



# A carbon-free lithium-ion solid dispersion redox couple with low viscosity for redox flow batteries



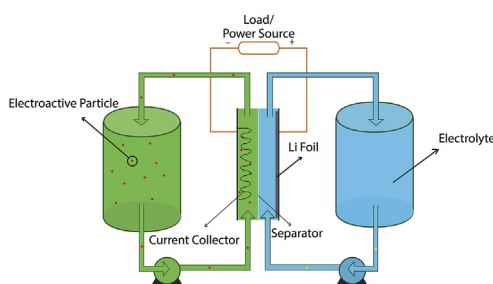
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## HIGHLIGHTS

- A carbon-free solid dispersion redox couple for a new type of flow battery is demonstrated.
- A unique characterization approach is used to study dispersion flow batteries.
- LTO suspensions with different loadings show shear-thinning behavior.
- Electrochemical behavior of LTO suspensions shows LTO loading dependence.

## GRAPHICAL ABSTRACT



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## 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.

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## 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

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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  $\text{LiFePO}_4$  [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 achieved in these SSFC-type systems as a result of the high energy density solid electroactive materials [16]. However, the operating cost of SSFC-type systems will likely be extremely high due to high viscosities ( $>1 \text{ Pa s}$  at the shear rate of  $35 \text{ s}^{-1}$ ) of the viscous electrolyte suspensions [16,21]. Inactive carbon conductive additives in these systems also reduce the total electrolyte energy density.

Herein, we first demonstrate a redox couple for a new type of flow battery without carbon additives and hence with a relatively low viscosity. The functional design of the system is similar to a SSFC, but the flowing suspension is comprised of only electroactive material particles dispersed in an organic lithium-ion battery electrolyte. In contrast to previous SSFC reports, electrochemical charge/discharge of our redox couple does not rely on an interconnected particle network throughout the electrolyte, but instead relies on the collisions of particles directly with the current collector (or through interparticle contacts to the current collector). For this initial experimental work, we took advantage of a lithium half cell configuration to characterize an electrolyte laden with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO). LTO was chosen because of its high capacity and good electrochemical performance at a variety of charge/discharge rates [22–24]. The details of LTO's material properties and electrochemical mechanisms have also been well described in the literature [25–28]. The flat charge/discharge profile for LTO should be advantageous at providing a consistent voltage during charge/discharge, regardless of the state of lithiation of the active material

in contact with the current collector at any given time. LTO is also a zero-strain lithium insertion material [25,29], which prevents fractures of the particles during electrochemical cycling. In addition, the charge/discharge potential of LTO ( $\sim 1.55 \text{ V vs. Li/Li}^+$ ) is within the stability window of the electrolyte, which removes the complication of significant electrolyte decomposition and solid-electrolyte interphase formation [30]. We note that at this voltage the long term goal is to use LTO as an anolyte paired with a catholyte that contains a lithium-ion battery solid cathode active material. Thus, although for initial half cell characterization studies reported here relative to lithium metal LTO is a cathode, the eventual goal is to use the LTO as an anolyte in a full cell flow battery.

Since this system was derived from conventional lithium-ion battery electrode materials, we adopted a distinct approach to demonstrate the as-proposed flow battery redox couple step-by-step. A conventional lithium-ion battery coin cell with LTO was prepared as a benchmark, and then a particle coin cell was constructed free of binders and conductive additives to show that the LTO active material could be successfully charged and discharged through direct contact with the current collector. After that, a vial cell was prepared to electrochemically characterize the LTO suspension during electrochemical cycling in a turbid flowing environment, and finally a flow cell was assembled to demonstrate the as-proposed flow battery redox couple. Rheological tests were conducted to demonstrate the viscosity of our particle-laden electrolyte as a function of particle loading and relative to other flow battery systems.

## 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 ( $\text{LiPF}_6$ ) 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  $\text{O}_2 < 1 \text{ ppm}$  and  $\text{H}_2\text{O} < 1 \text{ ppm}$ ) 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  $\text{Cu K}\alpha$  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 min and pasted (with a doctor blade with a gap height of 200  $\mu\text{m}$ ) 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 h. Electrodes composed of only LTO particles as the electrode material without binders or conductive additives on the aluminum foil were also

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