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Supporting Information

Solid electrolyte interphase in semi-solid flow batteries: a wolf in sheep´s clothing

Edgar Ventosa,[a]. Giorgia Zampardi,[b] Cristina Flox,[a] Fabio La Mantia,[b] Wolfgang Schuhamnn[b] and Joan Ramon Morante [a,c]*

Experimental Section

Materials for SSFB measurements.

The active material employed in this work was $Li_4Ti_5O_{12}$ (D50 1.9 μm) from MTI Corporation. All components of the electrolyte, namely ethylene carbonate, dimethyl carbonate, $LiPF_6$, and metallic lithium were purchased from Sigma-Aldrich (battery grade). Celgard 2500 and Ketjenblack EC-600JD were courtesy of Azelis and AkzoNovel Polymer Chemicals, respectively.

The oxygen-annealed $Li_4Ti_5O_{12}$ samples were obtained by treatment of commercially available $Li_4Ti_5O_{12}$ in flowing O_2 (20 vol %) at 650 °C for 120 min in order to remove organic impurities and adsorbed water.

Preparation of fluid electrodes

The fluid electrodes were prepared by mixing the active materials and carbon additive in the electrolyte (1 M $LiPF_6$ in EC:DMC 1:1 wt.) by magnetic stirring for overnight. The fluid electrode was passed through the cell for at least 1 h before starting the experiments to further homogenize the suspension. The reservoirs were constantly stirred during the electrochemical characterization.

For the suspensions, 1.5 g and 0.13 g of active and conductive additive, respectively, were added into 6 mL of electrolyte solution.

Electrochemical characterization of the fluid electrodes

A two-electrode configuration cell (more details below) was assembled in an Ar-filled glove box (O_2<1 ppm and H_2O<1 ppm) for the characterization of fluid electrodes. Pure lithium metal was used for counter and reference electrodes. Celgard 2500 and 1 M $LiPF_6$ in EC:DMC 1:1 wt. served as separators and electrolyte, respectively. The electrochemical cell employed for testing fluid electrodes is shown in Figure S1. The dimensions of the channel were 75×4×1 mm and the current collector was metallic copper. Electrochemical measurements were performed with a Bio-Logic VMP-3 (Bio Logic SAS).

Semi-solid flow battery in half-cell configuration

We have employed a modular electrochemical cell (filter-press cell) which provides great versatility. The filter press-cell configuration consists of several independent elements sandwiched (e.g. current collector, gaskets, channel frames) to define reaction zones (negative suspension and positive suspension compartments) separated by a Celgard 2500 film. Between each element, several gaskets must be introduced to avoid slurry leakages. Finally, the whole system is closed by metallic end-plates to give consistency to the system. This modular configuration offers several advantages, for example, the easy study of positive electrode and negative electrode materials in half-cell configuration as well as both compartments in full cell configuration. In addition, more compartments can be easily added to obtain a multi-cell (stack). Moreover, different channel geometries and thickness can be studied by simply changing one frame element

Figure S1 illustrates the two electrode configuration cell (half-cell) for the study of positive or negative electrode materials. The semi-solid suspension containing solvents (alkyl carbonates), conductive salt (LiPF6), conductive agent (carbon black) and electroactive particles is pumped through a Teflon plate, an Ethylene Propylene Diene Monomer (EPDM) gasket, and the positive (titanium plate) or negative (copper plate) current collector until reaching the channel frame. The channel frame consists of a 0.5 mm thick Teflon frame, sandwiched by two 0.5 mm thick gaskets made of expanded Teflon (ePTFE). Together they form a 75 mm long x 4 mm wide x 1 mm (approximately 0.3 mL slurry and 3 cm^2) deep channel. The working electrode zone is limited by a separator (Celgard 2500). Since it is a two-electrode half-cell configuration, the metallic lithium serves as counter and reference electrode. A sheet of metallic lithium covers the copper or titanium current collector for the evaluation of positive or negative electrode materials, respectively.

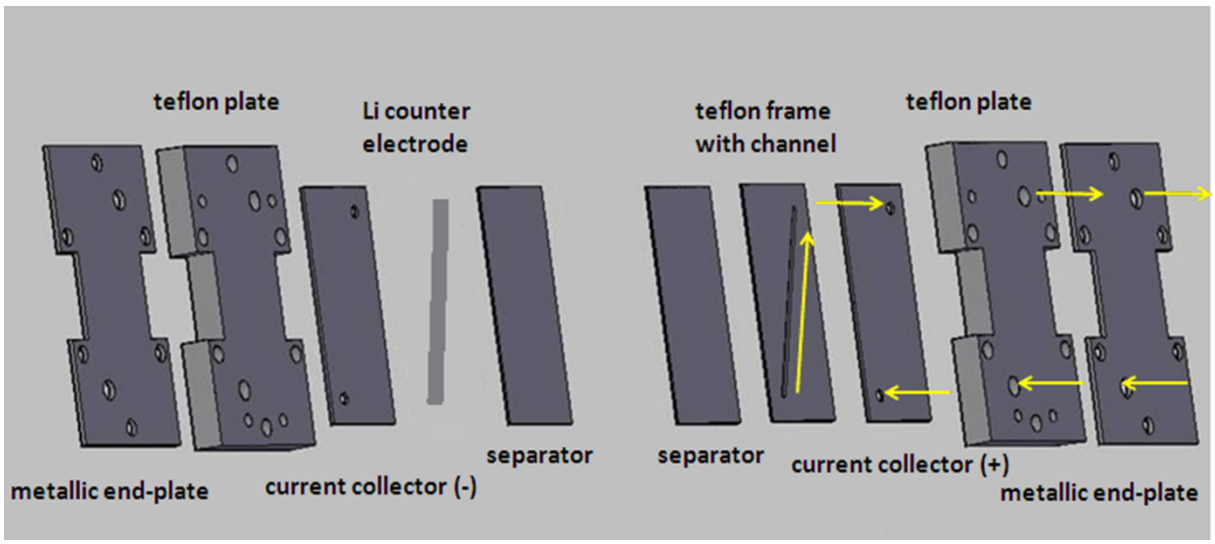

Figure S1. Schematic representation of the electrochemical flow cell.

Scanning Electrochemical Microscopy (SECM)

Feedback mode SECM provides information about the electrochemical reactivity of a sample surface by probing the reaction rate of a free diffusing redox mediator present in solution, through the current recorded at the SECM tip.[4] The SECM tip is positioned in close proximity to the sample surface and the measured current is a function of the tip potential and the tip-to-sample distance. In the bulk of the solution the current recorded at the SECM tip is the diffusion limiting one for the oxidation (reduction) of the redox mediator. The normalized feedback current is defined as the ratio of the current recorded at the SECM tip in close proximity of the sample surface (I_T) and the diffusion limiting recorded by the tip far away from the sample (I_{bulk}).

$$\frac{I_T}{I_{bulk}}$$

When approaching the tip to an electrochemically reactive and conductive sample surface, the normalized feedback current is higher than unity (positive feedback). If an inert or electronically insulating sample surface is approached, the normalized feedback current recorded at the tip is lower than unity (negative feedback).

The SECM experiment was carried out in a four electrodes electrochemical cell,[1-3] using a Li/Li^+ reference electrode consisting of metalling lithium immersed in a 1 M $LiClO_4$ (battery grade, dry, 99.99% Sigma Aldrich) EC:PC 1:1 %wt. (EC, ethylene carbonate, anhydrous 99% Sigma Aldrich)

(PC, propylene carbonate, anhydrous 99% Sigma Aldrich) separated from the electrolyte by a ceramic frit. The counter electrode was a cylindrical titanium mesh covered with TiS_2 (99.9% Sigma Aldrich) and carbon additive particles (Super C65, Timcal) held together by polyvinylene difluoride binder (Solvay) in a ratio 76:12:12. The working electrode was a copper foil placed at the bottom of the electrochemical cell, and a Pt wire with a diameter of 25 μm, sealed in a glass capillary as SECM tip. The exposed area of the Cu sample was 0.125 cm^2.

For the SECM experiment, the electrolyte solution contained 20 mM ferrocene (Fc) (98% Sigma Aldrich), and 1 M $LiPF_6$ (battery grade, ≥99.99% Sigma Aldrich) in EC:DEC (DEC, diethyl carbonate, anhydrous 99.7%, Sigma Aldrich) 1:1 %wt.

References

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