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► To cite this version:

Gaurav Assat, Stephen L Glazier, Charles Delacourt, Jean-marie Tarascon. Probing the thermal effects of voltage hysteresis in anionic redox-based lithium-rich cathodes using isothermal calorimetry. Nature Energy, 2019, 4 (8), pp.647-656. 10.1038/s41560-019-0410-6 . hal-02408292

HAL Id: hal-02408292

<https://hal.science/hal-02408292>

Submitted on 16 Dec 2019

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Probing the thermal effects of voltage hysteresis in anionic-redox-based lithium-rich cathodes using isothermal calorimetry

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Abstract

1 The commercialization of high-energy batteries with Li-rich cathode materials exhibiting
2 combined cationic/anionic redox processes awaits the elimination of certain practical bottlenecks.
3 Among these, large voltage hysteresis remains the most obscure from a fundamental
4 thermochemical perspective. Here we study this issue by directly measuring via isothermal
5 calorimetry the heat generated by Li/Li₂Ru_{0.75}Sn_{0.25}O₃ (Li/LRSO) cells during various cycling
6 conditions, with LRSO being a ‘model’ Li-rich layered cathode. We show how this heat
7 thermodynamically relates to the lost electrical work that is crucial for practical applications. We
8 further reveal that anionic redox on charging and discharging adopts different metastable paths
9 having non-identical enthalpy potentials such that the overall Li content no longer remains the
10 unique reaction coordinate, unlike in fully path-reversible cationic redox. We elucidate how quasi-
11 static voltage hysteresis is related with heat dissipated due to non-equilibrium entropy production.
12 Overall, this study establishes the great benefits of isothermal calorimetry for enabling energy
13 efficient electrode materials in next-generation batteries.

Introduction

14 Increasing the energy density of lithium-ion batteries requires denser positive electrodes
15 with higher voltage and/or capacity. Li_2MnO_3 -based Li-rich layered oxides (Li-rich NMCs), such as
16 $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$, can deliver specific capacities above 270 mAh g^{-1} to reach 1000 Wh kg^{-1}
17 of specific energy at the material level. Despite their slightly lower crystalline density than today's
18 Li-stoichiometric Ni-based layered oxides (NMCs and NCA), Li-rich cathodes remain very
19 promising for the long-term, as we will need to move away from Ni-rich towards Mn-rich materials
20 (Mn is inexpensive and environmentally benign) without compromising the energy density.¹⁻³ The
21 high capacity of Li-rich NMCs stems from cumulative anionic and cationic bulk redox processes.⁴⁻
22 ⁶. However, these electrodes currently fall short in other performance metrics⁷ because of large
23 voltage hysteresis^{5,8}, sluggish kinetics^{5,9,10}, and gradual voltage fade¹¹. These issues are concomitant
24 with anionic redox activity⁷ – the very same feature that enhances capacity. Therefore, further
25 investigations are needed to fundamentally understand the overall anionic redox process, which
26 constitutes not just of electron removal from oxygen-based electronic states, but also the ensuing
27 (local) structural/bonding rearrangements.⁷

28 The undesirable issue of voltage hysteresis in rechargeable batteries leads to energy
29 inefficiency, presumably dissipated as heat, consequently imposing an additional energy cost on the
30 end-users.¹² Voltage hysteresis would also complicate the state of charge (SoC) and thermal
31 management of such batteries. Li-rich NMCs show a relatively large difference between
32 charge/discharge voltages ($\sim 400\text{--}500 \text{ mV}$ after first cycle, $\sim 87\%$ energy efficiency, **Figure 1**). This
33 gap persists over cycling, even at extremely low rates ($C/300$)¹⁰, at high temperatures (55 or 85
34 $^\circ\text{C}$)¹³, and after long relaxation periods (100 hours)¹⁰. Such behaviour therefore cannot be explained
35 by simple electrochemical kinetics that fails to explain the observed path dependence and quasi-
36 static hysteresis. Interestingly and similar to Li-rich NMCs, many other newly-discovered Li- and
37 Na-based materials with reversible anionic redox also suffer from voltage hysteresis.⁷ These include

38 layered $\text{Li}_2\text{Ru}_{1-x}\text{Sn}_x\text{O}_3$ ⁹ (**Figure 1**), $\text{Na}_{2/3}[\text{Mn}_{1-x}\text{Mg}_x]\text{O}_2$ ¹⁴, and Na_2RuO_3 ¹⁵ as well as disordered
39 $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$ ¹⁶ and $\text{Li}_2\text{MnO}_2\text{F}$ ¹⁷.

40 Only a few studies have attempted to understand the origin of voltage hysteresis in this class
41 of cathodes. These include electrochemical measurements in different voltage windows to identify
42 correlated differential capacity (dQ/dV) peaks^{5,8,11,18,19}, ⁶Li nuclear magnetic resonance to observe
43 path-dependence in lithium site occupation²⁰, X-ray diffraction to claim back-and-forth (partially
44 reversible) transition-metal migration²¹, and bulk X-ray spectroscopies^{5,22,23} to demonstrate the
45 absence of hysteresis in the potentials at which transition-metals show redox-activity, unlike for the
46 hysteretic oxygen redox process. A couple of phenomenological models assuming either a Li-driven
47 phase change¹⁰ or an asymmetry in transition-metal migration²⁴ were also conceived. Despite such
48 widespread efforts, the general thermodynamic mechanism behind voltage hysteresis and its
49 thermal effects remain unclear. Two questions need answering: (i) how exactly is the lost energy
50 dissipated as heat so that it can be better managed/predicted? and (ii) what is the underlying
51 mechanism along with the corresponding thermochemical conditions that lead to hysteresis?

52 In light of this, we adopt a different approach herein and perform isothermal calorimetry
53 measurements during the cycling of a ‘model’ Li-rich layered cathode – $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ (LRSO)
54 or $\text{Li}[\text{Li}_{0.33}\text{Ru}_{0.5}\text{Sn}_{0.17}]\text{O}_2$. This high capacity (~ 250 mAh g^{-1} reversibly) material, although only
55 suitable for niche applications without cost batteries (e.g. space), shows remarkable structural and
56 electrochemical similarities with the practically important Li-rich NMCs (**Figure 1**).^{9,25} Overall, it
57 serves as a simplified ‘model’ compound to understand the general properties of Li-rich layered
58 electrodes. The magnitude of voltage hysteresis in LRSO (~ 200 – 300 mV) is lower than Li-rich
59 NMCs but the role of anionic redox activity is particularly similar, such that high potential charging
60 triggers the onset of hysteresis.^{9,23} Using isothermal calorimetry in this work, we report the heat
61 generation during different electrochemical stages of LRSO, starting with the classical cationic
62 redox step in first charge followed by the voltage plateau accompanying oxygen redox and finally

63 the hysteretic sloped voltage profiles that stabilize over cycling. These measurements allow us to
64 discuss the thermodynamics in terms of enthalpy change, entropy change, and entropy production.
65 We highlight the thermal asymmetry in the charge vs. discharge paths as well as the difficulties in
66 locating the true equilibrium properties of such hysteretic materials. A multi-step reaction scheme
67 for the solid-state oxygen redox reaction is finally proposed to comprehend the results.

[Figure 1]

Figure 1 | Comparison of voltage profiles of Li-rich NMC and LRSO. The first cycle (**a** and **b**) displays a two-stepped charge followed by a sloped discharge. The labels “**C**” and “**A**” denote respectively the cationic and anionic redox processes. The later cycles (**c** and **d**) display a quasi-static voltage hysteresis, leading to an energy inefficiency that is equivalent to the shaded area between the charge and discharge profiles. In **a** and **b**, the materials do not get back to their initial states after the first cycle, unlike for the already-formed materials in **c** and **d**.

Thermodynamic Considerations

68 The heat generated by an electrochemical cell in isothermal and isobaric conditions is
69 described in the Methods section.^{26,27} Because of large voltage hysteresis and path-dependence in
70 Li-rich cathodes^{5,9}, the position of their equilibrium potential U cannot simply be assumed in the
71 middle of the charge and discharge, unlike in classical path-reversible intercalation materials. We
72 therefore need a different approach herein. Neglecting heat of mixing^{27,28} and correcting for minor
73 parasitic heat flow (see details in Methods), the energy balance can be recast as

$$V - \frac{\dot{q}|_{T,P}}{I} = U - T \frac{\partial U}{\partial T} = U_H$$

74

Equation [1]

75 with

$$U_H = -\frac{\Delta H}{nF}$$

76 **Equation [2]**

77
78 where V is the cell voltage, $\dot{q}|_{T,P}$ is the heat generation rate (positive if heat is released by
79 cell), I is the current (positive for charging), T is the temperature, P is the surrounding pressure, n
80 is the number of electrons involved in electrode reaction, F is the Faraday's constant, and U_H is the
81 so-called "enthalpy potential".²⁷ Just as U is directly related to the partial change in Gibbs free
82 energy of the cell as its SoC is varied ($U = -\frac{\Delta G}{nF}$), U_H is directly related to the partial change in the
83 enthalpy H of the cell. In other words, U_H captures the energy change while U includes the entropy
84 change as well. U_H can thus simply be obtained by measuring V , I , and $\dot{q}|_{T,P}$. Knowing U_H can help
85 in predicting the heat generation under operating conditions for proper thermal management of
86 batteries.

87 Integrating

88 **Equation [1]** over a closed path, such as a charge–discharge cycle after which the material
89 returns to its original state, gives

$$\oint_{cycle} I V dt = \oint_{cycle} \dot{q}|_{T,P} dt$$

90 **Equation [3]**

91

92 because enthalpy H is a state variable and cancels out over a stable cycle as follows

93

$$\oint_{cycle} dH = -nF \oint_{cycle} U_H dx = 0$$

94 **Equation [4]**

95

96 **Equation [3]** demonstrates that the net electrical work due to hysteretic voltage profiles is
97 dissipated as waste heat. Note that the U_H measured via

98 **Equation [1]** (under applied current) can be path dependent, i.e. different on charge vs.
99 discharge for the same SoC, if the materials inside the cell remain as metastable phases under
100 dynamic conditions away from the true equilibrium. Nevertheless, even in that non-equilibrium
101 case, U_H over a stable cycle (i.e. having no net change in H) is constrained by **Equation [4]** and
102 therefore cannot form a hysteretic loop versus Li composition x , as schematized in **Supp. Figure 1**.
103 Note that Li-rich materials do not have a perfectly stable cycle because of gradual voltage fade.
104 However, these changes will turn out to be negligible for LRSO later in the paper.

105 In addition to the above energy balance, the Second Law of Thermodynamics relates the
106 entropy change to the heat exchange as²⁹

$$\frac{\dot{q}|_{T,P}}{T} = -\dot{S} + \dot{\sigma}_{prod} ,$$
$$\dot{\sigma}_{prod} \geq 0$$

107

Equation [5]

108

109 where \dot{S} is the rate of entropy change of the cell and $\dot{\sigma}_{prod}$ is the rate of entropy production
110 due to the irreversible processes inside the cell. $\dot{\sigma}_{prod}$ is close to zero only over a
111 thermodynamically reversible path. Since entropy is a state variable, its integration over a closed
112 path (e.g. a stable charge–discharge cycle) becomes

113

$$\oint_{cycle} \dot{S} dt = \oint_{cycle} \frac{dS}{dx} dx = 0$$

114

Equation [6]

115

116 Consequently, the integration of **Equation [5]** over a closed path, when combined with
117 **Equation [3]**, gives

118

$$\oint_{cycle} I V dt = \oint_{cycle} \dot{q}|_{T,P} dt = \oint_{cycle} T \dot{\sigma}_{prod} dt \geq 0$$

119

Equation [7]

120

121 The overall voltage hysteresis (both resistive and current-independent in nature) is therefore
122 a measure of entropy production that is dissipated as heat. Entropy production in the realm of
123 chemical reactions²⁹ is further described along-with **Supp. Figure 2**.

Isothermal calorimetry results for the 3.5 V cationic redox

124 Initial electrochemical de-intercalation of up to 0.75 Li per formula unit from
125 $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ (LRSO) takes place around 3.5 V with the oxidation of primarily Ru-based
126 electronic states (hence termed cationic redox). This redox step is completely reversible.^{9,23}
127 Isothermal calorimetry measurements at 40 °C (see Methods for details) were performed over this
128 step in coin-type Li half-cells at different C-rates, ranging from C/20 to C/5. **Figure 2a** shows the
129 resulting voltage profiles, which were used along with the simultaneously measured heat flow rates
130 to obtain the profiles of enthalpy potential U_H using

131 **Equation [1]**, as shown in **Figure 2b** for the slowest rate of C/20. The symmetric shape of
132 the heat flow profiles (orange curves) arises because of reversible entropic heat, whereas the net
133 positive shift is due to irreversible heat from overpotential (see Methods for further explanations).
134 The calculated U_H profiles (pink curves) superimpose neatly on charge and discharge, indicating
135 that the enthalpy change is path independent (**Supp. Figure 1a**) and is only a function of the Li

136 stoichiometry (SoC). Such behaviour is typical for classical electrochemical intercalation
137 reactions.^{26,30} Understanding the exact shape of entropic heat flow is beyond the scope of this study,
138 as it may be related to many aspects of the cathode material, such as the changes in Ru–Ru bond
139 distance ordering²³, charge ordering, Li vacancy ordering, or the shape of the dQ/dV profile (**Supp.**
140 **Figure 3**).

141 The deviation (early drop, marked by green arrows) of the discharge U_H profile from that on
142 charge in **Figure 2b** is likely because of concentration gradients and can be understood better by
143 studying the effect of varying C-rates. The U_H profiles obtained at different rates are compared in
144 **Figure 2c** (see **Supp. Figure 4** for the raw heat flow profiles). They converge over a broad range of
145 SoCs for both charge and discharge, however with some rate-dependent discrepancies at the
146 extremities, as highlighted with green backgrounds in **Figure 2c**. These kinetic effects arise from
147 the formation and relaxation of concentration gradients, most likely in the solid phase due to limited
148 lithium diffusion since the electrode is designed with a high (~60 %) porosity (electrode details in
149 Methods), and the associated heat of mixing effects^{27,28} that were neglected in

150 **Equation [1]**. Nevertheless, the U_H profiles at the slowest rate superimpose adequately and
151 reflect the enthalpy change of the electrochemical reaction. Moreover, the voltage and heat profiles
152 remain perfectly identical over consecutive cycles in this cationic redox regime (**Supp. Figure 5**).

153 Lastly, **Figure 2d** compares the net electrical work and the net heat generated from the cell
154 over a complete cycle at different rates. The heat and work are positive and match with each other,
155 in agreement with **Equation [7]**. Moreover, they exhibit a linear relationship with current that
156 approaches close to zero as the current diminishes. Overall, the calorimetric analysis of the 3.5 V
157 cationic redox step demonstrates its classical nature, i.e. it is path independent with minor quasi-
158 static voltage hysteresis, and can be thermodynamically treated as a single-step electrochemical
159 reaction.

[Figure 2]

Figure 2 | Isothermal calorimetry characterization of the 3.5 V cationic redox step. Voltage profiles (a) obtained with LRSO cycled inside the calorimeter at 40 °C using CCCV protocols after a few formation cycles. The polarization gradually increases with increasing C-rates. For C/20 (b), the measured profiles of cell voltage (blue) and heat flow rate (orange) that were used to obtain the U_H profiles (pink). U_H lies above the equilibrium potential U located somewhere between the charge and discharge voltages. Therefore, the entropic term is such that the cell's entropy increases on charge (causing heat absorption) and decreases on discharge (causing heat release). (c) Convergence of U_H profiles obtained at different rates, with green backgrounds highlighting the deviations possibly due to heat of mixing. As the C-rate increases, the charge U_H profiles develop a small distortion at the onset of charge and show an early rise towards the end of charge. Similarly, the discharge U_H profiles show an early drop towards the end of discharge. (d) Comparison of lost electrical work with dissipated waste heat over complete charge–discharge cycles. The slope and intercept are respectively related to the “SoC averaged” values of R_{int} and V_{hyst} in Equation [10]Error! Reference source not found..

Isothermal calorimetry results for the 4.2 V anionic redox

160 Further extraction of Li from LRSO takes place at the 4.2 V plateau (Figure 3a), which is
161 charge-compensated by the oxidation of bulk lattice oxygen (electron removal from oxygen non-
162 bonding levels, hence termed anionic redox).^{7,23} This step releases significantly larger heat than the
163 preceding cationic redox (Figure 3b). Such a large heat release cannot simply be explained by
164 electrochemical resistance, which we previously showed to remain small.⁹ We had additionally
165 reported very slow equilibration dynamics, such that the open-circuit voltage (OCV) slowly relaxes
166 away from the voltage under load for long periods of time. Note in this case that the direct
167 determination of the entropic term $\frac{\partial U}{\partial T}$ by temperature-dependent potential measurements, as
168 attempted for Li-rich NMC³¹, is questionable. Structure-wise, the anionic redox plateau leads to a
169 loss of crystallinity along with the onset of local distortion, in contrast to the preceding cationic
170 step.^{23,25} Moreover, the subsequent discharge adopts a different sloped S-shaped path (Figure 3c).
171 All these observations indicate that the 4.2 V plateau is an electrochemically-driven irreversible

172 phase transformation (hereafter termed as ‘activation’) from the crystalline partially-charged phase
173 to the disordered/distorted fully-charged one. This is reminiscent of conversion-type electrode
174 materials and cannot be treated as a single-step electrochemical reaction. We therefore propose a
175 two-step electrochemical/chemical (EC) mechanism to explain the anomalous heat generation. The
176 electrochemical (E) step consists of electron removal from states derived primarily from oxygen
177 (anionic oxidation) and the follow-up chemical (C) step is a stabilizing structural rearrangement,
178 e.g. the distortion of RuO₆ octahedra leading to the shortening of O–O distances and/or metal-ion
179 migration.^{7,23,25} This stabilizing chemical step explains the large heat generation observed over the
180 plateau.

181 The U_H profiles obtained from

182 **Equation [1]** are shown in **Figure 3c**. Note that these represent the overall changes in the
183 cell’s enthalpy (without any distinction of the underlying steps). Since the U_H profile on discharge
184 is well separated from the one on charge, as indicated by a double-headed arrow in **Figure 3c**, the
185 condition in **Equation [4]** cannot be fulfilled over the first cycle. Hence, there is a net change in
186 enthalpy, as further schematized in **Supp. Figure 1b**. In other words, the material does not return to
187 the pristine state after a full charge–discharge cycle, consistent with previous
188 characterizations.^{23,25,32} In summary, the large heat release during the voltage plateau may be due to
189 the underlying rearrangement step that accompanies anionic oxidation. The subsequent discharge
190 follows a thermodynamically different path.

[Figure 3]

Figure 3 | Isothermal calorimetry characterization of the full first cycle. (a) Voltage profile (blue) and (b) heat flow profile (orange) for the staircase-like first charge, followed by an S-shaped sloped discharge. An unintended interrupt of 104.4 mins (marked by *) occurred during the anionic oxidation plateau, which is further described in **Supp. Figure 6**. The steep rise in heat release at the end of the plateau is unrelated to the current interrupt and may be explained by the expected rise in

irreversible heat contribution due to poor kinetics when the reaction approaches its end. Other possibilities include partial oxygen release²⁵ and/or side reactions, possibly correlated with the small voltage feature near 4.5 V. The cell used here was the same as the one in **Figure 2** on partial cycling (cationic redox only), which is overlaid here for comparison with the full cycle. (c) The calculated enthalpy potential profiles (pink) are shown along with the cell voltage profile over the complete first cycle. A double-headed green arrow highlights the separation between charge versus discharge enthalpy potentials.

Isothermal calorimetry results for ‘activated’ LRSO

191 After some formation cycles, LRSO’s sloped S-shaped voltage profiles stabilize, with nearly
192 equal capacity contributions from cationic and anionic redox processes that take place at low and
193 high potentials respectively.^{9,23} To understand the electrochemical mechanism of this ‘activated’
194 phase, isothermal calorimetry was performed at different rates ranging from C/50 to C/5. The
195 resulting voltage profiles exhibit a significant voltage hysteresis that does not diminish by lowering
196 the current (**Figure 4a**). The heat flow for the slowest rate of C/50 (**Figure 4b**) is not symmetric
197 and remains largely above zero for the entire cycle, unlike the classical cationic redox in previous
198 **Figure 2**.

199 Again, the U_H profiles were calculated from
200 **Equation [1]**, as shown in **Figure 4b** for C/50 (other rates in **Supp. Figure 8**, comparison
201 with initial cycle in **Supp. Figure 9**). Interestingly, the U_H profiles on charge vs. discharge are
202 much closer in comparison to the hysteretic voltage profiles. A larger heat generation on discharge
203 indicates that the reaction’s enthalpy potential is located further away from the discharge voltage
204 than the charge voltage. Note that, despite a low rate of C/50, the U_H profiles on charge and
205 discharge do not fully superimpose, especially in the second half of SoCs (anionic redox region),
206 thus reflecting a slight path dependence in the cell’s enthalpy, as also schematized in **Supp. Figure**
207 **1c**. This effect was consistently observed for several cells (**Supp. Figure 10**). Whether this slight
208 mismatch is due to kinetic or thermodynamic reasons can be understood from **Figure 4c**. On either

209 charge or discharge, the U_H profiles obtained at different rates converge over almost the entire SoC
210 range, except possible heat of mixing effects at the end of charge and the beginning of discharge
211 (highlighted with green backgrounds). Therefore, enthalpy-wise, the charge and discharge paths are
212 rate-independent over the range of rates studied herein (from C/50 to C/5). Moreover, these paths
213 are slightly dissimilar as they do not converge to a single unique curve. ‘Activated’ LRSO thus
214 follows metastable paths having slightly different enthalpies on charge vs. discharge for the same
215 SoC. Therefore, the overall Li content is no longer the unique reaction coordinate to fully describe
216 the system, as discussed later.

217 Nevertheless, since ‘activated’ LRSO shows fairly stable heat profiles with negligible
218 voltage fade in consecutive cycles (**Supp. Figure 11**), the U_H profiles should satisfy **Equation [4]**,
219 despite being slightly different on charge vs. discharge, as also schematized in **Supp. Figure 1c**.
220 This can be verified from **Figure 4d** showing the match between net heat and work (over complete
221 cycles). The extra work needed due to voltage hysteresis is therefore dissipated as heat. The zero-
222 current intercept in **Figure 4d** is large ($\sim 70.4 \text{ Wh kg}^{-1}$), unlike **Figure 2d**, because of the large
223 quasi-static hysteresis. It is key here to note that this significant dissipation can be viewed,
224 according to **Equation [7]**, as entropy production and implies that the underlying steps are far away
225 from equilibrium even at the lowest rates (further discussion with **Supp. Figure 2**). Entropy
226 production (the value of the integrals in **Figure 4d**) should ideally vanish to zero at infinitesimally
227 small rates at which all the underlying steps would be near equilibrium. However, demonstrating
228 this is not trivial simply due to prohibitively long experiments as well as the interfering side-
229 reactions at extremely low C-rates. Such non-equilibrium arguments also explain the continuous
230 voltage relaxation observed for LRSO under open circuit conditions, despite long time periods (24
231 hours)⁹, because some of the underlying steps have slow equilibration dynamics with very large
232 time constants. Since similar slow dynamics plague Li-rich NMC¹⁰, equilibrium is never achieved
233 and the reported values of the entropic term $\frac{\partial U}{\partial T}$ are invalid as they violate **Equation [6]** during the

234 sloped cycles³¹. Likewise, distinguishing the true equilibrium potential U (unique) from path-
235 dependent metastable equilibrium potentials (non-unique) requires further thermodynamics
236 development.

237 Overall, it is clear that voltage hysteresis is linked to non-equilibrium entropy production,
238 which can be quantified over a complete cycle as the net dissipated heat or lost electrical work.
239 However, further deconvolution of the heat flow rate into entropy change and entropy production
240 rates, as per **Equation [5]**, is not possible without precise knowledge of the underlying mechanism.
241 Therefore, a multi-step mechanism consistent with calorimetry results is presented later.

[Figure 4]

Figure 4 | Isothermal calorimetry characterization of ‘activated’ LRSO. The hysteretic voltage profiles (a) obtained with LRSO cycled inside the calorimeter using CCCV protocols. dQ/dV curves are shown in **Supp. Figure 7**. The experiments were performed after a few formation cycles in the full potential range leading to complete ‘activation’. The quasi-static hysteresis appears to be larger in the higher potential anionic redox range. For C/50 (b), the measured profiles of cell voltage (blue) and heat flow rate (orange) that were used to obtain the U_H profiles (pink). A zoom in inset shows the slight differences in U_H profiles over the high potential region. (c) Convergence of U_H profiles obtained at different rates for charge (top) and on discharge (bottom), with green backgrounds highlighting the deviations possibly due to heat of mixing. (d) As a function of C-rate, the comparison of lost electrical work with dissipated waste heat over a complete charge–discharge cycle obtained by integrating respectively the cell voltage and the heat flow rate. These integrals scale linearly with current, with the slope and intercept respectively related to the “SoC averaged” values of R_{int} and V_{hyst} in **Equation [10]****Error! Reference source not found.**

242 Voltage window opening experiments were next performed. **Figure 5a** reveals that charging
243 to high potentials, particularly beyond 50% SoC, gradually triggers voltage hysteresis. Akin to the
244 discharge voltage profiles that are path dependent (i.e. they depend on the extent of charging), the
245 discharge heat flow profiles (**Figure 5b**) also exhibit path dependence. Consistent with voltage
246 hysteresis, discharging from the fully charged state results in a larger heat generation over a broad
247 range of SoCs (denoted by arrows) compared to discharge from partially charged states. The

248 corresponding U_H discharge profiles (**Figure 5c**) in the lower half of SoCs (cationic redox²³)
249 converge independently of the charging history. In contrast, for the upper half of SoCs (anionic
250 redox²³), the discharge U_H curves gradually evolve as a function of the extent of charge, thus
251 highlighting the distinctive role of the anionic redox process in causing voltage hysteresis. Lastly,
252 the net heat and work over complete cycles are compared in **Figure 5d** as a function of the charging
253 SoC. They again match with each other, consistent with **Equation [7]**. Instead of a linear trend with
254 current that is expected for path reversible intercalation materials, a non-linear rise is observed in
255 **Figure 5d** because of gradually worsening voltage hysteresis as the charging voltage window is
256 opened. In light of these unusual observations triggered by high potential charging, a multi-step
257 mechanism for the anionic redox process is proposed next.

[Figure 5]

Figure 5 | Isothermal calorimetry for charge voltage window opening of ‘activated’ LRSO. (a) Voltages profiles (blue). dQ/dV curves are shown in **Supp. Figure 12**. (b) Heat flow profiles (orange) on discharge only. Complete heat profiles in **Supp. Figure 13**. (c) The calculated U_H profiles (pink, for discharge only). U_H profiles on charge are identical as expected (see **Supp. Figure 14**). A dashed curve in the background shows the full range charge–discharge voltage profile. The initial kinks in U_H profiles at the onset of discharges is likely due to heat of mixing, as also observed in **Figure 4c**. (d) As a function of SoC to which the cell is charged, a comparison of lost electrical work with dissipated waste heat over a complete charge–discharge cycle obtained by integrating respectively the cell voltage and the heat flow rate. This non-linear trend was verified with a second cell (**Supp. Figure 15**).

Proposed multi-step mechanism for hysteretic anionic redox

258 The mechanism behind the hysteretic anionic redox process in ‘activated’ LRSO can now
259 qualitatively be understood in light of the above calorimetry results. From the point of view of local
260 structure, cationic redox can be treated as a single electrochemical step, therefore free from quasi-
261 static voltage hysteresis (**Figure 6a**). On the other hand, anionic redox can be described as a multi-

262 step process, consisting of sequential redox (electrochemical) and rearrangement (chemical) steps,
263 which form a “square-scheme”^{33–35} (**Figure 6b**) having a reaction energy landscape shown in
264 **Figure 6c**. On charge, the electrochemical oxidation of anions is followed by a stabilizing structural
265 rearrangement that could either enlist the distortion of octahedral symmetry leading to O–O
266 shortening^{7,23}, metal-ion migration^{6,8,11,20,21}, or a layer stacking change^{14,15}. Owing to this structural
267 modification, a different redox step is needed on discharge, which is again followed by a stabilizing
268 rearrangement to the original state with reduced anions. Interestingly, these steps are analogous to
269 the “square-scheme” mechanism that causes voltage hysteresis in certain molecular machines.^{34–36}
270 Note that the four elementary steps are thermodynamically constrained as they form a closed cycle,
271 but they do not necessarily take place close to equilibrium. A complementary experiment of
272 gradually opening the discharge voltage window (**Supp. Figure 16**) fully supports the proposed
273 mechanism.

274 Such a multi-step mechanism allows for non-equilibrium to exist if the kinetics of some of
275 the elementary steps, most likely the chemical rearrangements steps, is slow enough (much slower
276 than the C-rates used). In such a non-equilibrium case, the overall Li content of the electrode
277 material is not the only reaction coordinate (the other coordinates being related to species
278 repartitioning). The persistence of metastable paths can thus be explained, such that, independent of
279 current, charge predominantly occurs via the upper path in **Figure 6b** and discharge via the lower
280 one. Therefore, the non-equilibrium cell potentials during charge and discharge are respectively
281 closer to the thermodynamic potentials U_{ch}^{A} and $U_{\text{dis}}^{\text{A}}$ of the two redox steps, hence giving rise to
282 voltage hysteresis. This hysteresis leads, by definition, to dissipative entropy production²⁹, whose
283 value on charge and discharge is in part related to the Gibbs free energy of reaction of the respective
284 rearrangement step (**Figure 6c**). Nevertheless, the exact mathematical form of entropy production,
285 as described along-with **Supp. Figure 2**, depends on the underlying thermodynamics and kinetics
286 of the elementary steps that are, unfortunately, not easy to parametrize for LRSO. Thus, novel

287 methods need to be developed for determining the entropy change for such path-dependent
288 materials that show continuous OCV drift. Note that true equilibrium theoretically does exist in the
289 scheme of **Figure 6b**, i.e. when the four steps occur in unison, but this situation is never achieved at
290 practical C-rates, hence leading to metastability. This is the key difference in comparison to cationic
291 redox, which also involves local structural changes (RuO₆ octahedral expansion/contraction and
292 Ru–Ru distance change). However, these changes are energetically small and/or kinetically fast,
293 and therefore always in equilibrium with the redox step.

294 Concerning practical applications, the obstacle of quasi-static voltage hysteresis in Li-rich
295 electrodes can only be overcome by addressing directly the anionic redox process that triggers
296 atomic motion that is either kinetically slow and/or thermodynamically large in energy penalty,
297 hence causing metastable reaction pathways and voltage hysteresis. Towards these goals, revisiting
298 anionic redox chemistry in chalcogenides³⁷, owing to their lower chemical hardness, may prove
299 beneficial for fundamental understanding of the root cause behind hysteresis. Likewise, hysteresis-
300 free anionic redox in Na_{4/7}[□_{1/7}Mn_{6/7}]O₂ calls for further investigation of Na-based cathodes.³⁸

[Figure 6]

Figure 6 | Proposed mechanism for hysteretic bulk anionic redox in ‘activated’ LRSO. (a) Cationic redox can be described as a single step electrochemical reaction. **C** and **C⁺** are the reduced and oxidized cationic species (e.g. Ru⁴⁺ and Ru⁵⁺). (b) Anionic redox is described by a multi-step “square-scheme” mechanism. **A** denotes the anionic species in reduced state (e.g. O²⁻) that upon oxidation forms unstable **A⁺** (e.g. Oⁿ⁻ with $n < 2$). Structural reorganization spontaneously takes place to form stabilized **A_r⁺** (e.g. dimerized O–O²ⁿ⁻ with possible metal-ion migration^{6,7}). Reduction on discharge goes through the unstable **A_r** (e.g. O–O⁴⁻) that spontaneously rearranges back to the original state. **A⁺** and **A_r** are therefore the high-energy intermediates for the two respective paths. Note that electrons and Li ions are not explicitly shown in these schemes. Also, the cationic and anionic reactions may occur in a partially overlapped fashion depending of the precise kinetic and thermodynamic parameters. (c) A schematic reaction energy landscape, highlighting (i) the downhill nature of chemical (C) rearrangement steps, and (ii) their associated kinetic barriers. These two conditions explain path-dependence. If the larger heat generation experimentally observed on discharge is assumed primarily due to entropy production (i.e. minor contributions from reversible entropy), then $\Delta G_{\text{dis}}^{\text{r}}$ in ‘activated’ LRSO is expected to be larger than $\Delta G_{\text{ch}}^{\text{r}}$, implying that the O–O

dissociation is energy-wise costlier than its formation.

301 The above mechanism bears a similarity with the previously proposed “activated bonding
302 change” model for hysteretic hydrogen-containing carbons^{39,40}, or the phase-change-based model
303 for hysteretic Li-rich NMC^{10,24}, or the model based on limited ionic mobility for certain hysteretic
304 displacement reactions⁴¹. All these models lead to a non-equilibrium situation under operating
305 conditions, thus making it necessary to consider the heat associated with bonding change or phase
306 change, like previously done for hysteretic carbons.⁴²

307 Lastly, apart from providing mechanistic insights about anionic redox in Li-rich electrodes,
308 this work provides a new direction in the characterization of batteries with isothermal calorimetry.
309 A particular highlight is the importance of U_H , the enthalpy potential, that can greatly help in
310 predicting the total heat generation needed for battery thermal management. Therefore, we
311 recommend the measurement of U_H , especially for battery materials that either show large entropy
312 changes or a quasi-static voltage hysteresis (silicon, graphite, LiFePO₄, Li-S, Li-O₂, and conversion
313 electrodes). The non-equilibrium thermodynamics approach developed herein could be extended to
314 electrochemical systems beyond batteries, such as water-splitting catalysts showing large
315 overpotentials or to hysteretic solar cells.

Conclusion

316 In summary, isothermal calorimetry has elucidated the general thermodynamic mechanism
317 governing the ‘model’ Li-rich Li₂Ru_{0.75}Sn_{0.25}O₃ (LRSO) cathode’s electrochemistry. We proved
318 that charging LRSO through the anionic oxidation plateau leads to heat generation and a permanent
319 change of the material, such that it displays sloped and hysteretic voltage profiles with reversible
320 oxygen redox chemistry in the subsequent cycles. In a thermodynamically consistent manner, we
321 demonstrated that the electrical work lost due to such voltage hysteresis is dissipated as waste heat.
322 It is now clear that (i) metastable paths persist even under quasi-static conditions and that (ii)

323 voltage hysteresis is directly related to non-equilibrium entropy production instead of simply
324 originating from large differences in the enthalpy of charge vs. discharge paths. Far-from-
325 equilibrium is therefore an essential condition for quasi-static voltage hysteresis, which renders the
326 estimation of true equilibrium properties quite difficult. The extension of this work to the ‘practical’
327 Li-rich NMC, among other anionic redox cathodes, is imminent and similar results are expected.
328 Furthermore, the implementation of model-based simulations could help in generalizing the multi-
329 step “square-scheme” model proposed herein. Such fundamental understanding is necessary for
330 designing effective mitigation approaches that can lead to the eventual elimination of voltage
331 hysteresis. In the broader context, this new direction for battery characterization using isothermal
332 calorimetry would encourage the electrochemistry community to further exploit this tool as well as
333 to adopt the concepts of enthalpy potential and non-equilibrium entropy production. From an
334 applied perspective, the methodology developed herein calls for revisiting some known hysteretic
335 materials (silicon, conversion-based) and would also help in screening emerging materials for
336 minimizing heat generation.

Methods

337 **Energy balance for an electrochemical cell.** The general energy balance for an
338 electrochemical system was derived by Newman and co-workers.^{27,43,44} For a thermally thin
339 electrochemical cell in isothermal (constant temperature) and isobaric (constant pressure)
340 conditions, the heat generation rate $\dot{q}|_{T,P}$ (if heat of mixing is neglected^{27,28}) is given by

$$\dot{q}|_{T,P} = I(V - U) + IT \frac{\partial U}{\partial T} + \sum_i \Delta H_i r_i$$

342 **Equation [8]**

343
344 where $\dot{q}|_{T,P}$ is positive if heat is released by the cell, I is the current (positive for charging),
345 V is the cell voltage, U is the equilibrium potential, T is the temperature, P is the surrounding
346 pressure, and ΔH_i is the enthalpy of reaction of a chemical reaction i (other than the main
347 electrochemical reaction) occurring at a rate r_i . Recognizing the first term as irreversible heat
348 generation due to overpotential, the second term as reversible entropic heat, and the last term as
349 parasitic heat due to side reactions, **Equation [8]** Error! Reference source not found. can also be
350 equivalently formulated as²⁶

$$\dot{q}|_{T,P} = I\eta + \frac{IT}{nF} \left(\frac{dS_+}{dx} - \tilde{s}_{Li} \right) + \dot{q}_p$$

352 **Equation [9]**

353
354 where η is the cell's overpotential (the product $I\eta$ is always positive), n is the number of
355 electrons involved in electrode reaction, F is the Faraday's constant, x is the stoichiometric content
356 of Li in the positive electrode material, S_+ is the total entropy of the positive electrode material at a
357 given x , \tilde{s}_{Li} is the molar entropy of Li metal negative electrode, and \dot{q}_p is the parasitic heat flow due

358 to other chemical reactions. These formulations have extensively been used for investigating the
 359 entropic heat of intercalation materials⁴⁵ and more recently the parasitic heat in Li-ion cells^{30,46–49}.
 360 For quantifying the entropy change, one possibility (potentiometric method) is to perform
 361 temperature-dependent equilibrium potential measurements for directly determining $\frac{\partial U}{\partial T}$ in **Equation**
 362 **[8]**[Error! Reference source not found.](#)^{28,50–53} Another option (calorimetric method) is to measure V ,
 363 I , and $\dot{q}|_{T,P}$ over a charge–discharge cycle and obtain the terms in **Equation [9]** while considering
 364 these terms to be path independent (same on charge vs. discharge), which is a reasonable
 365 assumption for classical intercalation materials only.^{26,30,49} Lastly, a method called electrothermal
 366 impedance spectroscopy (ETIS) has also recently been developed.⁵⁴ To understand the effect of
 367 quasi-static voltage hysteresis, the irreversible heat term can be empirically modelled, when I is
 368 relatively low, as⁴⁹

$$I \eta = I^2 R_{int} + |I| V_{hyst}$$

Equation [10]

370
 371
 372 where R_{int} is the cell’s internal resistance and V_{hyst} the inherent quasi-static (extrapolated to
 373 zero-current) voltage hysteresis. This equation was successfully applied to empirically model the
 374 heat flow in $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2/\text{graphite}$ cells by including a small ($\pm \sim 4$ mV) voltage hysteresis
 375 equally on charge and discharge and by considering R_{int} as a function of SoC only.⁴⁹ However for
 376 the Li-rich electrodes, this approach is not suitable because (i) they show a much larger hysteresis
 377 (both Li-rich NMC and LRSO that are of interest in this work) and (ii) their R_{int} is known to vary
 378 differently on charge vs. discharge with SoC.^{5,9} Likewise, V_{hyst} can be expected to differ as a
 379 function of cell potential on charge vs. discharge in these highly path-dependent materials. In other
 380 words, the position of U in hysteretic Li-rich electrodes cannot simply be assumed in the middle of
 381 the charge and discharge profiles, unlike in classical intercalation materials. We therefore use a

382 different approach herein that is based on “enthalpy potential”, as described in the main text.

383
384 **Material synthesis and electrode fabrication.** Single-phase $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ (LRSO)
385 samples, as determined by X-ray powder diffraction, were obtained by solid-state synthesis reported
386 elsewhere.²⁵ The Bellcore plastic method⁵⁵ was used to prepare high-porosity self-standing
387 electrodes, as described in detail previously.⁹ The final electrode film was composed of 73% (by
388 weight) active material, 9% carbon SP (MM, Belgium), and 18% binder – poly(vinylidene fluoride-
389 co-hexafluoropropylene) (PVDF-HFP) (Arkema). The film was designed for an active material
390 loading of $\sim 20 \text{ mg cm}^{-2}$, $\sim 200 \text{ }\mu\text{m}$ film-thickness, and $\sim 60\%$ porosity. Such a relatively high
391 loading was needed to generate reliable amounts of heat flow from the coin cells. Owing to the high
392 porosity of carefully designed electrodes, in addition to the relatively low C-rates studied herein, the
393 liquid-phase transport limitations (and their associated entropy production^{56,57}) are expected to
394 remain very low compared to those in the solid phase, as also suggested via previous modelling^{57,58}
395 investigations.

396
397 **Coin-cell assembly.** Using $\sim 1 \text{ cm}^2$ circular discs of this electrode film, 2032 coin-type cells
398 with Li metal foil as the negative electrode were assembled in an argon-filled glove-box with two
399 layers of $12 \text{ }\mu\text{m}$ polyethylene film coated with $4 \text{ }\mu\text{m}$ alumina (W-SCOPE separators) along with one
400 layer of a WhatmanTM GF/D borosilicate glass microfiber sheet (GE Healthcare Life Sciences). The
401 electrolyte used was LP100 (Merck) having 1 M LiPF_6 in ethylene carbonate : propylene carbonate :
402 dimethyl carbonate in a 1 : 1 : 3 volume ratio. No stress build-up (mechanical work) is expected to
403 occur inside the cell owing to LRSO’s very small lattice volume change (maximum 3.7 %)²⁵, along
404 with the use of a soft and deformable glass microfiber separator that can accommodate any residual
405 strain. The C-rate in this work is defined such that 1C corresponds to the removal of 1 Li per
406 formula unit of LRSO in one hour ($1\text{C} = 160.13 \text{ mA g}^{-1}$).

407

408 **Isothermal Calorimetry.** Depending on the experiment, the cells were pre-cycled at room
409 temperature before being transferred into a TAM III Microcalorimeter (TA Instruments: stability \pm
410 0.0001 °C, accuracy \pm 1 μ W, precision \pm 10 nW) for isothermal calorimetry measurements at 40 °C.
411 A few formation cycles were again carried out once the cells were inside the calorimeter. Such pre-
412 cycling allows any possible side-reactions, such as gassing and/or surface stabilization in initial
413 cycles, to reach to a nearly steady state. The baseline drift over the course of the experiments did
414 not exceed \pm 0.5 μ W. The time constant of the calorimeter is about 5 minutes. All specifications
415 and information regarding microcalorimetry calibration, cell connections, and operation procedures
416 can be found in previous literature.^{30,46-49} The electrochemical cycling was performed with a
417 Maccor 4000 series cycler connected to the cells inside the calorimeter. Depending on the
418 experiment, either a constant current (CC) or a constant current constant voltage (CCCV) protocol
419 was used. The voltage hold of the CCCV step was terminated when current decayed to a low value
420 of C/100. The observed heat flow, defined positive when heat is generated by the cell, mainly arises
421 from the positive electrode. A constant and small value of background heat of +3.4 μ W, accounting
422 for parasitic reactions, was subtracted from the raw measured heat flow values, irrespective of
423 cationic or anionic redox regime. Such an assumption of constant parasitic heat is acceptable given
424 the scope of this study. Still, it must be kept in mind that parasitic heat depends on the complex
425 relationship among the cathode, the anode, the electrolyte, the operating conditions (cell voltage
426 etc.), the cell history over the course of the experiment, besides the continuous corrosion of inactive
427 cell parts.

Data availability.

428 The authors declare that the main data supporting the findings of this study are available
429 within the article and its Supporting Information files. Extra data are available from the
430 corresponding author upon reasonable request.

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Acknowledgements

431 J.M.T. and G.A. acknowledge the funding from the European Research Council (ERC)
432 (FP/2014)/ERC Grant-Project 670116-ARPEMA. S.L.G thanks NSERC and the Walter C. Sumner
433 Foundation for funding. We are grateful to Dr. Jeff Dahn for providing access to some of the
434 equipment used in this work.

Author Contributions

435 G.A. and S.L.G. conceived the idea. G.A. prepared the electrochemical cells and S.L.G.
436 performed the isothermal calorimetry experiments. G.A. and C.D. performed the thermodynamic
437 analysis. J.M.T. supervised the project. G.A. wrote the paper, with contributions from all authors.

Competing Financial Interests

438 The authors declare no competing financial interests.

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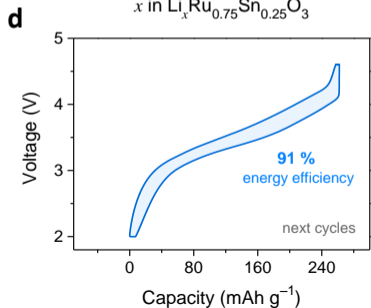
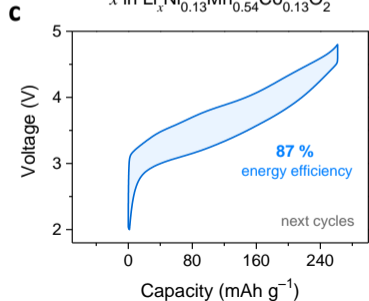
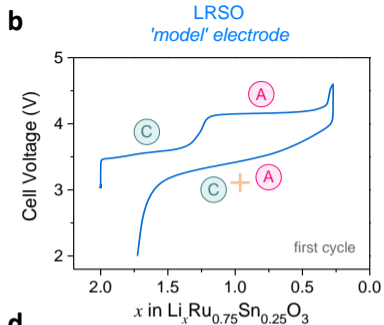
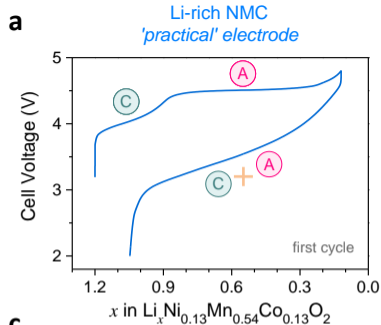
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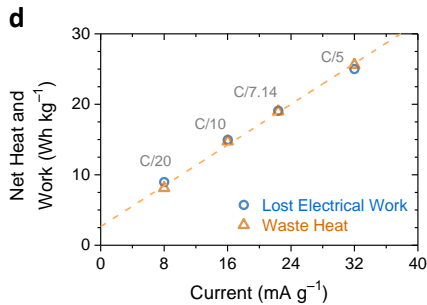
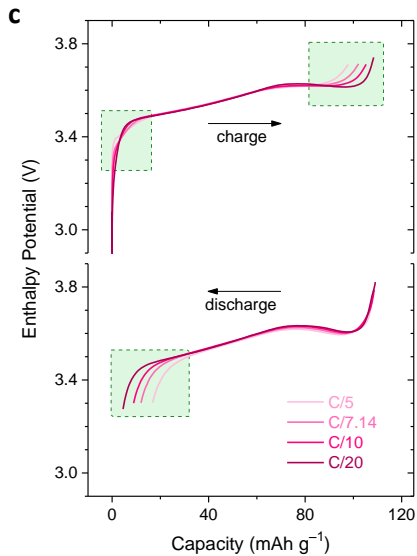
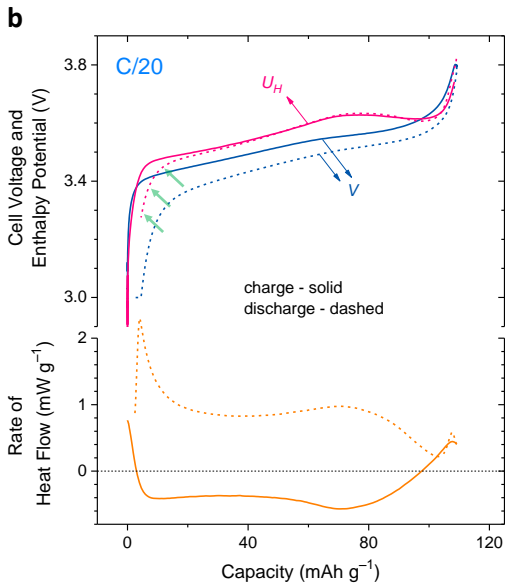
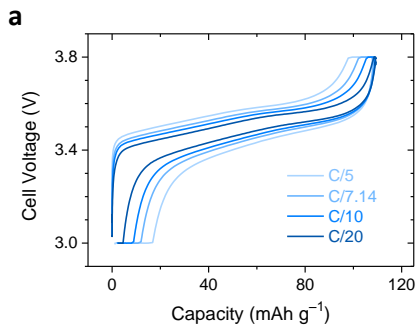
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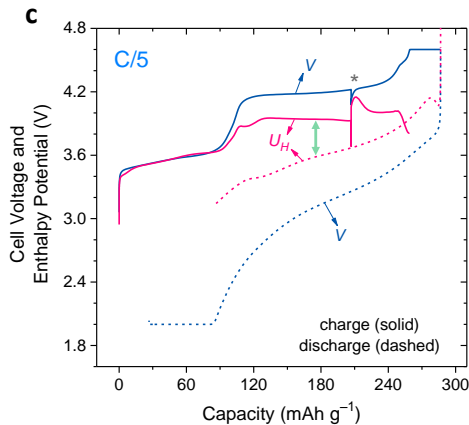
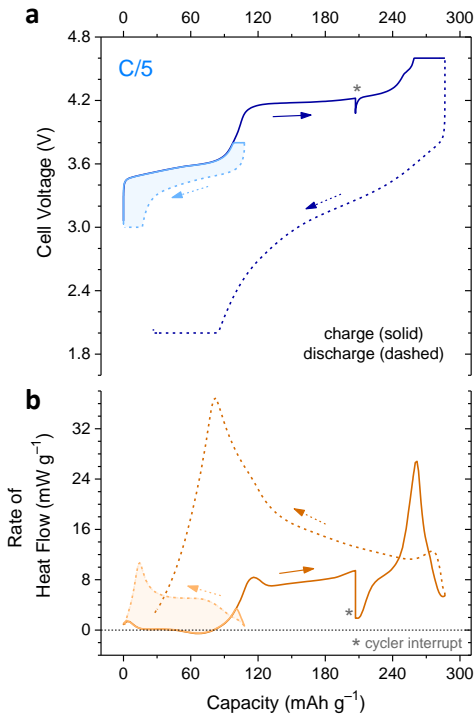
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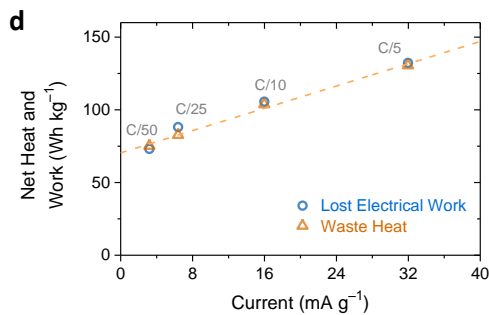
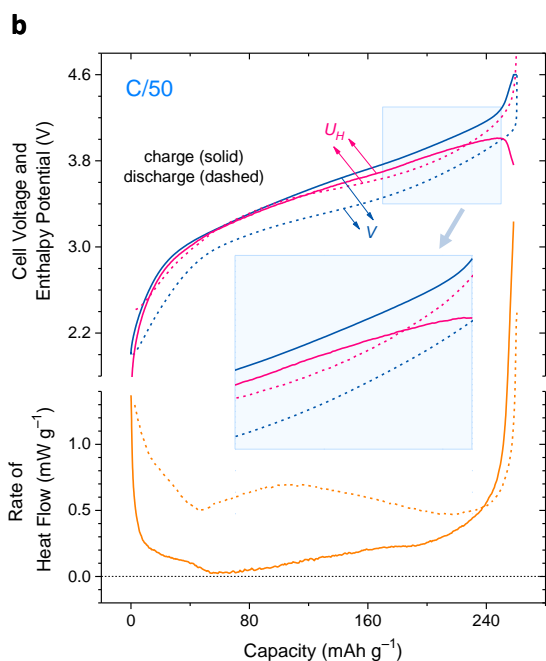
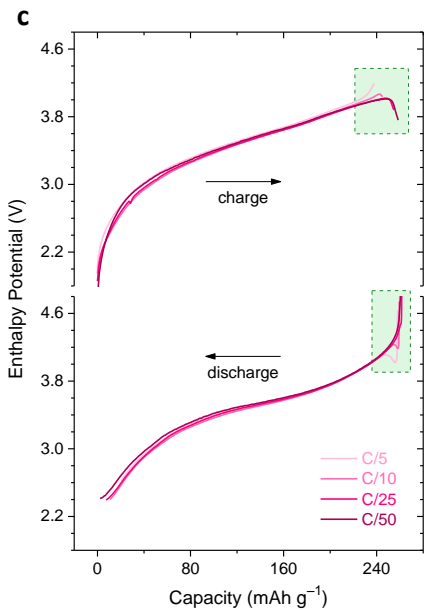
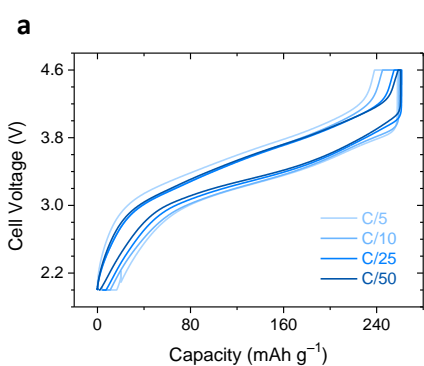
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charge window opening

