

Investigation of hysteresis and relaxation behaviour in graphite and $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ electrodes

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1 **INVESTIGATION OF HYSTERESIS AND RELAXATION BEHAVIOUR**
2 **IN GRAPHITE AND $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ ELECTRODES**

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9

10 **Abstract**

11 Li-ion battery electrode materials exhibit hysteresis between lithiation and delithiation due to
12 different thermodynamic equilibria at the same state of charge (SOC). The acquisition time for
13 the open circuit potential (OCP) and the hysteresis behaviour of graphite and
14 $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC) has been investigated using galvanostatic intermittent titration
15 technique in Lithium metal anode cells. The OCP at various stages of relaxation after each
16 current pulse have been recorded during lithiation and delithiation. The voltage hysteresis is
17 the difference between the potential at equilibrium after lithiation and delithiation. Hysteresis
18 is ~600 and ~300 mV below 0.1 SOC for graphite and NMC electrodes respectively, above 0.1
19 SOC the hysteresis is much lower 35-33 and 45-42 mV, with short rest requirements of 5-120
20 min. The error in hysteresis voltage with shorter relaxation times is compared to 120 min rest.
21 This analysis shows that 5 min. has an error of 16 mV for graphite and 2 mV for NMC between
22 0.1-1 SOC. Below 0.1 SOC, 90 min. (for graphite/NMC) and between 0.1-1 SOC, 30 min. (for
23 graphite) and 5 min. (for NMC) at charge rates below C/20 are appropriate relaxation times
24 and can shorten the OCP parameter acquisition test time significantly.

25 **Keywords**

26 Open circuit potential; hysteresis; relaxation; experimental duration; GITT, parameterization

27 **1. Introduction**

28 Li-ion battery parameters are required to model the electrochemical processes taking place
29 inside the battery. There are several variables/parameters governing the battery state of charge
30 (SOC), output voltage and capacity. Open circuit potential (OCP) is one of the most important
31 input variables to estimate the instantaneous cell voltage using numerical models [1]. However,
32 OCP has a significant hysteresis which corresponds to the different thermodynamic equilibria

33 of the material under charging and discharging processes [2-4]. The hysteresis in OCP varies
34 with SOC which needs to be considered in battery modelling [5]. Several studies to elucidate
35 the hysteresis in open circuit potential of the Li-ion batteries are reported [2-5]. Dreyer *et al.*
36 [2] explained the thermodynamic view point of having different equilibrium potential during
37 the lithiation and delithiation for the same SOC of the electrode. Barai *et al.* [3] investigated
38 the hysteresis of cylindrical and pouch cells with various rated capacities and cell chemistries.
39 Another study investigated the difference in equilibrium potential of LiFePO₄/Graphite cells
40 and reported the different hysteresis voltages with SOCs [4]. These studies have been carried
41 out on commercial full-cells where the computed hysteresis is the compound effect of the
42 hysteresis in the individual electrodes. For precise battery monitoring and control using
43 mathematical models the SOC dependent OCP and the hysteresis of each electrode need to be
44 gauged [4-9]. The time for the OCP parameter acquisitions can be long (2 weeks), and therefore
45 OCP has been estimated in some cases as the mid voltage between charge and discharge. This
46 practice doesn't take into consideration the voltage hysteresis observed between charge and
47 discharge, and in addition has polarization effects particularly below 10% SOC which are not
48 observed at steady state (equilibrium) OCP.

49 To obtain the OCP of the electrodes various studies have been conducted using galvanostatic
50 intermittent titration technique (GITT) at different currents (C/10-C/50), pulse durations (10-
51 60 min.) and relaxation durations (15-600 min.) [10-17]. However, very few studies have been
52 conducted on the OCP hysteresis of the individual electrodes [6,11]. Farkhondeh *et al.* [6] have
53 computed a voltage hysteresis of 8 mV for the LiFePO₄ and Croy *et al.* [11] have observed the
54 varying voltage hysteresis with SOC of the Ni and Mn based composite cathode, quantify the
55 voltage relaxation time at different SOC's required to reach OCP. GITT is usually used with
56 short current pulses and long arbitrary relaxation times to ensure that OCP has been reached,
57 this leads to long test times (up to two weeks). Too short a rest duration results in a non-steady

58 state OCP, with lithium concentration gradients between the electrode solid matrix and further
59 relaxation required to reach equilibrium voltage. Longer relaxation duration results in increased
60 test durations and cost. To date, no investigations have been carried out to investigate the effect
61 of rest duration on the OCP measurement of the battery electrodes and the change in rate of
62 voltage drop at different SOC.

63 The objectives of the present study have been directed towards the quantification of the OCP
64 relaxation for graphite and $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC) electrodes using in-house assembled
65 coin-cells in half-cell format. The voltage rate of change during relaxation to OCP is analysed
66 at different SOC's. This study reveals the sensitive SOC zone for the electrode OCPs and the
67 corresponding relaxation time in view of future model parameterization. This study
68 investigates the tradeoff between the experimental duration and the corresponding accuracy
69 required to guide researchers in selecting the relaxation duration for OCP measurements.

70 **2. Methodology**

71 Electrode slurry was prepared with a composition of Graphite: Carbon Black (CB): poly-
72 vinylidene fluoride (PVDF) in proportion of 92:2:6 [18,19] for anode and NMC: CB: PVDF in
73 proportion of 92:5:3 [18,19] for cathode in N-methyl-2-pyrrolidone. The slurries were coated
74 on copper and aluminum foil for anode and cathode, respectively, and subsequently dried over
75 a hot plate at 90°C for 30 min. and overnight in a vacuum oven at 45°C. Thereafter, coated
76 sheets were calendared up to 30-40% of porosity and circular disks of diameter 1.5 cm were
77 cut. The cut disks were used to assemble 2032 type coin cells with a lithium metal anode. A 20
78 μm thick polyethylene film of diameter 1.9 cm used as a separator. The electrolyte used was
79 1M LiPF_6 in EC/EMC 3/7(v/v) + 1%wt. VC, as previously described [20].

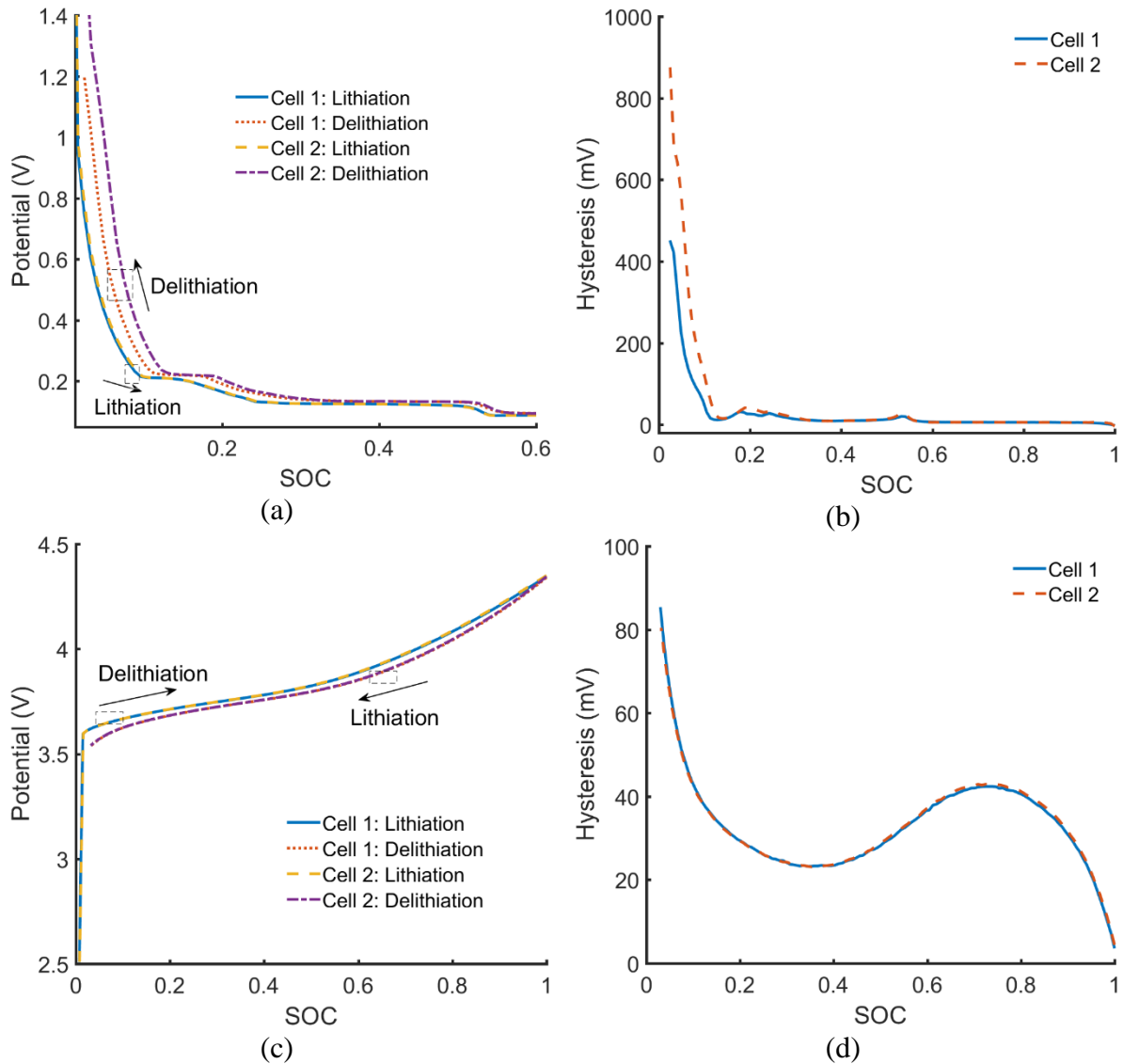
80 Two Li-graphite and Li-NMC cells were assembled and subjected to a formation process of 2
81 cycles between 0.005-3V [19] and 2.6-4.35V [18-19], respectively, at C/20 currents. The

82 experimental cells and of the experimental setup used in this study have been represented in
83 Figs. S1-S2 in supplementary materials. Afterwards, GITT was performed with consecutive
84 current pulses and relaxation durations. The applied current pulse was C/20 for 10 min. to
85 adjust the SOCs of the electrodes followed by 2 hour relaxation to attain an equilibrium state.
86 The voltage limits for the GITT test are 0.005-3V and 2.6-4.35V for the graphite and NMC
87 half-cells, respectively. The voltage change for graphite and NMC vs Li/Li⁺ was recorded over
88 the relaxation period, and the time to reach OCP for the various SOCs are shown.

89 **3. Results and Discussion**

90 GITT was performed during lithiation and delithiation for a set of two half-cells of Li-NMC
91 and Li-Graphite, and their voltage response analysed over a 120 min rest period. After 120 min
92 negligible change in voltage is observed, and we therefore assume the relaxation time is
93 sufficient for equilibrium OCP, and consequently the hysteresis evaluation over complete SOC
94 range. The OCPs during lithiation and delithiation and their hysteresis for each of the cells have
95 been compared in Fig. 1. Fig 1(a) shows that the lithiation OCP for the two Li-Graphite cells
96 are nearly overlapping for the entire range of the SOC. However, the delithiation OCP for the
97 two cells has significant variation between 0-0.13 SOC and around 0.2 SOC (0.014V) due to
98 the microstructural and porosity differences between two graphite electrodes. Above 0.23 SOC
99 the two cells have similar voltage profiles with less than 1mV variation. Furthermore, the
100 hysteresis for the two Li-Graphite cells shows (Fig. 1(b)) a large difference between 0.02-0.13
101 (up to 424mV at 0.02 SOC). Above 0.13 SOC, the two cells have insignificant difference in
102 hysteresis (within 0.5 mV) except at 0.2 SOC (up to 24 mV) and 0.53 SOC (up to 8 mV).
103 Similarly, the lithiation and delithiation OCPs shown in Fig. 1(c) demonstrate a very good
104 overlap (with a voltage difference within 2 mV) and repeatable behaviour for the two Li-NMC
105 cells for the entire range of the SOC. In addition, the hysteresis for the two cells is also closely

106 matching (within ~ 1.5 mV) to each other for the full SOC domain (Fig 1(d)). The results
 107 obtained for Cell 1 (of Li-Graphite and Li-NMC cells) will be discussed in the forthcoming
 108 sections.



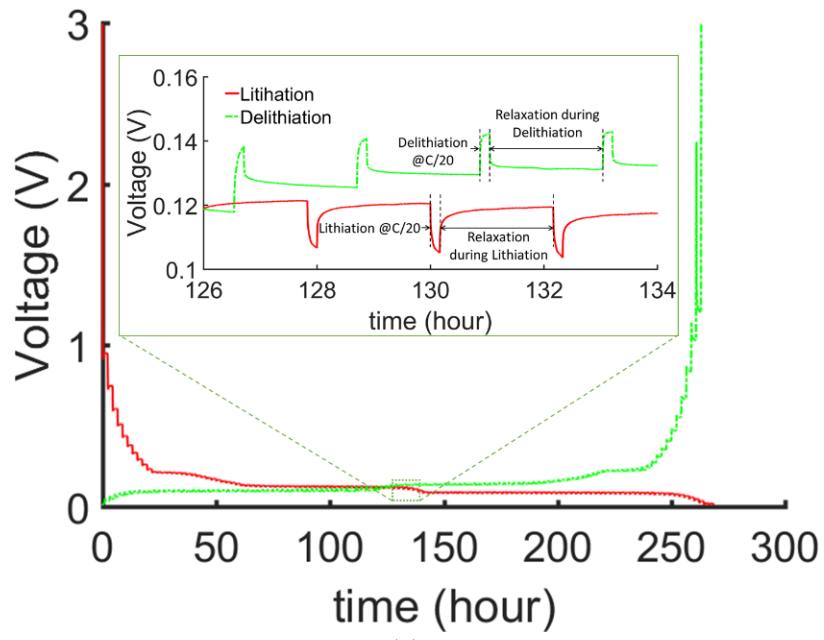
109 Figure 1: The comparison (a) Lithiation and delithiation OCPs and (b) Hysteresis of the two
 110 Li-Graphite cells; (c) Lithiation and delithiation OCPs and (d) Hysteresis of the two Li-NMC
 111 cells.

112 3.1 Graphite voltage relaxation investigation

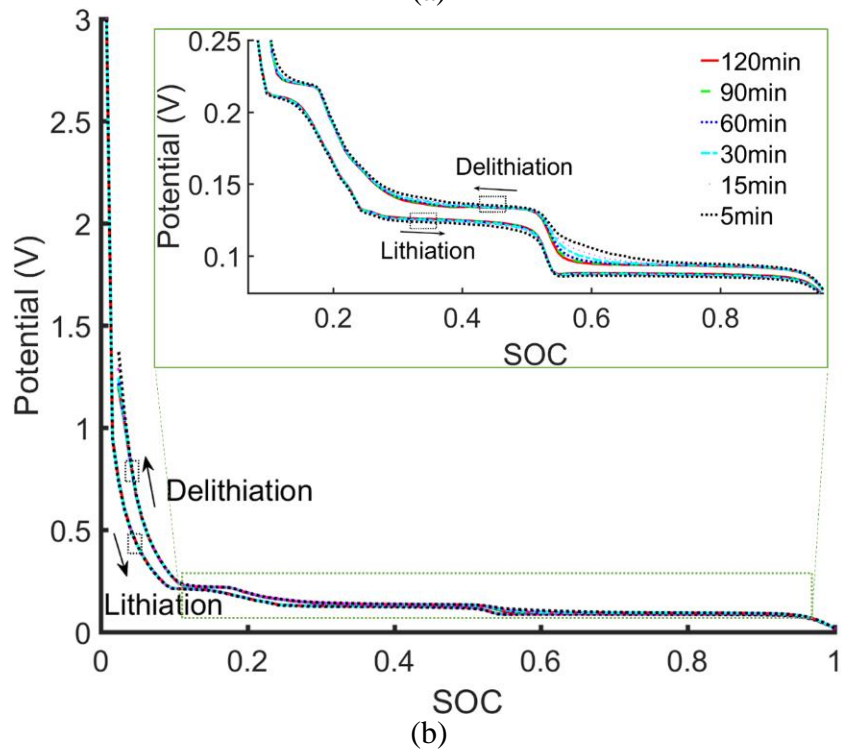
113 Figure 2(a) shows the lithiation and delithiation voltages, with respect to time, recorded using
 114 GITT. After removing the external current (at the end of the pulse) the voltage profile relaxes
 115 to an equilibrium potential (OCP). This is due to the lithium concentration at the surface of the

116 active material equalising to the bulk concentration of the material during relaxation. For a
117 lithiation step, this phenomena of lithium diffusion during relaxation, leads to higher cell
118 voltage at the end of relaxation compared to the potential at the end of current pulse (red line
119 in inset of Fig 2(a)). During the delithiation, lithium concentration at the surface will be lower
120 than the bulk of the electrode particle because lithium consumption at the surface take place at
121 a faster rate as compared to lithium diffusion from the inner matrix [21]. Therefore, after
122 removing the current pulse, lithium diffuses from the centre to the surface and leads to lower
123 cell voltages after relaxation compared to the voltage at the end of pulse (green line in inset of
124 Fig 2(a)).

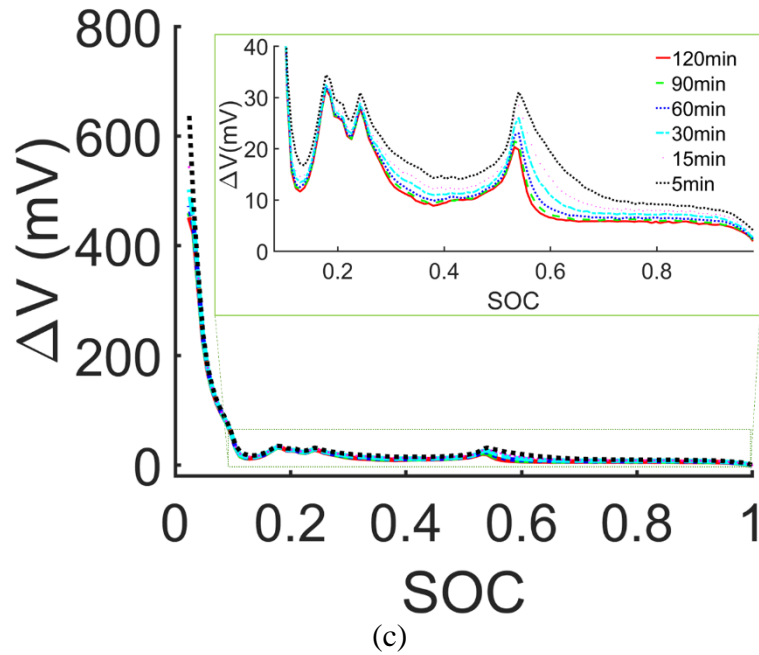
125 Figure 2(b) shows the Li-Graphite cell potential at different SOC's during the lithiation and
126 delithiation at 5, 15, 30, 60, 90 and 120 min. of the relaxations. The GITT test has been
127 conducted with 120 min. relaxation durations and the intermediate relaxation times have been
128 used to analyze the rate of change in voltage at different SOC's. The potential vs. SOC plot in
129 Fig. 2(b) shows the different voltage plateaus for the graphite in lithiation and delithiation. As
130 can be seen in the inset of the Fig. 2(b), the voltage during lithiation and delithiation (for all
131 relaxation intervals) are not overlaying and shows the voltage change at every SOC for the
132 voltages recorded at 5, 15, 30, 60, 90 including 120 min. relaxations. The inset of Fig. 2(b)
133 shows that the change in voltage with longer relaxation during lithiation is insignificant for the
134 entire SOC range while considerable change during delithiation is observed especially between
135 0.53-0.75 SOC.



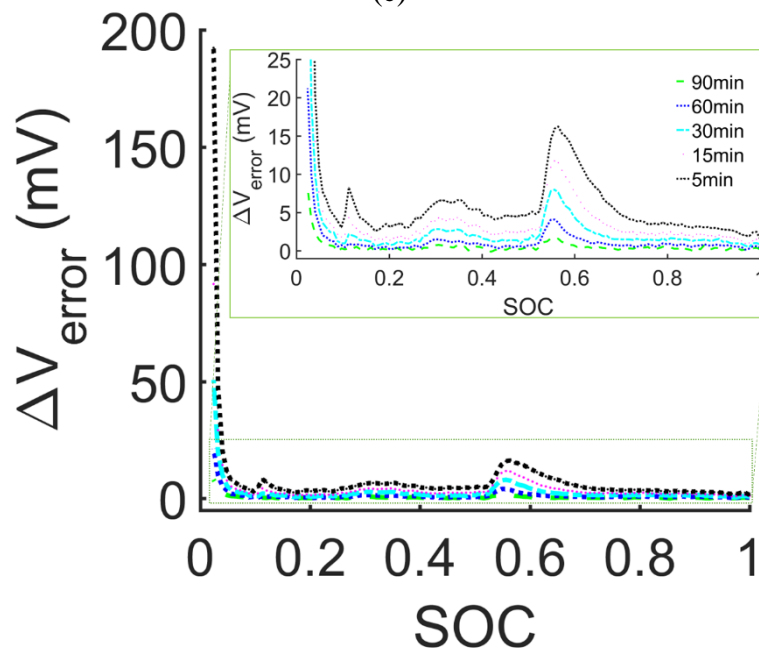
(a)



(b)



(c)



(d)

136 Figure 2: (a) Cell potential vs. time for lithiation and delithiation during GITT test, (b)
 137 Equilibrium potentials at various SOC during lithiation and delithiation, (c) Hysteresis (ΔV)
 138 between lithiation and delithiation OCPs with an enlarged view in the inset and (d) Error in
 139 voltage hysteresis (ΔV_{error}) with shorter relaxation duration with respect to the 120 min.
 140 relaxation and the inset in all subplots shows the zoomed view of the same for the visual
 141 clarity.

142 To analyze the rate of voltage change, the difference between delithiation and lithiation
 143 voltages over relaxation time with respect to the SOC has been plotted in Fig. 2(c). The highest
 144 voltage difference (ΔV) (ΔV is termed as hysteresis for 120 min relaxation) is observed at 0.02

145 SOC, ranging from 643-451 mV for 5-120 min. relaxations as listed in Table 1. The ΔV shows
 146 a decreasing trend as rest duration increases. At 0.02 SOC the ΔV between 5-15 min. is ~101
 147 mV and ~92 mV for the subsequent 15-120 min. A greater change in voltage with time
 148 indicates that, at low SOC, small changes in lithium concentration lead to a significant change
 149 in voltage during lithiation and delithiation. The voltage hysteresis steeply decreases between
 150 0.02-0.1 SOC and less than 35 mV (inset of Fig. 2(c)) is observed between 0.1-1 SOC. This
 151 inset also shows that at 0.18, 0.25 and 0.53 SOC which have ΔV of ~34, ~31 and ~28 mV for
 152 5 min. relaxation (listed in Table 1). However, the ΔV between 0.3-0.5 and 0.6-1 SOC are
 153 below 15 mV (inset of the Fig. 2(c)) which correspond to the OCP hysteresis of the graphite
 154 between these SOC.

155 Table 1: Voltage difference (ΔV) for the various stages of relaxation of graphite electrode
 156 correspond to peaks shown in Fig 2(c).

Rest (min.)↓	ΔV (mV)			
	SOC = 0.02	SOC = 0.18	SOC = 0.24	SOC = 0.53
5	643.72	34.38	30.92	27.96
15	542.97	33.24	29.42	25.96
30	502.05	32.41	28.79	24.50
60	472.67	32.06	28.28	22.61
90	459.55	31.78	28.20	21.43
120	451.44	31.67	27.85	20.32

157
 158 The error in ΔV_{error} ($\Delta V_x - \Delta V_{120}$, where $x = 5, 15, 30, 60$ and 90 min.) has been analysed and
 159 plotted in the Fig. 2(d). The ΔV_{error} is high for low SOC (0.02-0.06) because of the large rate
 160 of change of voltage with lithium concentration. At 0.02 SOC ΔV_{error} is 8 mV at 90 min. which
 161 decreases with SOC to less than 1 mV above 0.06 SOC. Above 0.06 SOC ΔV_{error} is 4, 8, 12,
 162 16 mV for 60, 30, 15 and 5 min., respectively, as can be seen in inset of Fig. 2(d).

163 Finally, the total time required to conduct the GITT test has been analysed with various
 164 relaxation durations (Table 2). Overall 124 and 122 current pulses at C/20 have been employed

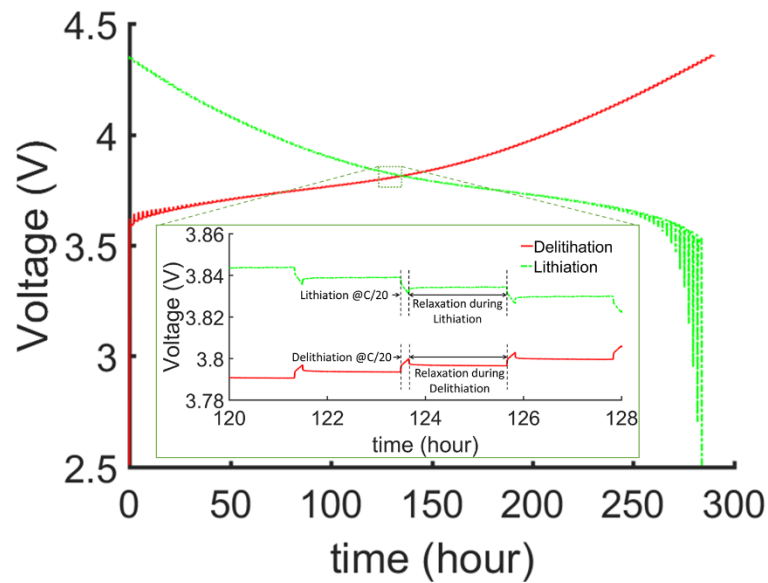
165 to completely lithiate and delithiate the Li-Graphite cell, respectively. The total time required
 166 to complete the cycle with a 5 min. relaxation is ~61.5 hrs. The ΔV_{error} for 5 min. rest is below
 167 16 mV at 0.1-1 SOC and with the full 120 min. relaxation the test taking 533 hrs. The
 168 corresponding values for 30 and 60 min. relaxation are 164 and 287 hrs. with a ΔV_{error} of 8 and
 169 4 mV, respectively. In summary, the selection of the relaxation duration for the OCP and
 170 hysteresis measurement can be reduced whilst retaining accuracy and also reducing the time
 171 required to obtain these parameters.

172 Table 2: Time required to conduct the GITT test with various relaxation durations for Li-
 173 Graphite cells.

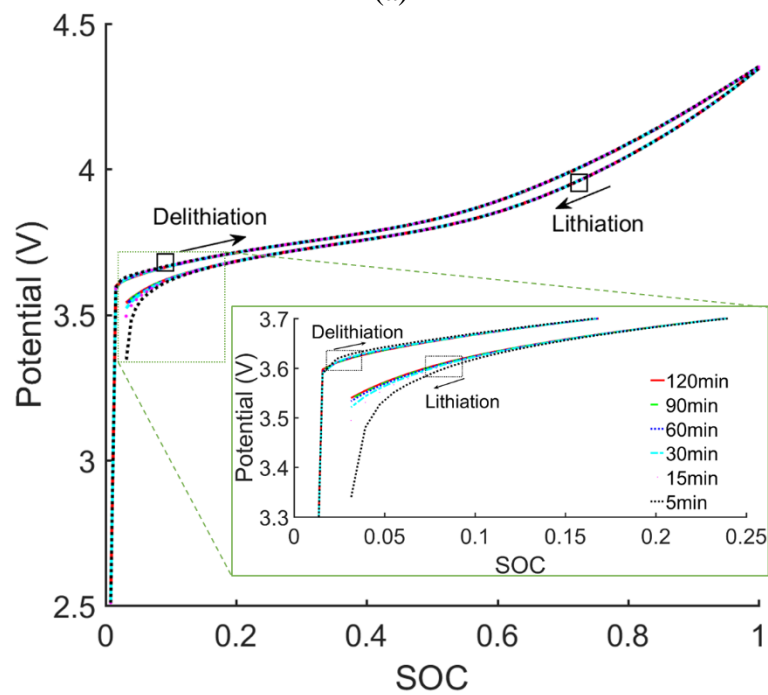
With relaxation of (min.)	5	15	30	60	90	120
Total Lithiation Relaxation time (Hrs.)	10.3	31.0	62.0	124.0	186.0	248.0
Total Lithiation Pulse time (Hrs.)	20.7	20.7	20.7	20.7	20.7	20.7
Total Lithiation time (Hrs.)	31.0	51.7	82.7	144.7	206.7	268.7
Total Delithiation Relaxation time (Hrs.)	10.2	30.5	61.0	122.0	183.0	244.0
Total Delithiation Pulse time (Hrs.)	20.3	20.3	20.3	20.3	20.3	20.3
Total Delithiation time (Hrs.)	30.5	50.8	81.3	142.3	203.3	264.3
Total Cycle time (Hrs.)	61.5	102.5	164.0	287.0	410.0	533.0
Max. ΔV_{error} (mV) above 0.1 SOC	16	12	8	4	1	0

174 3.2 NMC voltage relaxation investigation

175 Figure 3(a) shows the delithiation and lithiation voltages with respect to time for Li-NMC
 176 between 4.35-2.5V. With delithiation the cell voltage increases and during relaxation the cell
 177 voltage decreases caused by gradient relaxation after turning off the current pulse (red line in
 178 inset of Fig 3(a)). This process was repeated until the cell voltage reached the upper cut-off
 179 which was accomplished in 127 intermittent current pulses. During lithiation, the cell potential
 180 decreases with the application of current and during relaxation the cell potential increases due
 181 to concentration gradient relaxation (green line in inset of Fig 3(a)). The potential profiles
 182 shown in Fig. 3(a) have been further utilised in OCP, time to reach OCP and hysteresis
 183 quantification of the NMC electrode.



(a)



(b)

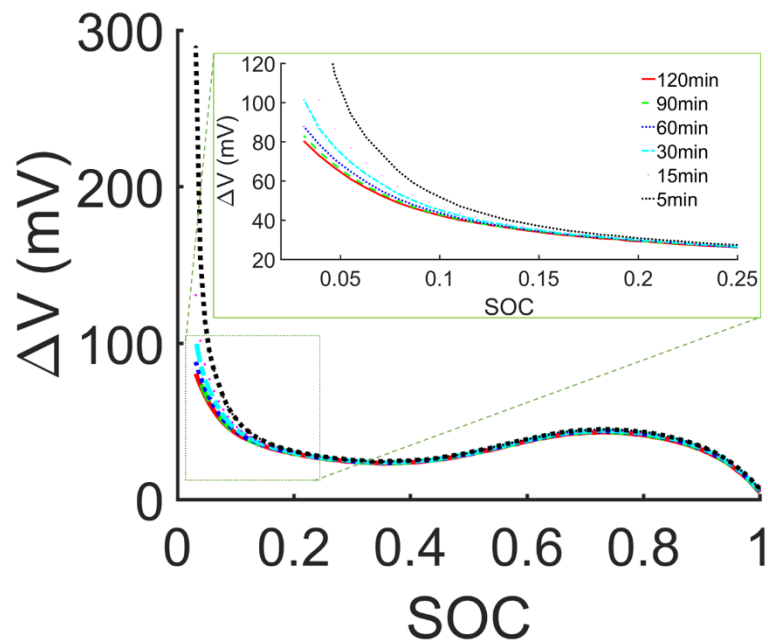
184 Figure 3: (a) Li-NMC Cell potential vs. time during lithiation and delithiation using GITT
 185 test which has been enlarged in the inset for the visual clarity (b) Equilibrium potentials
 186 (OCP) at various SOC during lithiation and delithiation of Li-NMC cells and inset shows
 187 magnified view of the voltages at different relaxation stages.

188 The relaxation potentials after every current pulse during delithiation and lithiation of the Li-
 189 NMC cells have been extracted at 5, 15, 30, 60, 90 and 120 min. of rest and plotted in Fig 3(b)
 190 with respect to SOC. At all SOC different voltages during lithiation and delithiation are
 191 observed at all relaxation durations, illustrating the different rates of change in voltage for
 192 NMC when charging or discharging. Similar behaviour for NMC has been reported in Lu *et al.*

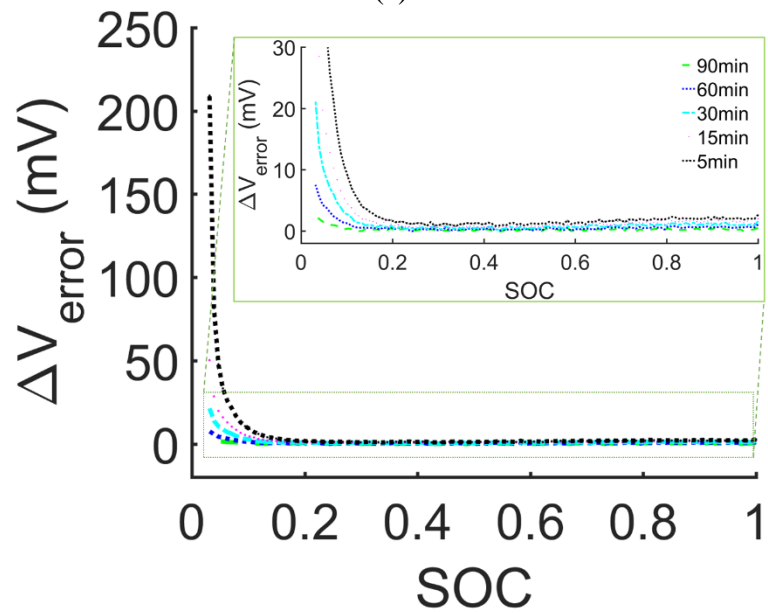
193 [22] who showed the voltage gap between lithiation and delithiation varies with SOC.
194 Furthermore, the potential profile at different relaxation stages (of lithiation and delithiation)
195 are overlapping which shows very fast gradient relaxation in the NMC solid matrix for 0.1-1
196 SOC (Fig. 3(b)). However, below 0.1 SOC the lithiation of the NMC shows a considerable
197 change in potential with relaxation time especially below 30 min. rest (inset of the Fig. 3(b))
198 due to the slower solid phase lithium diffusivity in NMC at low SOC. In contrast, the voltage
199 (Fig. 3(b)) at different stages of the relaxation during delithiation has insignificant change for
200 entire range of SOC

201 The voltage difference from OCP (ΔV) over time between lithiation and delithiation for each
202 SOC of the Li-NMC cell has been analysed and is shown in Fig. 4(a) for 5, 15, 30, 60, 90 and
203 120 min. of relaxation. As can be seen in the plot that the ΔV at 0.03 SOC are 290, 130, 101,
204 88, 83 and 80 mV with increasing relaxation durations, respectively. This analysis shows a
205 large change (189 mV) in ΔV during the 5-30 min. of the relaxation compared to the successive
206 90 min. (21 mV) (see the inset of the Fig 4(a)) due to the high rate of change of voltage in the
207 0-0.1 SOC range. With rise in SOC the ΔV decreases and dropped to 25-23 mV for 5-120 min.
208 of the relaxation time at 0.35 SOC. The further increase in the SOC leads to further rise in the
209 ΔV can be seen in Fig 4(a). Above 0.73 SOC, the ΔV decreases with the lowest ΔV of 7-4.5
210 mV for 5-120 min. relaxation at the full SOC of the NMC electrode.

211 The ΔV_{error} for selecting shorter relaxation (5, 15, 30, 60 and 90 min.) with respect to the 120
212 min. rest has been computed and shown in Fig. 4(b). Highest ΔV_{error} are 210, 50, 21, 8 and 3
213 mV, at 0.03 SOC for the corresponding stages of relaxation, respectively. As the SOC increases
214 the error drops down rapidly and above 0.1 SOC it stabilises below 0.3 and 0.4 mV for 60 and
215 90 min. rests, respectively. The ΔV_{error} above 0.2 SOC with the 5, 15 and 30 min. relaxations
216 are below 2, 1.5 and 1 mV, respectively (see the inset of Fig. 4(b)).



(a)



(b)

218 Figure 4: (a) ΔV between lithiation and delithiation OCPs at various stages of the relaxation
 219 (b) ΔV_{error} for the shorter relaxation with respect to the 120 min. relaxation of the Li-NMC
 220 cells. Both subplots have the zoomed view in the inset for the sake visual clarity.

221 Lastly the time span required to conduct the GITT test with these relaxation durations and
 222 corresponding percentage ΔV with respect to 120 min. relaxation have been analysed and listed
 223 in Table 3. The total time for lithiation and delithiation with a $C/20$ current pulse for 10 min.
 224 followed by 5 min. relaxation is 62.75 hrs. With elongated relaxation the cycle can be

225 completed in ~167, 293 and 544 hrs. for the 30, 60 and 120 min. rest durations, respectively.
 226 The test durations with 120 min. rest would be approximately nine times longer compared to 5
 227 min., however, the computed ΔV in case of 5 min. are 360, 104 and 125% of the 120 min. at
 228 0.03, 0.5 and 0.99 SOC, respectively. The tabulated data shows that the percentage ΔV drops
 229 with a faster rate in case of early 30 min. of the relaxation compared to the following 90 min.
 230 This analysis elucidate that further increasing the relaxation has only significant reduction in
 231 ΔV at low and high SOC (Fig 4(a)). In order to have (for example) 5% difference between
 232 observed and OPC voltage, the 10 initial and last pulses should have 30 min. relaxation, and
 233 intermediate pulses can have 5 min. relaxations which save 450 hrs. to conduct the GITT test
 234 for the Li-NMC cells.

235 Table 3: Time required to conduct the GITT test with various relaxation durations for Li-
 236 NMC cells.

With relaxation of (min.)	5	15	30	60	90	120	
Total Lithiation Relaxation time (Hrs.)	10.6	31.8	63.5	127.0	190.5	254.0	
Total Lithiation Pulse time (Hrs.)	21.2	21.2	21.2	21.2	21.2	21.2	
Total Lithiation time (Hrs.)	31.8	53.0	84.7	148.2	211.7	275.2	
Total Delithiation Relaxation time (Hrs.)	10.3	31.0	62.0	124.0	186.0	248.0	
Total Delithiation Pulse time (Hrs.)	20.7	20.7	20.7	20.7	20.7	20.7	
Total Delithiation time (Hrs.)	31.0	51.7	82.7	144.7	206.7	268.7	
Total Cycle time (Hrs.)	62.8	104.7	167.4	292.9	418.4	543.9	
Max. ΔV_{error} (mV) at 0.03 SOC	210	50	21	8	3	0	
Percentage ΔV (against 120 min.)	SOC=0.03	360	162	126	109	103	100
	0.25	105	102	102	101	100	100
	0.50	104	103	101	100	101	100
	0.75	104	103	102	101	100	100
	0.99	125	116	112	108	104	100

237 4. Conclusions

238 In this work, the OCP, rate of change in voltage, and voltage difference to OCP with respect to
 239 time (ΔV) of graphite and NMC electrodes has been investigated using in-house fabricated

240 half-cells. For this study, the GITT test has been conducted with a C/20 current pulse for 10
241 min. followed by 120 min. relaxation, and the voltage at different stages of the relaxation during
242 lithiation and delithiation have been analysed. The voltage change (ΔV) over time to
243 equilibrium (OCP) has been elucidated over the full SOC and voltage range for lithiation and
244 delithiation. ΔV is shown to vary with SOC with the highest in magnitude below 0.1 SOC, for
245 both Li-Graphite and Li-NMC, above 0.1 SOC, the hysteresis (ΔV) is limited to 35-33 and 45-
246 42 mV, for the relaxation of 5-120 min, respectively. Below 0.1 SOC, the ΔV_{error} with 5 min.
247 relaxation is high, i.e., up to 200 mV for both cells. However, above 0.1 SOC this ΔV_{error} is
248 approx. 16 mV and 7 mV for Li-Graphite and 1.5 mV and 0.5 mV for the Li-NMC cells, with
249 5 and 30 min. rest, respectively. The total experimental time required for the GITT test with 30
250 and 120 min. relaxations are ~ 2.7 and ~ 8.7 times longer compared to 5 min. relaxation for both
251 the cells. In summary, the OCP and ΔV of the Li-Graphite cell are more sensitive to the
252 relaxation duration compared to the Li-NMC cells. In order to have a desired accuracy with
253 reduced experimental duration for OCP and hysteresis measurement a variable rest duration is
254 highly recommended with longer relaxation during the fast rate of change in voltage and shorter
255 rest time in the voltage plateaus. The recommended relaxation for the Graphite and NMC
256 electrodes are 30 min. and 5 min., respectively, beyond the 0.1 SOC. However, below 0.1 SOC
257 at least 90 min. relaxation is appropriate to attain the accuracy (ΔV_{error}) of ~ 5 mV for both of
258 the electrodes.

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