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A Combined Thermodynamics & Computational Method to Assess Lithium Composition in Anode and Cathode of Lithium Ion Batteries

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ABSTRACT

With aim to address the open question of accurate determination of lithium composition in anode and cathode at a defined state of charge (SOC) of lithium ion batteries (LIB), we developed a method combining electrochemical thermodynamic measurements (ETM) and computational data fitting protocol. It is a common knowledge that in a lithium ion battery the SOC of anode and cathode differ from the SOC of the full-cell. Differences are in large part due to irreversible lithium losses within cell and to electrode mass unbalance. This implies that the lithium composition range in anode and in cathode during full charge and discharge cycle in full-cell is different from the composition range achieved in lithium half-cells of anode and cathode over their respective full SOC ranges. To the authors knowledge there is no unequivocal and practical method to determine the actual lithium composition of electrodes in a LIB, hence their SOC. Yet, accurate lithium composition assessment is fundamental not only for understanding the physics of electrodes but also for optimizing cell performances, particularly energy density and cycle life.

In this study thermodynamics data, including open-circuit potential (OCP), entropy (ΔS) and enthalpy (ΔH) are collected on full-cells and on their derived lithium half-cells. Fundamentally, the thermodynamics data of a full-cell is the arithmetic difference between the corresponding data of cathode and anode achieved in half-cells. However, as we show here misfits exist between experimental data and the arithmetic difference indicating cells data depart from theory. Misfits were significantly reduced by applying linear transforms to the half-cells data and by iterative computational method. The fitting parameters are adjusted independently for anode and cathode to minimize differences between experimental and computed thermodynamics data. This method enables accurate Li composition in anode and cathode over the full SOC range of the full-cell to be assessed. It is found that both anode and cathode in the full-cell operate under lower Li composition ranges than those achieved in half-cells, which significantly reduces the full-cell energy density. Moreover, the effect of full-cell cycle ageing at the ambient and high temperatures on electrodes composition is investigated independently for anode and cathode so as to understand their respective contribution to cell' capacity losses.

1. Introduction

Lithium ion batteries (LIB) are currently the main power source in a wide range of applications including mobile electronics, electric vehicles and in stationary energy storage [1,2]. During charge and discharge lithium ions are shuttled between anode and cathode through the electrolyte owing to lithium intercalation/de-intercalation and/or alloying/de-alloying electrode processes. Accordingly, lithium composition in anode and cathode varies with cell's SOC. In an ideal cell design the SOC of anode, cathode and full-cell should be equal to maximize energy storage performances. In practical cells, however, the SOC matching is hard to achieve mainly because of: 1) electrode processes causing irreversible active lithium losses such as formation (and reformation) of a solid interphase electrolyte (SEI) on the surfaces of anode and following thermal ageing, trapped lithium, active material electrical disconnection, and 2) unbalanced anode and cathode active masses in cell starting from inception. Irreversible lithium losses cause the full-cell, hence anode and cathode to become lithium deficient. Therefore, lithium composition range in anode and cathode in the full-cell departs from the one achieved in half-cells.

Typically, lithium half-cells contain excess metallic lithium so as to fully charge and discharge the working electrode (anode or cathode). Excess lithium also compensates for lithium losses

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during cycling and ageing. In half-cells the SOC of the working electrode is usually determined by Coulomb counting and voltage measurements the lithium being used as a counter and a reference electrode. Commercial full-cells, however, are two-electrode cells which voltage is the difference between cathode and anode voltages. Full-cell's voltage reading doesn't teach on individual electrode voltages therefore, not on their composition. Should a reference electrode be used, the voltage-composition relationship is not unequivocal since for example electrodes such as the graphite anode and the lithium iron phosphate cathode show voltage plateaus over a wide range of lithium composition.

Electrochemical thermodynamics measurements technique (ETM) was introduced by us over a decade ago and has since been used as investigation method for electrode materials and full-cells [3–6]. In ETM the temperature is used as additional parameter enabling entropy and enthalpy profiles to be achieved.

A new combined ETM and computational technique will be introduced in this work with aim to determine the actual lithium composition in anode and cathode at any SOC of the full-cell. Thermodynamics data are collected on anode and cathode half-cells and then data are processed in order to best fit the experimental data on full-cell. ETM data including open-circuit potential (OCP), entropy (ΔS) and enthalpy (ΔH) are processed independently with same fitting parameters so as to minimize differences between experimental and computed data, thus accurately revealing lithium composition in anode and cathode.

2. Principles of the combined ETM-computational method

2.1. The linear transform ("shift and stretch")

At a defined SOC of a full-cell, 'X_{fc}', cell's OCP, E^0_{fc}, equals the difference between the cathode ('ca') and anode ('an') potentials at their respective SOC, $X_{ca} and X_{an}$:

$$E^0_{fc}(X_{fc}) = E^0_{ca}(X_{ca}) - E^0_{an}(X_{an}) \tag{1}$$

In a half-cell OCP relates to free energy ΔG of cell reaction according to:

$$\Delta G_{ca}(X_{ca}) = -nFE^0_{ca}(X_{ca}), \tag{2}$$

and

$$\Delta G_{an}(X_{an}) = -nFE^0_{an}(X_{an}), \tag{3}$$

where n = number of exchanged electron per mole (n = 1 for lithium).

The SOC of an optimized full-cell should be equal to the SOC of each electrode:

$$X_{fc} = X_{ca} = 100 - X_{an} \tag{4}$$

("$100 - X_{an}$" formula applies because anode and cathode have complementary SOC in the full-cell.)

The free energy relates to enthalpy $\Delta H(X)$ and entropy $\Delta S(X)$ according to:

$$\Delta G_{ca,an}(X_{ca,an}) = \Delta H_{ca,an}(X_{ca,an}) - T\Delta S_{ca,an}(X_{ca,an}) \tag{5}$$

Deriving Eq. (5) vs. T yields ΔS and ΔH according to:

$$\Delta S_{ca,an}(X_{ca,an}) = F\frac{\partial E^0_{ca,an}(X_{ca,an},T)}{\partial T} \tag{6}$$

$$\Delta H_{ca,an}(X_{ca,an}) = -F\left[E^0_{ca,an}(X_{ca,an},T) + T\frac{\partial E^0_{ca,an}(X_{ca,an},T)}{\partial T}\right] \tag{7}$$

By combination of the above equations, one gets:

$$\Delta S_{fc}(X_{fc}) = \Delta S_{ca}(X_{ca}) - \Delta S_{an}(100 - X_{an}), \tag{8}$$

and

$$\Delta H_{fc}(X_{fc}) = \Delta H_{ca}(X_{ca}) - \Delta H_{an}(100 - X_{an}) \tag{9}$$

Practical full-cells most of the times depart from optimized electrode mass balance and incur lithium losses; therefore, Eqn. (4) doesn't apply. In order to determine the actual SOC of anode and cathode at a well-defined SOC of the full-cell, our approach here consists of fitting OCP, ΔS and ΔH data of full-cells and half-cells by applying a linear transform ofX_{ca}andX_{an} vs. X_{fc}, a process called 'shift and stretch' according to:

$$X_{ca} = \alpha_{ca}X_{fc} + \beta_{ca}, \tag{10}$$

and

$$X_{an} = \alpha_{an}X_{fc} + \beta_{an}, \tag{11}$$

where $\alpha_{ca}, \beta_{ca}, \alpha_{an}$ andβ_{an} are adjustable parameters to best fit Eqn. (8) and (9).

Let 'H' be a lithium host electrode structure. The electrode reaction can be schematized as:

$$H + xLi^+ + xe^- \leftrightarrow Li_xH \quad x_{min} \le x \le x_{max}, \tag{12}$$

The electrode theoretical specific capacity (mAh/g), q_{th} is given by Eq. (13):

$$q_{th} = \Delta x\frac{F}{3.6M(H)}, \Delta x = x_{max} - x_{min}, \tag{13}$$

where F = Faraday constant (~96500 C) and M(H) = molecular mass of H (g/mole).

Assuming x_{max} andx_{min}correspond respectively to 100% and 0% SOC of electrode H the relationship between SOC 'X' and Li composition 'x' is given by:

$$x = x_{min} + \frac{X}{100}\Delta x = x_{min} + \frac{X}{100}\frac{3.6M(H)q_{th}}{F} \tag{14}$$

Should 100% and 0% SOC correspond to x_{min}andx_{max}, respectively, Eq. (14) becomes:

$$x = x_{max} - \frac{X}{100}\Delta x = x_{max} - \frac{X}{100}\frac{3.6M(H)q_{th}}{F} \tag{14′}$$

Eq. (14) and (14′) will be used to convert SOC to lithium composition in anode and cathode, respectively.

2.2. Fitting parameters assessment

In order to verify the effectiveness of the proposed 'shift and stretch' method, five sets of data OCP vs. SOC, ΔS vs. SOC, ΔS vs. OCP, ΔH vs. SOC and ΔH vs. OCP are used to compute the four parameters$\alpha_{ca}, \beta_{ca}, \alpha_{an}and\beta_{an}$of Eqns. (10) and (11). The purpose of the curve fitting is to find the optimal values of these four parameters by shifting and stretching the curve of cathode and anode so that the reformed curves in full cell can match with its measured values for entropy, enthalpy and OCP. In this work, the root mean square error (RMSE) is used to evaluate the difference between the reformed curve and the measured curve in the full cell. Since the three curves (E^0, ΔS, ΔH, vs. SOC) shift and stretch in the same format, we combine the RMSE of these three functions. Thus, the problem of finding optimal values of these four parameters can be simplified as a optimisation problem by