



# A thermodynamic and crystal structure study of thermally aged lithium ion cells



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## HIGHLIGHTS

- Effect of thermal ageing on cells' thermodynamic and kinetic properties.
- Degradation of electrochemical performance with the ageing temperature and time.
- Strong correlation between cells thermodynamic changes and electrodes degradation.
- Thermodynamics method allows a distinction between different ageing modes.

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## ABSTRACT

Lithium ion batteries in the coin-cell form factor (2032) initially charged to 4.2 V at ambient temperature are stored at 60 °C and 70 °C for up to 8 weeks. The cells discharge capacity ( $Q_d$ ) and thermodynamic properties, including open-circuit potential (OCP), entropy ( $\Delta S$ ) and enthalpy ( $\Delta H$ ) are measured after each completed ageing week. Post-mortem analysis of aged anodes and cathodes is investigated by X-ray diffractometry (XRD) and Raman Scattering spectrometry (RS) in an attempt to correlate thermodynamic data to changes in the crystal structure characteristics. It is found that degradation of the electrode materials' crystal structure accounts for most of the observed changes in the cells' thermodynamics with well quantified and distinct contributions from anode and cathode.

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## 1. Introduction

There are several well established causes of performance degradation of lithium ion batteries (LiB) including long charge/discharge cycling [1–3], thermal ageing [4–13], high rate charge and discharge [14–16], overcharging [17–20] and over discharging [17]. Performance degradation includes decays in discharge capacity, in discharge potential [21–23] and in power output [4,10,21]. Cells performance decays relate to irreversible changes in

the anode, the cathode and the electrolyte physical properties such as crystal structure degradation in anode [24–26] and cathode [26–28] and in the electrode/electrolyte interfacial properties [29–31]. Other processes such as metal dissolution [32–34], electrolyte decomposition [35–39] and electrode mechanical properties degradation due to active materials electrical disconnection from the current collector [40] may also account for battery decaying performances.

In a recent study we investigated the effect of overcharge and long cycling of LiB cells on electrochemical performances and on thermodynamics properties [41,42]. We assigned the cells' performance decay to crystal structure degradation of the cathode and anode materials, which correlate well with changes in the entropy and enthalpy profiles. In this study we investigate the effect of high temperature ageing on the cells' thermodynamic and kinetic

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properties. This includes open-circuit potential (OCP), entropy and enthalpy profiles, discharge capacity, average discharge potential and energy output.

A new thermodynamics based approach will be introduced in this paper. It enables a clear distinction between contribution to the cell performance decay arising from anode and cathode [43]. Post-mortem analyses of anode and cathode materials by XRD and RS support the point that crystal structure degradation is the main cause of the changes in the cells' thermodynamic and kinetic properties in thermally aged cells.

## 2. Experimental

### 2.1. Storage condition and capacity loss determination

LiB coin cells' (2023) of initial capacity  $Q_0 \sim 44$  mAh are used in this study.

The cells were conditioned, aged and tested according to the following steps:

- i. A charge to 4.2 V under 10 mA constant current ( $\sim C/4$ -rate) at ambient temperature using an Arbin Instruments battery cycler.
- ii. A thermal storage of charged cells at  $60^\circ\text{C} \pm 1^\circ\text{C}$  and  $70^\circ\text{C} \pm 1^\circ\text{C}$  for a period up to 8 weeks.
- iii. Four cells were retrieved at completion of each week and naturally cooled to the ambient temperatures.
- iv. The four cells are then charged to 4.2 V and discharged to 2.75 V under  $\pm 10$  mA, a step in which the cells' discharge capacity  $Q_d(T_s, n)$ , capacity loss  $(Q_0 - Q_d(T_s, n))/Q_0 \times 100$  (in %), and average discharge potential  $\langle e_d(T_s, n) \rangle$  are assessed, where  $n$  = number of ageing weeks ( $0 \leq n \leq 8$ ;  $n = 0$ ) corresponds to a fresh cell) and  $T_s$  = the storage temperature).

The cells discharge energy 'E' is then assessed using Eq. (1):

$$E(T_s, n) = Q_d(T_s, n) \times \langle e_d(T_s, n) \rangle \quad (1)$$

### 2.2. Thermodynamics measurements

The four discharged cells of step iv. are transferred into the Electrochemical Thermodynamics Measurement System (ETMS, BA-2000®, KVI PTE LTD, Singapore) then the following processes are carried out:

- i. Conditioning cycle: cells are charged to 4.2 V under 9 mA then a constant 4.2 V voltage is applied until the charge current dropped below 0.05 mA. Cells are then discharged to 2.75 V under 9 mA and constant 2.75 V voltage is held until the discharge current dropped below 0.05 mA. In these steps the ETMS assesses the cells' charge and discharge capacity, which is close to  $Q_d(T_s, n)$ .
- ii. Electrochemical thermodynamics measurements (ETM) test: discharged cells are charged at C/6-rate for 18 min corresponding to 5% increment in state of charge ( $\Sigma$ ). Therefore, after the  $j$ th charge increment the cells' state of charge  $\Sigma_j$  is given by:  $\Sigma_j(\%) = 5j$  ( $1 \leq j \leq 20$ ).
- iii. At  $\Sigma_j$  the cells temperature  $T$  is decreased from ambient ( $\sim 25^\circ\text{C}$ ) to  $10^\circ\text{C}$  by  $5^\circ\text{C}$  steps while keeping the circuit open and monitoring the OCP. Each  $T$  is kept constant for 30 min and the cells' OCP ' $E_0(\Sigma_j, T)$ ' is measured. Typically, after 30 min relaxation time  $E_0(\Sigma_j, T)$  varies by less than

$40 \mu\text{V min}^{-1}$ , which is considered close enough to thermodynamic equilibrium.

From linearity of  $E_0(\Sigma_j, T)$  vs.  $T$  in step iii., the ETM system automatically determines the entropy  $\Delta S(\Sigma_j)$  and the enthalpy  $\Delta H(\Sigma_j)$  according to Eqs. (2) and (3), respectively

$$\Delta S(\Sigma_j) = \frac{\partial S(\Sigma_j)}{\partial \Sigma_j} = F \frac{\partial E_0(\Sigma_j, T)}{\partial T} \quad (2)$$

$$\Delta H(\Sigma_j) = \frac{\partial H(\Sigma_j)}{\partial \Sigma_j} = F \left( E_0(\Sigma_j, T) - T \frac{\partial E_0(\Sigma_j, T)}{\partial T} \right), \quad (3)$$

where  $\partial S(\Sigma_j)/\partial \Sigma_j$  and  $\partial H(\Sigma_j)/\partial \Sigma_j$  are, respectively, the slope of  $S$  and  $H$  vs.  $\Sigma_j$  at well-defined  $\Sigma_j$ .

By iteration of steps i. to iii., twenty one entropy and enthalpy data points are acquired and plotted vs.  $\Sigma_j$  and vs. OCP.

### 2.3. Post-mortem crystal structure analyses

At the last charge increment of step iii. ( $j = 20$ ), one or two cell samples are retrieved from the ETMS and discharged to 2.75 V at 10 mA then opened in a glove box filled with argon. The anode and the cathode are separated and washed with DMC of 99% purity used as received, then dried in argon at ambient temperatures and in vacuum at  $60^\circ\text{C}$  for about 1 h.

The anode and cathode samples are analysed by XRD (Bruker D8 Advance diffractometer) using  $\text{CuK}\alpha$  radiation in the angular range of  $15^\circ$ – $90^\circ$  ( $2\theta$ ) for cathode and  $20^\circ$ – $90^\circ$  ( $2\theta$ ) for anode with  $0.02^\circ$   $2\theta$ -steps and by RS (Renishwa inVia Raman microscope) in the backscattering geometry; with the 514 nm radiation by an argon ion laser of 20 mW power.

## 3. Results and discussion

### 3.1. Thermodynamics and kinetics data

#### 3.1.1. Initial OCP and discharge data

The cells' OCP measured at ambient temperature immediately after ageing at  $60^\circ\text{C}$  and  $70^\circ\text{C}$  is plotted versus the ageing time in Fig. 1A, a and b, respectively. The two traces almost lie on the top of each other for the first 5 ageing weeks. Then they split from each other as cells aged at  $70^\circ\text{C}$  feature a sharp decrease in OCP compared to those aged at  $60^\circ\text{C}$ . The corresponding discharge capacity ( $Q_d(T_s, n)$ ) profiles are plotted in Fig. 1B, a and b, respectively. For the first two weeks the  $Q_d(T_s, n)$  traces are quite close to each other. Only after the third week they depart as the capacity of cells aged at  $70^\circ\text{C}$  becomes increasingly lower than the ones aged at  $60^\circ\text{C}$ .

From an initial discharge capacity of 44 mAh in fresh cells, the discharge capacity dropped to about 37 mAh and 32.5 mAh after 8 ageing weeks at  $60^\circ\text{C}$  and  $70^\circ\text{C}$ , respectively, corresponding to irreversible capacity losses of 15.9% and 26.1%, respectively. It is generally admitted that above *circa* 20% capacity loss, a LiB is considered no more operational, which is the case of the cells aged at  $70^\circ\text{C}$  for 8 weeks.

Fig. 1C, a and b shows the average discharge potential  $\langle e_d(T_s, n) \rangle$  profiles of cells aged at  $60^\circ\text{C}$  and  $70^\circ\text{C}$ , respectively.  $\langle e_d(T_s, n) \rangle$  is defined in Eq. (4):

$$\langle e_d(T_s, n) \rangle = \frac{1}{t_d} \int_0^{t_d} e(t) dt, \quad (4)$$

where  $e(t)$  = time dependent cell discharge voltage and  $t_d$  = total discharge time. Fig. 1D, a and b shows the corresponding energy

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