TITLE: Methodology that provides quick information about the effectiveness of the Solid Electrolyte Interface (SEI) layer in newly manufactured batteries

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SHORT DESCRIPTION: This document's intention is to provide a generic and instrument-unspecific guideline to help in the process of acquiring reliable and reproducible data with a Coulometry method. Areas covered are pouch batteries handling, fabrication-redox mediator addition and a few comments on data analysis. Extensive advice on data analysis is beyond the document's scope.

ABBREVIATIONS / TERMINOLOGY:
SEI –Solid Electrolyte Interface

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Unlike commonly-used, well-established and time-consuming quality control procedures in Lithium – ion batteries fabrication lines, which usually takes several weeks and are based on measurements of the cell voltage evolution after the fabrication, this concept is a methodology that provides quick information about the effectiveness of Solid Electrolyte Interface (SEI) layer in newly manufactured batteries. The invention consists on a methodology that requires injecting organic redox molecules in the pouch cell and use the coulombic efficiency during the first few galvanostatic cycles to diagnose the presence of failures or micro cracks on the SEI surface and even the influence (positive or negative) of electrolyte additive and/or specific SEI forming protocols on the quality of the SEI. Such organic redox molecules are able to be reduced in contact with the negative electrode through defects or cracks in the SEI layer. Once reduced, it travels to the positive electrode where it is oxidized and then it can travel back to the negative electrode where it can be reduced again. This shuttle behavior consumes a significant fraction of the charge supplied during the charge of the battery cell, therefore reducing its coulombic efficiency.
This is a practical methodology to address the quality control of freshly made Lithium – ion batteries in a timeframe of 24 - 48 hours instead of the usual 2 to 3 weeks. There are three sections that are described as follows: *I)* The first one deals with lab considerations such as setting up, pouch cell fabrication procedure and sample and data storage. This serves as the foundation and, in the best case, should only be followed once, but reviewed on a regular basis; *II)* The second part provides advice on the measurement process which is to be followed in day-to-day activities; *III)* The last part provides some general advices on the analysis of Coulometry method data.

I) GENERAL:

Manufacturing lithium – ion batteries at pouch cell scale might expose the operator to dangerous situations such as short circuits, sharp objects, chemicals, flammability and explosion hazards thus it is important to ensure proper training of the operator according to local safety regulations and device specificities. This includes familiarity with available glovebox which hosts a dry nitrogen or other atmosphere and thus avoids any chemical reactions, and condensation or water layers on samples and materials. Familiarity in lab regulations or other available documentation specific to local premises and instruments is also a premise.

Ensure stable lab climate (temperature, humidity) to enable stable operation of the electrical charge – discharge pulses with minimum mechanical, thermal, and electrical drift. Avoid opening windows, direct sunlight on the experiment, sources of electromagnetic radiation, etc. In the best-case, humidity, temperature and pressure are logged to allow tracing back implausible battery tester measurements and check possible influences of one of these parameters.

Ensure calm, vibration-free environment for the battery testers including the interfacing cables, especially while experiments are conducted. The battery testers should be placed in a calm position in the lab, away from noise sources, ventilation and passersby. In the best scenario, the battery tester should be shielded from external changes in electromagnetic field e.g. by putting it in a Faraday's cage. To reach maximum control on environmental variables, the electrical tests, the battery testers and the pouch cells can be placed in a climatic chamber which maintains an adequate temperature and humidity control.

Ensure proper and unambiguous sample labelling to avoid mixing up during storage and testing.

When handling samples and sensitive parts of the Pouch cells it is advisable to wear nitrile gloves and use tweezers where appropriate.

Where necessary, avoid electrostatic discharge by proper grounding of the operator. Moreover, while handling electrodes, it is recommended to avoid any mechanical contact to the electrodes surface or to the terminals, which can cause both mechanical and electrical damages.

Work according to local IT policies and ensure safe data storage with regular backups. Best to avoid local hard drive and use a server storage.

Keep raw data and post-processed data separate and make sure to not overwrite raw data during analysis treatment.

## II) MEASUREMENT:

Make sure that the battery format allows for the injection of microliters of an electrolyte containing a given concentration of certain compound and subsequent sealing, preferably pouch format. Introduce the battery in the glovebox under a dry nitrogen or other inert atmosphere. Make an opening hole in the pouch and add 1 μmol of the mediator per $cm^2$ of geometric electrode area. Then the battery has to be vacuum-sealed under −90 kPa gauge pressure in a vacuum sealer and be removed from the glovebox to connect it to a battery tester in a climatic chamber at 20ºC.

Make sure that the battery tester is switched on. Confirm voltage status and make sure connections are in proper shape for measurements. Make sure to log all relevant metadata (sample, experimental settings, environmental conditions, etc.). Perform 7 galvanostatic charge – discharge cycles at C/3 rate.

Even though pouch cells are very reproducible, it is a must to replicate the experiments (i.e. 3 replicas) for deviation features and statistical analysis.

It is highly recommended to calibrate the battery tester to ensure the traceability of measurements, i.e. to get reliable and comparable quantitative results.

Save data according to local naming convention using unique names. Useful schemes should include sample ID, C-rate, type of battery, timestamp.

## III) ANALYSIS:

One type of data is usually generated during charge - discharge measurements:

- The capacity, obtained from the current versus time integration, expressed as follows:

  $$Q = \int_{t_0}^{t_f} I \times t \, dt$$

  where *Q* is the charge, *I* is the applied current, *t* is time, $t_0$ is the start time and $t_f$ the final.

- The coulombic efficiency is calculated as the ratio between the charge delivered and the charge stored:

  $$\eta = \frac{Q_{discharged}}{Q_{charged}} \times 100$$

- Data are stored in .csv format files to allow analysis and graphical representation.

The evolution of coulombic efficiency versus cycles is analyzed to evaluate the SEI quality, assuming that low efficiency (unwanted) corresponds to low quality SEI while experiments rating high efficiency (wanted) correspond to high quality SEI.

Even though pouch cells are very reproducible, it is necessary to replicate the experiments for deviation features and statistical analysis. A minimum of 3 replicas is recommended. To consolidate the results, a statistical analysis will be carried out using the average value and the standard deviation as a measure of the experimental error whose equations are expressed as follows:

$$X = \frac{\sum_{i=1}^{N} x_i}{N}$$

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - X)^2}{N - 1}}$$

where *X* is the average value, *η* the coulombic efficiency, $x_i$ coulombic efficiency measured for the replica *i*, *i* is the number of the replica (from 1 to N), *N* is the total number of replicas, and *S* is the standard deviation.