



Research Paper

Influence of electrochemical cycling on the rheo-impedance of anolytes for Li-based Semi Solid Flow Batteries



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ABSTRACT

The recently launched concept of Semi-Solid Flow Batteries (SSFBS) shows a strong potential for flexible energy storage, but the liquid-dispersed state of the electrode materials introduces several aspects of which a scientific understanding is lacking. We studied the effect of electrochemical cycling on the rheological and electrical properties of a SSFB anolyte containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and Ketjen Black (KB) particles in EC:DMC solvent with 1M LiPF_6 , using an adapted rheometer that allows in situ electrochemical cycling and electrical impedance spectroscopy. Charging (lithiation) caused a reduction in the electronic conductivity, yield stress and high shear viscosity of the fluid electrode. For mildly reducing voltages (1.4 V), these changes were partially reversed on discharging. For more reducing voltages these changes were stronger and persistent. The finding of comparable trends for a fluid electrode without the LTO, lends support to a simplistic interpretation, in which all trends are ascribed to the formation of a surface layer around the conductive KB nanoparticles. This Solid Electrolyte Interphase (SEI) insulates particles and reduces the van der Waals attractions between them. SEI layers formed at less reducing voltages, partially dissolve during the subsequent discharge. Those formed at more reducing voltages, are thicker and permanent. As these layers increase the electronic resistance of the fluid electrode by (more than) an order of magnitude, our findings highlight significant challenges due to SEI formation that still need to be overcome to realize SSFBs.

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1. Introduction

Semi-Solid Flow Batteries (SSFBS), as recently introduced by Duduta et al. [1], comprise a promising addition to the spectrum of rechargeable battery systems. The advantages of SSFBs over conventional batteries lie in the decoupling of power (cell size) and energy (tank size), and the potential for adjusting the chemistry of the system during operation. In particular non-aqueous SSFB systems are interesting, since they offer much higher energy densities as compared to more conventional aqueous redox flow systems [1]. The ability of non-aqueous SSFBs to provide and store energy in a flexible way makes them particularly promising for grid applications.

However, a key aspect in which SSFBs are yet unproven is their performance after repeated electrochemical cycling. While many SSFBs use the same materials [1,2] as conventional lithium-ion batteries, they may potentially degrade in different ways due to the dispersed state of the solid matter. In SSFBs (de)lithiation takes place in electrochemically active particles while the electrons are transported to the current collectors via conductive nanoparticles (CNPs). The occurrence of both particles in the (sub)micron size range has several consequences: i) the surface-to-volume ratio is relatively large, and ii) Brownian motion and interparticle interactions now play a role. Electrochemistry induced changes can therefore manifest themselves in different ways. They can directly affect individual particles (e.g. electronic conductivity, lithium uptake) but also collective effects are possible, because colloidal particles show a tendency for self-assembly into a microstructure. The colloidal interactions, which drive this assembly, are likely to be affected by the electrochemical cycling, and since the structure is kept dynamic by Brownian motion

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and/or shear flow, the microstructure may adapt to electrochemical changes.

While the precise microstructure of SSFB fluids is still to be ascertained, the generally accepted view [1–3] is that in the absence of flow, the CNPs assemble into a branched percolating network. This network provides electronic conduction and sustains static forces, thereby resisting the sedimentation of particles. In flow, the network gets broken down into agglomerates with a size that depends on the shear rate [3–5]. The contribution of active particles to the microstructure is less understood. They are expected to behave like a disordered fluid that surrounds the CNP network. This lack of order is inferred from the insignificance of both attractive and long-ranged repulsive forces; the former since otherwise the viscosity would be very high, the latter from the strong screening by the dissolved salt [6].

These differences between SSFBs and conventional lithium-ion batteries raise the question, how degradation processes such as volume and structural changes of the active materials upon (de-) lithiation [7] or the formation of solid electrolyte interface (SEI) [8,9] affect SSFBs. Several consequences of such processes for fluid electrodes are conceivable. Considering the CNP network, both the nature of the interparticle contacts and their number density can change: the former as a consequence of surface processes, and the latter due to (for flow batteries inherent) mechanical rejuvenation: shear-induced fragmentation of the CNP network creates a possibility for the fragments to re-assemble into a different microstructure when the fluid returns to the quiescent state³. Macroscopically, the electronic conductivity and the yield stress are likely affected by these microscopic processes. While critically relevant to SSFBs, the above phenomena can potentially also affect other types of battery systems that use self-assembling colloidal particles, such as polysulphide [10] and carbon free [11] flow batteries. Recent work on carbon slurry based iron redox flow batteries has shown electronic conductivity enhancement through changes in the interparticle contacts due to iron plating [12].

The objective of the present work is twofold: to quantify changes in rheological and electrical performance due to repeated electrochemical cycling, and to gain a mechanistic understanding of these macroscopic changes. To achieve these goals, a commercial rheometer was extended to allow parallel electrical impedance measurements, as well as a controlled cycling of the fluid electrodes via the inclusion of a lithium counter electrode. The studied fluid electrode consists of a mixture of Ketjen Black (KB) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) particles dispersed in EC:DMC 1:1 with 1 M LiPF_6 . LTO has previously been identified as a promising active material for SSFBs [13] as lithiation occurs at about ~ 1.55 V vs Li/Li^+ , within the safe operating range of the non-aqueous electrolyte [2,14,15]. To examine the role of electrochemical state (and history), we cycle the fluid electrode to a series of increasingly reducing voltages, measuring the rheological and electrical properties before and after each charge and discharge step. Comparisons are also made before and after mechanical rejuvenation, to probe the changes in self-assembly. To facilitate interpretation of the various changes we also make a comparison between the results for the KB-LTO electrode, and a fluid electrode without the LTO.

2. Materials and Methods

2.1. Fluid Electrode Preparation

Ethylene carbonate (EC) and dimethyl carbonate (DMC) were obtained from Sigma Aldrich (anhydrous, 99%+ purity). Binary mixtures of EC and DMC were 1:1 by mass. LP30 (EC:DMC 1:1 with 1 M LiPF_6) was obtained from BASF. Ketjen Black EC 600JD powder (KB) was obtained from AkzoNobel. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder was obtained

from Südcemie. Lithium foil was purchased from Alfa Aesar (99.9%). All sample preparations and experiments were carried out in an MBraun Argon-filled glove box (O_2 , H_2O below 1 ppm). Two fluid electrodes were prepared: a mixture of 1 wt.% KB and 5 wt.% LTO, and a reference sample at 1 wt.% KB. The dry particles were first wetted by EC-DMC solvent for 8 hours to improve their dispersibility; from an earlier study it is known that KB is colloidally unstable in carbonate solvent with large amounts of salt [6]. The KB reference contained 2.9 wt.% KB while for the mixture it was 2.6 wt.% KB and 13.4 wt.% LTO at this stage. Afterwards, LiPF_6 salt (Alfa Aesar (98%)) was added via a concentrated solution ($\text{LP30} + \text{LiPF}_6$) to reach a concentration of 1 M (viscosity 4 mPas [16]). After an additional 8 h, the samples were homogenized by rotor stator mixing (Ultraturrax) at 15000 rpm for 2 min, and loaded in the rheo-impedance setup.

2.2. Cycling-rheo-impedance setup

Electrochemical cycling and rheo-impedance measurements were performed on a stress controlled rheo-meter (Haake RS 600) with a home-built adaptation (Fig. 1) comprising an extension of a previously described system [3]. Briefly, the 60 mm parallel plate geometry of the rheometer was used as a base. A copper plate attached to the upper rheometer rotor served as a shearing surface, current collector and electrode for electrical impedance spectroscopy (EIS). A perforated stainless steel (316) plate was used as the bottom shearing surface. Due to the small size (1 mm radius) and fraction (< 40%) of the holes, rheological measurements could be performed with reasonable accuracy (within 5%; test with 1.231 Pas and 0.01 Pas calibration oils). This plate also served as a second electrode for EIS. A Celgard 2500 separator was used to separate the perforated plate from a second compartment with a lithium foil (on a titanium current collector). This allowed the foil to be in contact the electrolyte but not the particles. In the solvent trap of the rheometer (not shown), mercury was used as a working fluid to ensure a low friction and low noise electrical connection to the rotating upper geometry [3]. During rheological tests all electrodes were disconnected.

EIS measurements were performed (between the upper and perforated plate, with S1 closed and S2 open) in a four-terminal configuration. The perforated plate was excited by a sinusoidal voltage of < 50 mV in the frequency range from 10 MHz to 0.01 Hz. Amplitude sweeps on the KB-only fluid had indicated that the response was linear (and hence the impedances the same) at least up to 100 mV (Note: these voltages were applied at the HF2 output. The actual voltage across the sample was typically much smaller). Currents were measured by a transimpedance amplifier (HF2CA, Zurich Instruments) on the virtually grounded rotor. A buffer pre-amplifier (HF2TA, Zurich Instruments) was used to measure the potential difference between the perforated plate and the rotor. An impedance spectroscopy (HF2IS, Zurich instruments) was used to

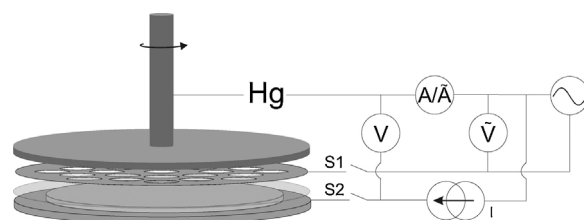


Fig. 1. Schematic of rheo-impedance setup. dark grey: upper geometry, perforated plate, bottom current collector translucent gray: membrane, beige: lithium foil on current collector. Either switch S1 or S2 is closed, to allow EIS or electrochemical cycling.

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