] to 71 vol% [47, 68]. The energy density for the
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20 carbon-free solid dispersion redox flow battery system is only dependent on the
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22 energy density of the solid active material itself and the volume fraction of the
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24 active material that can be stably dispersed and efficiently pumped.
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4. Conclusions

A carbon-free solid dispersion redox flow couple consisting of an organic lithium-ion electrolyte laden with LTO was demonstrated and characterized electrochemically with a unique and systematic approach. It was found that LTO-to-LTO particle contacts provide sufficient electronic conductivity to allow particles multiple LTO particle distances from the current collector to contribute to battery capacity. The LTO suspension has a shear-thinning behavior and the current output of the LTO suspensions was linearly dependent on the LTO concentration. Electrochemical characterization of LTO dispersions in custom flow geometries indicates electrochemical capacity is provided by collision of LTO particles with the current collector, and that design of a flow cell relying on collision from a particle dispersion can be successfully reversibly electrochemically oxidized and reduced.

A carbon-free solid dispersion flow battery system inherits the advantages of conventional redox flow batteries to decouple the power and the energy in the system, providing the flexibility to independently adjust and design the power and energy requirements for an application. This system also has the potential to provide a much higher energy density with a lower viscosity compared with vanadium flow battery and semi-solid flow battery, provided the anolyte described in this study can be paired with a suitable catholyte and sufficient capacity utilization of active materials can be achieved. Future research efforts will need to be directed towards improving the power output of the carbon-free

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4 solid dispersion redox flow couple. The characterization methods described in
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6 this paper provide a systematic step-by-step method to study dispersed solid flow
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8 batteries.
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Figures:

Figure 1. Cartoon schematic of cell configurations: (a) a vial cell with the aluminum wire in the LTO suspension as the cathode current collector and the lithium foil in the glass tube as the anode; (b) a flow cell with an aluminum wire current collector in the channel containing the LTO suspension and lithium foil attached on the stainless steel foil as the anode.

Figure 2. XRD patterns for (a) the LTO powder, as well as reference patterns for (b) spinel-phase LTO material (obtained from PDF 00-049-0207) and (c) rutile TiO₂ (obtained from PDF 00-001-1292).

Figure 3. Scanning electron microscope (SEM) image of the LTO particles.

Figure 4. First discharge and charge cycle of (a) a conventional Li/LTO half cell and (b) a Li/LTO particle coin cell, both charged/discharged at a rate of $\sim 0.1C$.

Figure 5. The viscosity as a function of shear rate for the particle-free electrolyte (1.2 M $LiPF_6$ in EC/EMC = 3:7 solvents, black squares) and the electrolyte laden with 5 (red circles), 10 (blue triangles), and 20 (purple pentagons) vol% LTO.

Figure 6. (a) Chronoamperometry (CA) profiles at 1.2 V and (b) cyclic voltammetry (CV) scans at the rate of 5 mV s^{-1} for the particle-free electrolyte and the electrolyte laden with 5 (red), 10 (blue), and 20 (purple) vol% LTO as measured in the vial cell. Inset in (a) is the steady state current as a function of the LTO concentration in the suspension.

Figure 7. (a) Chronoamperometry (CA) profiles at 1.2 V with the stirring halted during the test, (b) Chronopotentiometry (CP) profiles with applied discharge currents 0.02, 0.05, 0.10 mA (0.002, 0.005, and 0.010 mA cm⁻², respectively), and (c) discharge and charge curves for the vial cell with an LTO concentration of 10 vol%.

Figure 8. (a) Chronoamperometry (CA) profile at 1.2 V, (b) cyclic voltammetry (CV) scan at the rate of 5 mV s⁻¹, and (c) discharge and charge curve for the flow cell with an LTO concentration in the electrolyte of 10 vol%.

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