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# Influence of charge status on the stress safety properties of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cells

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## ABSTRACT

In order to improve the safety management, the stress changes of  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  (NMC) cells are real-time monitored using non-destructive strain gauges, and the effects of gauge substrate, temperature and state-of-charge (SOC) have been investigated. The shell exhibits elastic deformation behaviour, and the strain-stress relationship is established. As the temperature increases from 25 to 80 °C, the stress of the NMC cells increases from 0 to 275 MPa, especially greatly at 70 °C and sharply at 80 °C after 18 h. The stress increases from 0 to 9.2 MPa when the potential increases from 2.8 to 4.3 V. However, the value rises from 10 to 55 MPa when the voltage increases from 4.6 to 5.0 V during overcharge process; while an obvious increase of stress appears when the cut-off voltage is below 0.6 V during over-discharge tests. The facile method is significant for the non-destructive inspection and emergency management of batteries.

**Keywords:** Mechanical analysis; Real-time monitoring;  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ ; State of charge; Temperature effects

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## 20 1. Introduction

21 Continuous environmental deterioration and traditional fossil fuel resource depletion make (hybrid)  
22 electric vehicles highly attractive for city transport. As one of their key power sources, lithium-ion  
23 batteries have gained tremendous attentions because of their unique advantages such as high energy  
24 density, low weight and high environmental compatibility. However, the safety issues, especially  
25 swelling, leakage, burning and explosion, restrict their sustainable and fast development as well as  
26 large scale applications. Such typical hazards usually take place when the maximum inner stress is  
27 higher than the strength of the outer shell and could cause the severe damage on the whole battery.  
28 Therefore, it is vital and essential to monitor the stress changes and take precaution of the potential  
29 dangers for the safety management of batteries. A few methods have been reported to investigate  
30 the stress changes in batteries, with a focus on the stress of the microscale particles in the active  
31 materials <sup>1,2</sup> and the safety simulation of the shell of battery <sup>3,4</sup>. However, the typical safety issues  
32 are directly related to the macroscopic stress in a battery shell, which has not yet been carefully  
33 considered. Such macroscopic stress, including the stress of particles and other stresses, is highly  
34 complex as a result of the interaction between particles, thermal expansion, interaction between  
35 electrode and electrolyte, electrochemical reaction, and so on. Actually, a battery is a sealed can  
36 with a thin shell, of which the inner pressure can be tested via the outer surface. A mechanical strain  
37 gauge (or strain gage) is a useful device to accurately measure the pressure/stress via the small  
38 changes in electrical resistance of wire grids under strain. If the battery shell is under linear elastic  
39 deformation, the strains measured by the strain gauge on the shell surface without destruction can  
40 be used to determine the macroscopic stress of batteries according to the Hooke's law.

41 As one of the popular cathode materials with high mass density, NMC can meet the requirements of  
42 pulse power characteristics for transport applications in a small volume, but the safety problems

43 (especially large deformations and/or leakage due to abuse or elevated temperature) hamper its  
44 extensive applications <sup>5,6</sup>. Various studies of NMC have been reported, attempting to understand  
45 and solve these problems. For example, the thermal stability of charged NMC <sup>7</sup> and the gas  
46 generation of  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{NMC}$  cells at 80 °C <sup>8</sup> have been investigated. The production of heat and  
47 gas can cause runaway reactions and trigger explosion of batteries <sup>9</sup>, which will be very hazardous  
48 under abnormal operating conditions <sup>10</sup>. According to the production processes, such problems  
49 would result in the large deformations and then leakage of batteries. If the stresses that are closely  
50 related to the deformations of the battery surface can be monitored and corresponding measures can  
51 be taken in advance, the hazards like leakage, burning or explosion could be efficiently prevented.  
52 Therefore, it is necessary to monitor the macroscopic stress changes of NMC batteries in order to  
53 develop further measures for safe applications.

54 In this paper, strain gauges are adopted to real-time monitor the strains and stresses of  
55  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  lithium ion cells under various conditions. The reliability of the monitoring  
56 tests, along with the relationship between macroscopic mechanical stress and electrochemical  
57 performance, has been analysed. The reasons for such stress changes have also been discussed.

58

## 59 **2. Experimental**

### 60 **2.1. Synthesis of NMC**

61 Powders of  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$  and  $\text{LiOH}\cdot\text{H}_2\text{O}$  (molar ratio of 1:1.05) were fully mixed to form  
62 a rheological precursor using alcohol as the dispersing agent by a planetary ball milling at 180 rpm  
63 for 4 h. The milled precursor was preheated at 550 °C in air for 4 h in a muffle oven and further  
64 calcined at 750~850 °C in air for 12 h. The as-synthesized black product was ground for  
65 physicochemical characterization and stress tests.

## 66 **2.2. Physicochemical characterization**

67 In order to eliminate the unexpected influence of anode materials, common lithium cells composed  
68 of NMC and lithium metal are chosen for stresses and strains monitoring tests under different  
69 conditions. The as-synthesized powder sample for electrochemical characterization was well mixed  
70 with 10 wt.% of conductive additive of super P and 7 wt.% of commercial PVDF binder to form a  
71 homogeneous viscous slurry to coat a cleaned aluminium foil using a doctor blade. After being  
72 dried at 100 °C, the aluminium foils loaded with active materials were cut into 1.2 cm<sup>2</sup> wafers  
73 which were further dried at 100 °C under vacuum for 12 h before being used as the working  
74 electrodes. Using pure lithium metal as the counter and reference electrodes, CR2032 coin cells  
75 were assembled in an argon-filled glove box by sandwiching a Celgard 2300 microporous separator  
76 between the working electrode and lithium disc. The electrolyte was 1 M LiPF<sub>6</sub> in a mixture of  
77 ethyl carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 in vol.,  
78 Shenzhen Capchem Chemicals Co. Ltd., China).

79 Galvanostatic charge/discharge cycling tests of the above devices were carried out with different  
80 potential windows, current rates and working temperatures on a Neware battery-testing instrument  
81 (Shenzhen Neware Technology Ltd., China). Electrochemical Impedance Spectroscopy (EIS)  
82 measurements were conducted before and after stress tests under different conditions in the  
83 frequency range from 100 kHz to 0.01 Hz with a sinusoidal excitation voltage of 10 mV, and the  
84 impedance curves were fitted using Zsimpwin and Zview softwares. Cyclic voltammetry (CV)  
85 technique was used in the voltage window of 2.8 ~ 4.3 V to investigate the electrode reaction  
86 process after different cycles. Both EIS and CV tests were carried out on an electrochemical  
87 workstation consisting of a PAR 273A potentiostat/galvanostat and a signal recovery model 5210  
88 lock-in-amplifier controlled by a Powersuit software (Princeton Applied Research, USA).

89 In order to compare the changes of phase composition and structure of NMC electrodes under  
90 different states, X-ray diffraction (XRD) tests were carried out using Cu-K $\alpha$  radiation in the range  
91 from 10 to 70 ° at a scanning rate of 0.04 ° s<sup>-1</sup> on a Philips X'Pert pro MPD machine.

### 92 **2.3. Measurement of cell strains**

93 The testing cell is a sealed container composed of 304 stainless steel (SS), so resistance strain  
94 gauges for metals (Zhonghang Electronic Measuring Instruments Co. Ltd., China) were chosen for  
95 measuring the strains and consequently evaluating the stresses in lithium cells under different  
96 conditions. The gauge has a size 0.3×1.8 mm and a maximum strain range of 2%. The accuracy and  
97 the resistance are about 1  $\mu\epsilon$  and 120 Ohm, respectively. The strain gauge consists of a grid of wire  
98 filament on an insulated rear side which supports a metallic foil pattern. To allow the strains to be  
99 transferred from the test specimen to the foil through the adhesive and strain gauge, the strain gauge  
100 needs to be properly mounted onto the shell surface. The cathode shell was firstly polished with  
101 sandpaper, and cleaned by ethanol. Glue was pasted on the dried clean surface for adhering the  
102 strain gauge. After being well adhered to the cathode shell surface, the gauge was connected to a  
103 stress-strain testing system (Donghua testing technology Co. LTD, China). At the same time, the  
104 cell was connected to the electrochemical testing system to evaluate the relationship between strains  
105 and electrochemical performance of NMC cells under different operating conditions, and the  
106 principle diagram and images of the testing systems are shown in Fig. 1.

107

## 108 **3. Results and discussion**

### 109 **3.1. Influence of strain gauge installation on the electrochemical performance**

110 In order to evaluate the influence of strain gauge installation on the electrochemical performance of  
111 the lithium cells, galvanostatic charge/discharge tests before and after installing strain gauge were

112 carried out at 25 °C, and the typical curves are compared in Fig. 2. After installing the strain gauge,  
113 the galvanostatic charge/discharge curves from 2.8 to 4.3 V at 1.0 C current rate are coincidence  
114 under the same testing conditions, indicating that the installation of strain gauge has a negligible  
115 effect on the electrochemical performance of NMC cells. Therefore, such non-destructive method  
116 can reflect the stress changes of lithium ion cells without altering their performance.

117

### 118 ***3.2. Temperature correction and deformation analysis of the cells***

119 Because the most desirable strain gauge materials are sensitive to temperature variations, resistance  
120 wires of the strain gauge will deform when the surrounding temperature is changed, which will  
121 result in resistance change and produce test inaccuracies and even errors. Due to the low thermal  
122 expansion coefficient<sup>11</sup>, the quartz glass was chosen to characterize the test accuracy, and the  
123 measured strain data will be calibrated to authentically reflect the safety properties of the battery  
124 materials and combined electrolyte system. The strain changes could be caused by the active  
125 material decomposition or volume changes of electrolyte, and/or the expansion of the cell case and  
126 related accessories. In order to obtain the strain changes from the NMC electrode material, two  
127 types of lithium ion cells were assembled under the same conditions, *i.e.* one is a normal cell  
128 (abbreviate C) with active material and electrolyte, and the other is a reference cell (abbreviate R)  
129 which is same as the normal cell but with no active material. These test specimens were heated to  
130 the evaluated temperatures and kept for a period before being naturally cooled down by air. As the  
131 temperature increases from 25 to 50 °C, the strain changes of the normal cell, reference cell, and  
132 quartz glass are compared in Fig. 3(a). The strain values of the quartz glass decrease quickly to -580  
133  $\mu\epsilon$  in less than 1 h, while that of the reference cell decrease slowly to -120  $\mu\epsilon$  in about 2 h. However,  
134 the strain value reaches more slowly +100  $\mu\epsilon$  in 5 h when NMC electrode is added. Noticeably, the

135 strain values of the quartz glass and the reference cell decrease very quickly in a short time before  
136 reaching a stable state. However, the strain values of the normal cell increase and reach a constant  
137 state much more slowly. The same strain gauges were used and the tests were carried out under the  
138 same environmental conditions, so the strain difference is from the substrates. The substrates with  
139 larger deformation than that of the resistance wires will cause the negative strain (compression),  
140 while the deformation of the substrates lower than that of the resistance wires will cause the positive  
141 strain (tension). If the substrates change little, the compression and tension of resistance wires will  
142 produce negative strain and positive strain, respectively. The normal cell has the highest  
143 deformation, and the deformation of the reference cell is much higher than that of quartz glass. The  
144 quartz glass has a negligible deformation at 50 °C, so the maximum negative strain is from the  
145 compression of resistance wires, and the as-obtained strain values reflect the changes of strain  
146 gauge itself. As the substrate changes from quartz glass to the SS shell of reference cell, the strain  
147 values increase greatly under the same conditions, indicating that the deformation of the SS  
148 substrate increase to make the compression of resistance wires weak. The strain values change from  
149 negative to positive and reach maximum when NMC electrode is added to the reference cell,  
150 indicating that electrode causes the increase of substrate deformation to change the resistance wires  
151 from compression to tension. Therefore, the test strain values are the combination from both the  
152 strain gauge and test specimens, and the substrate deformation from the swelling of SS shell causes  
153 the increase of strain values. As for the cells at open-circuit states, the normal cell has much higher  
154 strain values than that of the reference cell under the same conditions, indicating the higher  
155 deformations of the normal cell is due to the NMC electrode. The quartz glass reflects the  
156 temperature effect of the strain gauge, so all the strain values used for calculating stresses will be  
157 corrected by eliminating the temperature effect of the strain gauge.

158 In order to determine the stresses from the measured strains, the stress-strain relationship of cathode  
 159 shell needs to be determined. The deformations of the SS cathode shell and quartz glass were  
 160 further tested within a wide temperature range of 25 ~ 80 °C. The strain values obtained from the  
 161 tests during the increasing/decreasing processes of temperature are summarized in Fig. 3(b).  
 162 Apparently the strain values can be recovered to 0 when the temperature decreases from 80 to 25 °C,  
 163 indicating only elastic deformation occurs, thus elastic theory can be used for calculating the  
 164 stresses using the measured strains, as discussed in the next section.

165

### 166 **3.3. Strain-stress relationship of lithium cells**

167 The radius (R) and thickness (t) of the SS cathode shell of the cells are 10 mm and 0.15 mm,  
 168 respectively. Thus the ratio of t/R is 0.015/10 which is much smaller than 0.1, and the cathode shell  
 169 can be regarded as a thin-walled plate. As aforementioned the cathode shell of the cells exhibits  
 170 small elastic deformation during the testing processes. If the distribution of the stresses  $P_z$  along the  
 171 longitudinal direction of the cathode shell is assumed to be uniform, a rigorous relationship between  
 172 the  $P_z$  and the stresses can be found using the elastic theory for shells as follows.

173 The construction of the cell is illustrated in Fig. 4(a), and the cathode shell laminate is cut off by  
 174 two cylinders and two radial transverse sections to produce a small element, as shown in Fig. 4(a-1)  
 175 and (a-2). The radius of the two cylinders are  $r$  and  $r + dr$ , respectively. The angle between the  
 176 two transverse sections is  $d\theta$ . From Fig. 4(a-3) and (a-4), axial bending moment and transverse  
 177 shear stress on the two cylinders are  $M_r$ ,  $M_r + (dM_r / dr) dr$  and  $Q_r$ ,  $Q_r + \left(\frac{dQ_r}{dr}\right) dr$ , respectively.  
 178 Circumferential bending moment on the two cylindrical surfaces is both  $M_\theta$ . External stress on two  
 179 cylindrical surfaces is  $P_z$ .

180 According to the moment equilibrium of the element, algebraic sum of all internal moments and

181 external moments on the tangent line of cylinders is 0:

$$182 \left( M_r + \frac{dM_r}{dr} \right) (r + dr) d\theta - M_r r d\theta - 2M_\theta dr \sin \frac{d\theta}{2} + Q_r r d\theta dr + P_z r d\theta dr \frac{dr}{2} = 0 \quad (1)$$

183 with  $\sin \frac{d\theta}{2} \approx \frac{d\theta}{2}$  when  $\theta$  is small. Ignoring the second-order terms, this becomes

$$184 M_r + \frac{dM_r}{dr} r - M_\theta + Q_r r = 0 \quad (2)$$

185 The deformation of mid-plane caused by the uniform pressure is axially symmetrical. Therefore, the  
186 deformation,  $w$ , only depends on the radius  $r$ . As shown in the Fig. 4(b),  $AB$  is a line on the  
187 radial section whose vertical distance to mid-plane is  $z$ . The radius of A and B are  $r$  and  $r + dr$ ,  
188 respectively, so  $AB = dr$ . The lines of  $mn$  and  $m_1n_1$  pass through the points of A and B,  
189 respectively. Both lines are vertical to the mid-plane. When the cathode laminate deforms, A and B  
190 move to  $A_1$  and  $B_1$ , respectively. Therefore, the strains are

$$191 \varepsilon_r = \frac{z(\varphi + d\varphi) - z\varphi}{dr} = z \frac{d\varphi}{dr} \quad (3a)$$

$$192 \varepsilon_\theta = \frac{2\pi(r + z\varphi) - 2\pi r}{2\pi r} = z \frac{\varphi}{r} \quad (3b)$$

193 Under small deformation,  $\varphi = -\frac{dw}{dr}$ , Equations (3) and (4) are rewritten as

$$194 \varepsilon_r = -z \times \frac{d^2 w}{dr^2} \quad (4a)$$

$$195 \varepsilon_\theta = -\frac{z}{r} \times \frac{dw}{dr} \quad (4b)$$

196 By Kirchhoff-love assumption every point in the laminate is under the two-direction stress state  
197 when the cathode laminate deforms. According to the generalized Hooke's law, the physical  
198 equations of the cathode laminate are:

$$199 \sigma_r = \frac{E}{1 - \mu^2} (\varepsilon_r + \mu \varepsilon_\theta) \quad (5a)$$

$$200 \sigma_\theta = \frac{E}{1 - \mu^2} (\varepsilon_\theta + \mu \varepsilon_r) \quad (5b)$$

201 Combining above equations and substituting (4) into (5), the stresses can be written as:

$$202 \quad \sigma_{\theta} = -\frac{Ez}{1-\mu^2} \left( \frac{1}{r} \frac{dw}{dr} + \mu \frac{d^2w}{dr^2} \right) \quad (6a)$$

$$203 \quad \sigma_r = -\frac{Ez}{1-\mu^2} \left( \frac{\mu}{r} \frac{dw}{dr} + \frac{d^2w}{dr^2} \right) \quad (6b)$$

204 After integration, the bending moment can be obtained:

$$205 \quad M_r = \int_{-\frac{t}{2}}^{\frac{t}{2}} \sigma_r z dz = -D \left( \frac{d^2w}{dr^2} + \frac{\mu}{r} \frac{dw}{dr} \right) \quad (7a)$$

$$206 \quad M_{\theta} = \int_{-\frac{t}{2}}^{\frac{t}{2}} \sigma_{\theta} z dz = -D \left( \mu \frac{d^2w}{dr^2} + \frac{1}{r} \frac{dw}{dr} \right) \quad (7b)$$

$$207 \quad \text{where } D = \frac{Et^3}{12(1-\mu^2)}.$$

208 Substituting (7(a)(b)) into (1) and with some arrangements, the following equation can be obtained.

$$209 \quad \frac{d}{dr} \left[ \frac{1}{r} \frac{d}{dr} \left( r \frac{dw}{dr} \right) \right] = \frac{Q_r}{D} \quad (8)$$

210 The distribution of the transverse load is assumed to be uniform. As shown in the Fig. 4(c), the

211 shearing force on the cross section of the cylinder whose radius is  $r$  is as follows:

$$212 \quad Q_r = \frac{\pi r^2 p}{2\pi r} = \frac{pr}{2} \quad (9)$$

213 Substituting (9) into (8) we have

$$214 \quad \frac{d}{dr} \left[ \frac{1}{r} \frac{d}{dr} \left( r \frac{dw}{dr} \right) \right] = \frac{pr}{2D} \quad (10)$$

215 After integrations, the bending deformation of the mid-plane is:

$$216 \quad w = \frac{pr^4}{64D} + \frac{C_1 r^2}{4} + C_2 \ln r + C_3 \quad (11)$$

217 where,  $C_1, C_2, C_3$  are the constants to be determined. Since the deformation and slope of the

218 laminate are limited values,  $C_2=0$ . The rim of the cathode laminate is assumed to be clamped, so

$$219 \quad r=R, \quad \frac{dw}{dr} = 0, \quad \text{and} \quad w = 0$$

220 Finally the deformation is calculated as:

$$221 \quad w = \frac{P}{64D} (R^2 - r^2)^2 \quad (12)$$

222 Substituting (12) into (11) gives:

$$223 \quad M_r = \frac{P}{16} [R^2(1 + \mu) - r^2(3 + \mu)] \quad (13a)$$

$$224 \quad M_\theta = \frac{P}{16} [R^2(1 + \mu) - r^2(1 + 3\mu)] \quad (13b)$$

225 So the stresses are:

$$226 \quad \sigma_r = \frac{M_r}{t^2/6} = \frac{3P}{8t^2} [R^2(1 + \mu) - r^2(3 + \mu)] \quad (14a)$$

$$227 \quad \sigma_\theta = \frac{M_\theta}{t^2/6} = \frac{3P}{8t^2} [R^2(1 + \mu) - r^2(1 + 3\mu)] \quad (14b)$$

228 The stresses at the centre of the cathode laminate (*i.e.*  $r=0$ ) are found to be:

$$229 \quad \sigma_r = \sigma_\theta = \frac{E}{1 - \mu} \varepsilon_\theta \quad (15)$$

230 The material of the cell shell is 304 stainless steel which has a Young's modulus  $E$  of =193 GPa and  
 231 a Poisson's ratio  $\mu$  of 0.28 at 25 °C<sup>12</sup>. Therefore, the stress at the centre of the cell shell can be  
 232 calculated using the measured strain according to Eq. 15. From Eq. 14(a)(b), the maximum stress is  
 233 at the centre of the cell plate, and the stress distribution along the radius across the whole surface of  
 234 the cell is supplied in Fig. 4(d), which is of most interest for evaluating the safety issues of the cell.  
 235 The normalized stress and normalized radius are obtained by dividing the maximum stress and  
 236 maximum radius, respectively. The stresses along the axial direction and radial direction decrease  
 237 differently with the increase of radius, which is significant to analyse the stress distribution and the  
 238 possible failure position of the cell surface.

239

#### 240 **3.4. Influence of ambient temperature on the stresses in cells**

241 Since both the strain gauge and the specimen are sensitive to ambient temperature, the strain gauges  
242 are designed to minimize the sensitivity to temperature by compensating the thermal expansion of  
243 the specimen materials. In order to eliminate the influence of electrochemical activation on the  
244 stresses, the cells were galvanostatically charged/discharged for 10 cycles and discharged to 2.8 V  
245 to reach a stable state. The cycled and stable cells were kept for over 20 h in an oven with various  
246 temperatures to evaluate the effects of ambient temperature on the stresses of the electrode. Under a  
247 series of ambient temperature (i.e. 25, 50, 60, 70, 80 °C) the stress changes of the normal cells and  
248 the reference cells at the same charge states were monitored, and the testing results are shown in Fig.  
249 5. The stable stress values of the normal cell C and the reference cell R are almost zero and have no  
250 change at 25 °C. However, the values of C and R respectively increase gradually to 125 MPa and 95  
251 MPa when the ambient temperature reaches 50 °C. The values of C and R respectively increase  
252 quickly to 126 MPa and 113 MPa when the temperature further increases to 60 °C. The values of C  
253 and R respectively increase to 175 MPa and 162 MPa when the temperature further increases to  
254 70 °C. As the temperature further increases to 80 °C, the stress values of the normal cell C increase  
255 quickly and continuously above 200 MPa, and have a jump above 240 MPa when the heating period  
256 is 18 h, while that of the reference cell R have an abrupt increase and reach a stable value of 170  
257 MPa gradually. Under the same conditions, the stresses of the normal cells are always higher than  
258 that of the reference cells, and higher temperature results in higher stress values. Comparing the  
259 stress values of the cells under the same conditions, the higher stress values of the normal cells are  
260 from the NMC electrode.

261 No obvious signal for Mn, Ni, and Co is detected in the electrolyte when the charged  
262  $\text{Li}_{1.1}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3})_{0.9}\text{O}_2$  cell is stored in a 55 °C oven for 3 weeks<sup>6</sup>, and the amounts of Ni, Co,  
263 and Mn dissolved in the electrolyte are respectively 48.0, 50.5, and 42.4 ppm when

264 Li[Mn<sub>1/3</sub>Ni<sub>1/3</sub>Co<sub>1/3</sub>]O<sub>2</sub> electrode is immersed in the electrolyte at 55 °C for 10 days<sup>13</sup>. Correlating  
265 this information with the stress changes of the normal cells and reference cells, the stress is mainly  
266 caused by the thermal expansion of cell case in the temperature range of 50 ~ 60 °C, and the extra  
267 stress values of the normal cells are contributed from the volume expansion of the NMC electrode,  
268 including active material, conductive additive and binder. Though the stable stress values of the  
269 normal cell at 60 °C is close to that at 50 °C, the stress values at 60 °C increases much faster than  
270 that at 50 °C, indicating that the volume expansion of the NMC electrode reaches a maximum state  
271 at different rates within the temperature range and a higher temperature enhances the increasing rate  
272 of the stress. The stress values of the reference cells at 70 °C are similar to that at 80 °C, indicating  
273 the thermal stress of the SS cell case reach a maximum state when the temperature is 70 °C, and  
274 quickly becomes stable when the temperature is 80 °C. LiPF<sub>6</sub> can be resolved into PF<sub>5</sub> at 70 °C, and  
275 PF<sub>5</sub> will react with the solvents of EC and DMC at 85 °C<sup>14</sup>. Therefore, the extra increment of the  
276 stress values of the normal cells is mainly from the decomposition of LiPF<sub>6</sub> when the temperature  
277 increases to 70 °C, and the much more increment is mainly from the reaction of the decomposition  
278 product of PF<sub>5</sub> with the solvents in the electrolyte at 80 °C. The produced gases in the normal cells  
279 will produce continuously increasing stress with the prolonging of the heating time at 80 °C.

280

### 281 **3.5. Stress changes during cycles**

282 In order to investigate the stress changes during galvanostatic charge/discharge cycles at low current  
283 density, the stresses of the fresh cells were real-time monitored at 25 °C. The stress curves  
284 corresponding to the charge/discharge curves at 0.5 C rate between 2.8 V and 4.3 V are shown in  
285 Fig. 6. During the charge process of NMC material, lithium ions are continually extracted from the  
286 structure and the decrease of lithium ions result in the increase of the reduced ions of Ni, Co and

287 Mn in oxidation state to keep charge balance, so the lattice constants of  $a$  and  $c$  change in the  
288  $\alpha$ -NaFeO<sub>2</sub> layered crystal structure. The  $a$  decreases whilst the  $c$  increases due to an increasing  
289 electrostatic repulsion<sup>15</sup>. These changes of the parameters of  $a$  and  $c$  produce microscale stress  
290 between particles, which further develop to the macroscale stress monitored by the strain gauge.  
291 From the curves, such stress increases at different rates during a charge/discharge cycle. At the  
292 beginning of the charge process, the potential increases quickly from 2.8 V to 3.6 V, while the  
293 corresponding stress increases gradually from 0.0 to 0.3 MPa. At the potential platform from 3.6 to  
294 3.8 V, the stress value increases from 0.3 MPa to 4.6 MPa, indicating lithium ions extraction causes  
295 the change in lattice volume of the crystal in the single phase region of electrode material<sup>16</sup>, which  
296 results in the increase of stress. When the potential is increased from 3.8 V to 4.3 V, the stress  
297 increases quickly to the maximum value of 9.2 MPa at the highest potential, along with the large  
298 volume changes from the high electrostatic repulsion. Therefore, the stress value of the cell is  
299 closely related to the charge state of the cells, which has also been reported in<sup>17</sup>. The stress  
300 increases with the potential within the testing window, and both stress and potential reach maximum  
301 values simultaneously at the end of charge process, indicating the increased stress is caused by the  
302 volume changes of the NMC electrode into which lithium ions are inserted. During the discharge  
303 process, the stress decreases differently with the decrease of potential. During initially discharge,  
304 from 4.3 V to 3.8V, the stress decreases rapidly to 3.9 MPa, followed by a gradual relaxation as  
305 more lithium ions are inserted. At the discharge platform from 3.8 V to 3.6 V, the stress value  
306 decreases from 3.9 MPa to 1.1 MPa. However, the stress value is 0.5 MPa, not initial 0, when the  
307 potential restore to 2.8 V, indicating there is a residual stress during the charge/discharge cycle,  
308 which is similar to the irreversible increase in stack stress to permanent volumetric expansion of  
309 graphite anode<sup>18</sup>. Such residual stress will accumulate and lead to the unrecoverable deformation of

310 the cell during cycles, which could evolve into safety problems like swelling or bulging.

311 In order to investigate the relationship between the capacity fade and residual stress at high current  
312 density, the normalized capacities and corresponding residual stress values of the cell during 100  
313 cycles between 2.8 V and 4.3 V at 1 C rate are summarized in Fig. 6 (c). After 100 cycles, the  
314 residual stress accumulates from 0 to 37.8 MPa, and the capacity declines to 88.7 % of the initial  
315 capacity. During the continuous charge/discharge cycles, the capacity fades gradually but the  
316 residual stress increases quickly, as a result of the deformation from the loss of cycled lithium ions,  
317 similar to that in graphite <sup>1</sup>.

318 CV tests are carried out on the cells which are discharged to 2.8 V after different cycles to better  
319 understand the increased residual stress and decreased capacity, and the results are shown in Fig.  
320 6(d). The oxidization potential ( $E_O$ ), reduction potential ( $E_R$ ), potential difference between  
321 oxidization peak and reduction peak ( $\Delta E$ ), oxidation peak current ( $I_O$ ) and reduction peak current  
322 ( $I_R$ ) are listed in Table 1. The 2<sup>nd</sup> and 3<sup>rd</sup> CV curves are almost coincident except the higher  
323 oxidization peak intensity of the 2<sup>nd</sup> curve and the lower oxidization peak potential of the 3<sup>rd</sup> curve,  
324 indicating the higher reaction activity of the 2<sup>nd</sup> cycle and the lower polarization degree of the 3<sup>rd</sup>  
325 cycle. The oxidization peak at around 3.87 V and the reduction peak at around 3.68 V are associated  
326 to the de-intercalation and intercalation of lithium ions inside the host matrix, respectively. The  
327  $Ni^{2+}/Ni^{4+}$  accounts for the oxidation peak at 3.87 V <sup>19</sup> and the reduction peak at 3.67 V <sup>20</sup>. However,  
328 the redox peak intensities decrease greatly after 100 cycles and the potential difference between  
329 oxidization peak and reduction peak increases overwhelmingly, suggesting the reaction activity  
330 decreases and the reaction resistance increases during cycling process, which results in the decrease  
331 of capacity and the increase of residual stress.

332

### 333 3.6. Stress and structure changes during overcharge and over-discharge processes

334 From above analysis, charge state is found to greatly affect the stress values. In order to investigate  
335 the stress changes of the cells under some extreme conditions like overcharge (abbreviate OC) and  
336 over-discharge (abbreviate OD), the stress changes were monitored when they are respectively  
337 charged to 5 V and discharged to 0 V at 1.0 C rate at 25 °C, and the results are summarized in Fig. 7.  
338 As shown in Fig. 7 (a), the stress increases slowly and almost linearly from 0 to 9.9 MPa with a low  
339 slope of 7.6 MPa/h when the potential of the cell increases from 2.8 V to 4.3 V, close to that in the  
340 normal potential window shown in Fig. 6. So, the battery is under a normal state in this charge  
341 process. However, the stress increases abruptly from 10.0 MPa to 55.5 MPa when the potential  
342 increases from 4.7 V to 5.0 V, and the slope jumps to 225.5 MPa/h. The cell above 4.7 V is regarded  
343 as in an overcharge state <sup>21</sup>, so the stress increases rapidly in the overcharge state, which is  
344 attributed to the decomposed gases from the electrolyte <sup>15</sup>.

345 During the over-discharge process from 4.3 V to 2.8 V, the stress drops slowly from 10.0 MPa to 0.2  
346 MPa in an almost liner way, as shown in Fig. 7(b), similar to above results. However, the stress  
347 decreases linearly to -1.5 MPa when the potential decreases to 1.2 V. Furthermore, the decreasing  
348 slope of the stress keeps constant when the potential drops from 4.3 V to 1.2 V. The cyclability of  
349 the cell affects little by over-discharge to 2.0 V or 1.5 V, and the capacity loss is close to that of the  
350 similar cell cycled between 3.0 and 4.2 V <sup>22</sup>. Below 1.2 V, the potential decreases slowly and  
351 exhibits a quasi-plateau till 0.6 V, where the corresponding stress decreases in a stair step till -5.0  
352 MPa. Below 0.6 V, the potential decreases quickly to 0.0 V, but the stress increases abnormally in a  
353 linear way to -1.8 MPa. The stress values change from positive to negative during the  
354 over-discharge process, indicating the stress changes from tension to compression, which is from  
355 the negative deformation of the surface shell. With the decrease of the cut-off potential, lithium ions

356 continuously intercalate the electrode material to destroy the crystals<sup>23,24</sup>, which results in the  
357 decrease of volume and the increase of the negative stress values when the potential decreases from  
358 1.2 V to 0.6 V. Over-discharge to 1.0 and 0.5 V leads to cell's capacity loss of 29 and 38 %,  
359 respectively, which is significantly higher than normally cycled cells<sup>22</sup>. Large amount of CO<sub>2</sub> and  
360 hydrocarbons as well as CO have been found in the over-discharged cell<sup>25</sup>, and electrolyte  
361 decomposition is accelerated in the over-discharged state<sup>26</sup>. The decomposition of the electrolyte is  
362 dependent on the changes of surface conditions at the cathode. Therefore, with the continuous  
363 increase of inserted lithium ions, the crystal structure of the NMC material starts to breakdown to  
364 reduce deformation when the potential drops to 1.2 V, so the discharge process becomes difficult  
365 and the corresponding stress exhibits negative values. The completed destruction results in the  
366 lowest negative stress when the potential is 0.6 V. The produced gases or hydrocarbon will increase  
367 anomaly the stress below 0.6 V, as shown in the curve. Though the potential decreases slowly below  
368 1.2 V, the stress has several plateaus during the decreasing process. The plateaus may correspond to  
369 the damage process of the crystals. The possible mechanisms are further confirmed by the following  
370 XRD and EIS tests.

371 In order to detect the composition and the microstructure of the active materials under different  
372 charge states, the NMC electrodes were analysed by XRD technique, and the patterns are supplied  
373 in Fig. 7. Considering the low loading density of active material, the aluminium current collector of  
374 the NMC electrode was not removed for XRD characterization. In these patterns, all the index  
375 peaks except the obvious Al peak at around 65 ° are attributed to the samples at different charge  
376 states. Noticeably, the XRD patterns of the pristine and the overcharged samples are almost  
377 identical and the average crystallite size of the pristine and the overcharged is 46.265 and 52.765nm,  
378 respectively, indicating the crystal structure changes during the overcharge process. All peaks of

379 both samples match well with that of the hexagonal  $\alpha$ -NaFeO<sub>2</sub> structure with the R3m space group,  
380 indicating the existence of layered structure<sup>27-29</sup>. After overcharge, lithium ions are extracted from  
381 the NMC, the peak densities of the (101), (102) and (104) decline, and the lattice constants of the *a*  
382 and *c* of the NMC change from 2.860 and 14.225 Å to 2.831 and 14.322 Å, respectively.

383 Furthermore, the high potential will lead to the decomposition of electrolyte. These changes cause  
384 the increase of stress during overcharge process, in consistent with above stress analysis results.

385 However, the main characteristic peaks of the NMC disappear in the over-discharged pattern, and  
386 more amorphous characteristics appear except the peak at around 38 °, suggesting the crystal  
387 structure of the over-discharged sample destroys, which also confirms with above stress changes.

388 The amorphous products are probably the X-ray undetectable nano-sized mixtures, similar to that in  
389 the over-discharged LiFePO<sub>4</sub>, LiNiO<sub>2</sub>, and LiMn<sub>2</sub>O<sub>4</sub><sup>24</sup> such products result in the decrease of  
390 volume and electrostatic repulsion to produce negative deformation of shell to produce negative  
391 stress, agreeing well with above results.

392 In order to compare the interface behaviour of the electrodes under different charge states, the cells  
393 were further analysed with EIS technique, and the curves are supplied in Fig. 7(d). The fresh cells  
394 were galvanostatically charged or discharged to the referred potential for the EIS tests. Except that  
395 of the over-discharged curve, all the curves at other charge states have two semicircles in the  
396 high-to-medium frequency region, indicating a similar electrode reaction process. The zoomed-in  
397 section in Fig. 7(e) clearly shows the constitutions of the semicircles. In the curves of 2.8 V and 4.3  
398 V, the two semicircles grow with the increase of charge voltage limit, similar to Zheng's report<sup>27</sup>.

399 The semicircle in the medium-to-low frequency region becomes big abnormally when the cell is  
400 overcharged. The intercept of the curves on the *Z'* real axis in the high frequency region is attributed  
401 to the ohmic resistance of the electrolyte solution (*R<sub>s</sub>*). The semicircle in the high-to-medium

402 frequency region corresponds to the impedance of the solution film resistance ( $R_f$ ) on the electrode  
403 surface. The semicircle in the medium-to-low frequency region is related to the solid electrolyte  
404 interface ( $R_{SEI}$ ) and charge transfer resistance ( $R_{ct}$ ). The oblique line in the low frequency region is  
405 concerned to Warburg impedance  $W$  which concerns the semi-infinite diffusion of lithium ions in  
406 the bulk electrode. Using ZsimpWin and Z-view softwares with the  $R(QR)(QR)(QR)W$  model  
407 supplied in Fig. 7(f), the EIS curves are fitted well, indicating lithium ions diffuse in the crystal  
408 structure after reacting with electrode materials. Due to the non-homogeneity such as porosity,  
409 roughness, and geometry in the system, constant phase element (CPE)  $Q$  is substituted for  
410 traditional capacitance  $C$  in the model. In the equivalent circuit, the  $Q_f$ ,  $Q_{SEI}$  and  $Q_d$  correspond to  
411 the constant phase elements of the electrolyte film, SEI film and film/electrode interface,  
412 respectively<sup>30</sup>. During the charge process, lithium ions are extracted from the NMC material to  
413 form  $Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$  with high metal valences, so the charge transfer reaction becomes difficult  
414 and the high metal valences accelerates the oxidization of the electrolyte to produce gases to form a  
415 thick film on the electrode surface. All these result in the big semicircles, agreeing with the testing  
416 results. According to the simulation results supplied in Table 2, the Ohmic resistances of liquid  
417 charge-transfer resistance of the 2.8 V and 4.3 V are close, but that of the over-discharged and  
418 overcharged increase greatly, indicating the conductivity of the electrolyte near the electrode surface  
419 changes, which is from the changed composition after over-discharge or overcharge. The large  
420 differences of film resistance and charge transfer reaction resistance show that the electrode surface  
421 changes greatly under different charge states, which may be from the different compositions or  
422 structure of the NMC electrode material. All these changes cause the stress change in the cell shell  
423 to produce possible safety issues.

424 In order to detect the stress from lithium anode, the strain gauge was adhered to anode shell, and the

425 stresses were real-time monitored under the same testing conditions with NMC cathode. From the  
426 testing results in Figure S1, the stress values are close to the minimum detection limit of the strain  
427 gauge, indicating the stress change of the lithium anode shell is too low to be detected by the strain  
428 gauge with a detection limit of 1  $\mu\epsilon$ . Lithium ions are extracted from NMC cathode to deposit on  
429 the lithium surface which is in the electrolyte during charge process, while lithium ions are  
430 extracted from lithium anode to insert NMC cathode during discharge process. As for lithium anode,  
431 lithium ions are excessive in the test cells, and lithium ions extraction/deposition reactions take  
432 place at the lithium surface wetted by the electrolyte, instead of the crystal lattice like that in NMC  
433 cathode to cause volume changes. Furthermore, lithium is a soft metal which can resist the strain  
434 during electrode reaction processes, and the flexible polymer separator along with electrolyte can  
435 buffer the large volume change of NMC cathode. Therefore, the stress change from the lithium  
436 anode is low enough to be neglected, and the strain of the NMC shell is mainly from the lithium  
437 ions processes of NMC electrode in the test cells.

438

### 439 ***3.7. Relationship between charge states and stress changes***

440 According to above analysis, the relationship between charge states and stress changes at 25 °C is  
441 constructed in Fig. 8. The stress continuously increases from -5.0 MPa to 55.5 MPa when the  
442 state-of-charge (SOC) changes from over-discharge OD to overcharge OC, but the cell exhibits  
443 good electrochemical performance in the normal region with SOC increasing from 0 to 100%.  
444 Beyond the normal region, the electrochemical performance becomes poor, and the stress increases  
445 differently. As the potential discharges to 2.8 V, the residual stress value reaches 0.2~0.5 MPa when  
446 the current rate is 1C. As mentioned before, the residual stress accumulates to 37.8 MPa after 100  
447 cycles, and the polarization become high and the capacity fades to 88.7 %, so the increased residual

448 stress undermines the electrochemical performance. The stress value ranges from 9.9 MPa to 55.5  
449 MPa during overcharge process from 4.3 V to 5.0 V, while that from 0.2 MPa to -5.0 MPa during  
450 the over-discharge process from 2.8 V to 0.0 V. Under the over-discharge state, the stress of the cell  
451 first decreases and then increases because of the different reaction process. Therefore, the  
452 emergence of high pressure on the surface of the cell case means the degradation of the  
453 electrochemical performance, which is significant for the safety management of batteries in  
454 applications.

455

#### 456 **4. Conclusions**

457 A non-destructive method has been developed to real-time monitor the surface stress changes of a  
458 SS cell case for the safety management. The temperature sensitivity and stress properties of the  
459 strain gauges have been investigated, and temperature correction has been conducted. The  
460 stress-strain relationship of the cell case has been established according to the derived stress  
461 calculation formula. The stress values of the NMC cells under different states have been discussed.  
462 As the cells are open circuit, the surface stress mainly originates from the thermal stress of case at  
463 temperatures from 50 to 70 °C, but the continuously increasing stress at 80 °C is due to electrolyte  
464 decomposition in addition to the volume expansion of electrode and thermal stress of case. The  
465 surface stress is greatly affected by charge state, and the stress value increases from 0.0 to the  
466 maximum value of 9.2 MPa when potential increases from 2.8 to 4.3 V at 0.5 C current rate, but the  
467 stress does not restore to 0.0 MPa when potential decreases to 2.8 V. The accumulated residue stress  
468 is 37.8 MPa, while the capacity degradation is 11.3 % compared to the initial capacity after 100  
469 cycles at 1.0 C current rate. During the overcharge to 5.0 V, the stress increases slowly to 10.0 MPa  
470 at 4.7 V, and then increases quickly to 55.5 MPa. During the over-discharge to 0.0 V, the stress

471 value decreases linearly from 10 to -2.0 MPa when potential decreases from 4.3 to 1.2 V, and then  
472 decreases to -5.0 MPa from 1.2 to 0.6 V, while increases abnormally to -1.8 MPa from 0.6 to 0.0 V.  
473 Various techniques have been used to analyse the electrode reaction processes. The increased  
474 surface stress worsens the electrochemical performance, and their relationship has been analysed.  
475 The relationship between stress and potential can potentially serve as a useful tool to monitor the  
476 electrochemical performance and failure of batteries.  
477 The surface stress changes can be monitored successfully by strain gauges in lithium cells. A sealed  
478 battery can be regarded as a pressure vessel where electrode reaction takes place, and the inner  
479 pressure would cause the deformation of the shell to produce stress, so strain gauge could be used to  
480 monitor the strain-stress of a full battery, and some pictures of the stress testing system for a  
481 practical full battery are supplied in Figure S2. The stress measurements can be further combined  
482 with computer simulation calculations on the surface for cross validations and to predict the stress  
483 changes in the complex processes involving chemical reaction and thermal effects. Compared the  
484 surface stress to the stress threshold value of the battery package, special techniques (including  
485 ending, blocking, cutting, or injecting chemicals, *etc.*) could be utilized to eliminate safety issues.  
486 Therefore, this initial work demonstrates the possibility to monitor the surface stress changes of  
487 cells using strain gauges as an effective and economical way which may greatly improve the safety  
488 management of batteries.

489

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494

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568 Tables

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570

571 **Table 1. Values of  $E_O$ ,  $E_R$ ,  $\Delta E$ ,  $I_O$  and  $I_R$  of  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  after different cycles.**

Cycle	$E_O$ (V)	$E_R$ (V)	$\Delta E$ (V)	$I_O \times 10^{-4}$ (A)	$I_R \times 10^{-4}$ (A)
2 <sup>nd</sup>	3.87	3.67	0.20	12.83	-6.16
3 <sup>rd</sup>	3.84	3.67	0.17	11.93	-6.28
100 <sup>th</sup>	3.87	3.53	0.34	3.23	-1.80

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**Table 2 Values of  $R_s$ ,  $R_f$ ,  $R_{SEI}$ ,  $R_{ct}$  and  $W$ .**

State of charge	$R_s(\text{ohm/cm}^2)$	$R_f(\text{ohm/cm}^2)$	$R_{SEI}(\text{ohm/cm}^2)$	$R_{ct}(\text{ohm/cm}^2)$	$W \times 10^{-3}(\text{ohm/cm}^2)$
0.0V	9.82	108.07	4.75	1145.61	$1.60 \times 10^9$
2.8V	3.83	13.33	15.55	224.56	11.52
4.3V	3.89	12.33	63.60	128.95	6.53
5.0V	4.50	222.89	2310.53	988.60	1.53

577

## 1 **Figure Captions**

2 Figure 1. Images of the NMC coin cell adhered with strain gauges and the corresponding testing  
3 platform.

4 Figure 2. Comparisons of the charge/discharge curves of NMC before/after installing gauges.

5 Figure 3. (a) Strain curves of the NMC cell, reference cell and quartz glass at 50 °C, and (b) strain  
6 curve of the cell shell and quartz glass from 25 to 80 °C.

7 Figure 4. (a) Schematic diagrams of the stress distribution (a-1), (a-2) and internal forces (a-3), (a-4)  
8 of the cell, and (b) deformation analysis when the cathode laminate bends; (c) shearing force of the  
9 laminate under uniformly distributed loading; (d) normalized stress distribution along radius.

10 Figure 5. Stress changes of the NMC cell and reference cell at different ambient temperatures.

11 Figure 6. (a) Typical galvanostatic charge/discharge curves, and (b) the corresponding stress changes  
12 at 0.5 C current rate; (c) the residual stress during cycles at 1.0 C current rate; (d) different CV curves  
13 of the NMC cell at a scanning rate of 0.2 mV s<sup>-1</sup>.

14 Figure 7. The stress changes of the NMC cell during (a) overcharge process, and (b) overdischarge  
15 process; (c) XRD patterns of the NMC material, and (d) EIS curves of the NMC cell at different  
16 charge states; (e) part amplified, and (f) the corresponding fitting model of the EIS curves.

17 Figure 8. The relationships between stress changes, state of charge and electrochemical performance  
18 at room temperature.

19

20

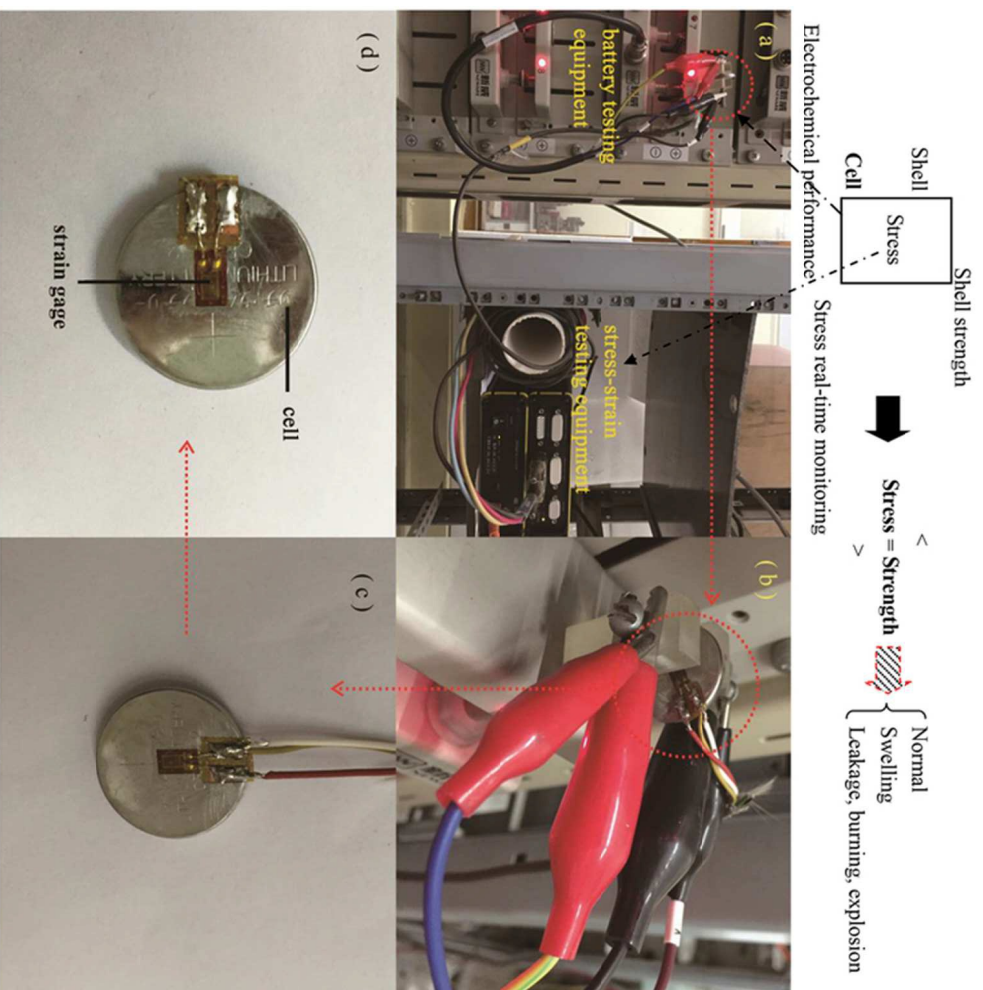


figure 1  
64x64mm (300 x 300 DPI)

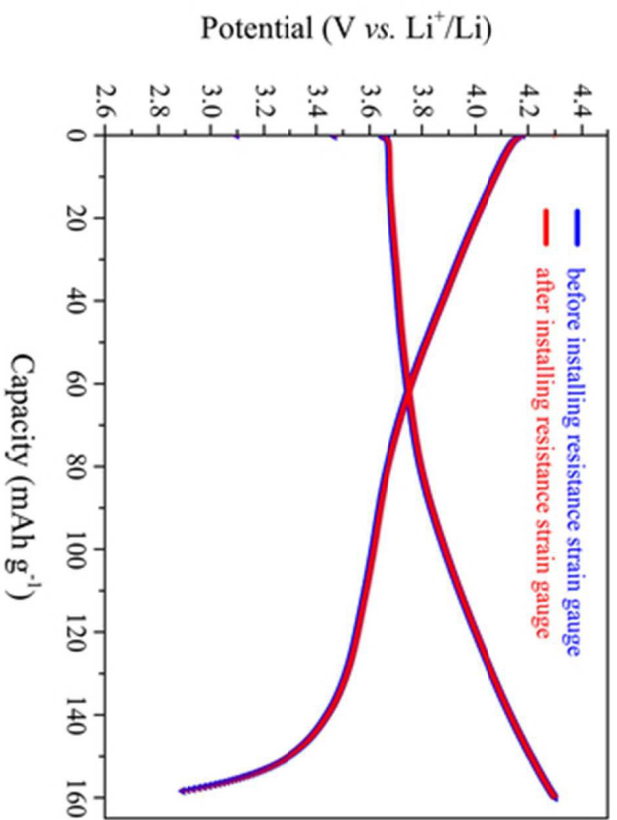


figure 2  
44x31mm (300 x 300 DPI)

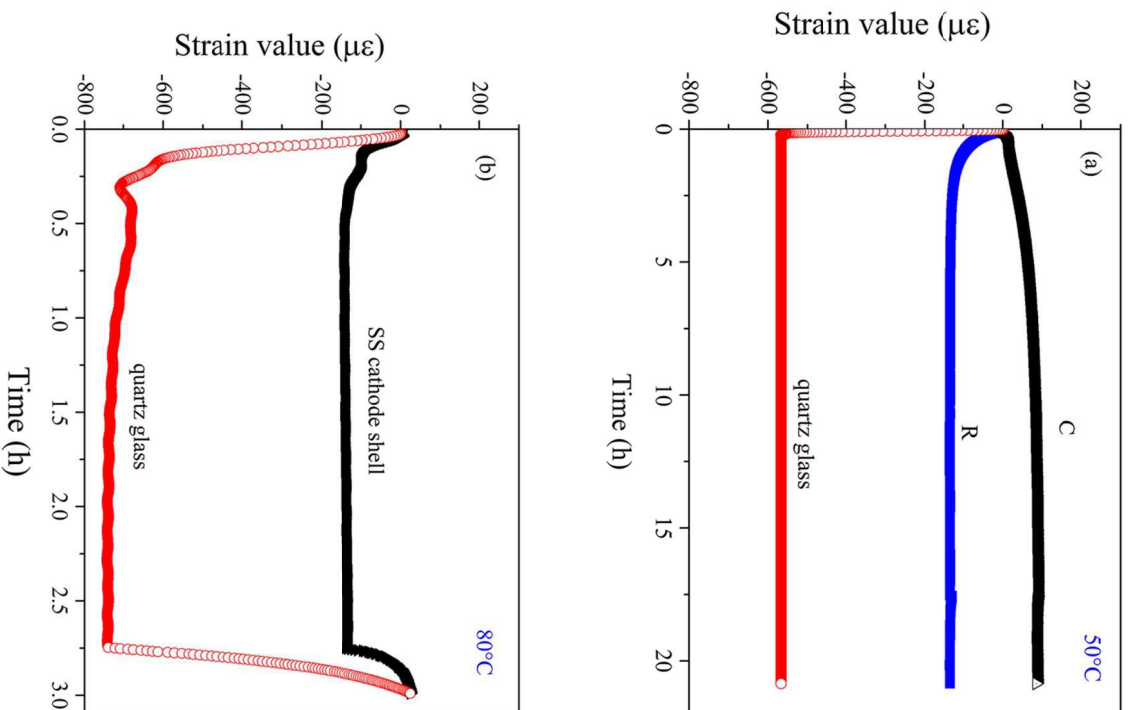


figure 3  
88x124mm (300 x 300 DPI)

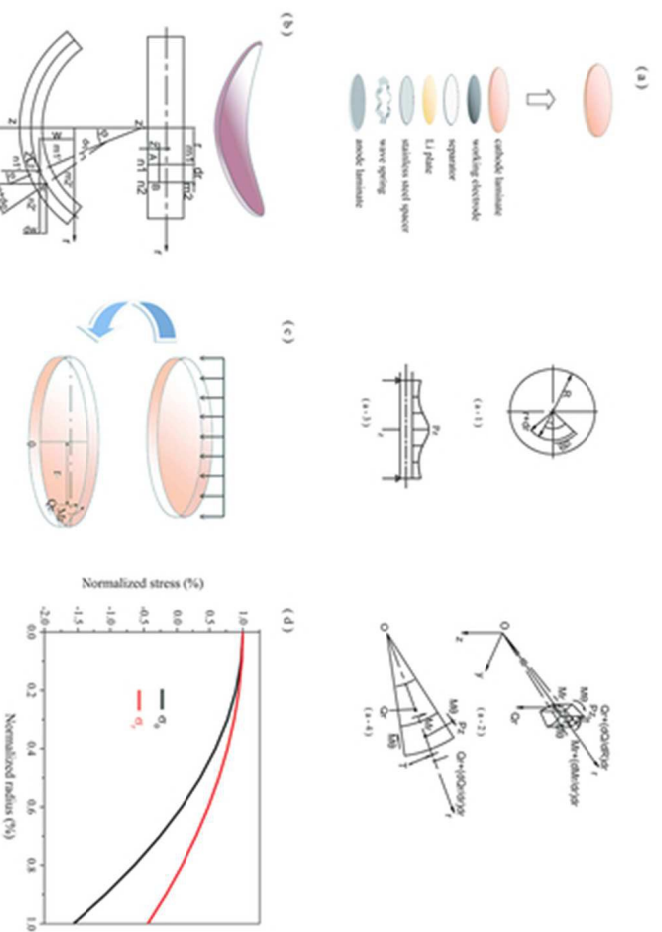


figure 4  
44x31mm (300 x 300 DPI)

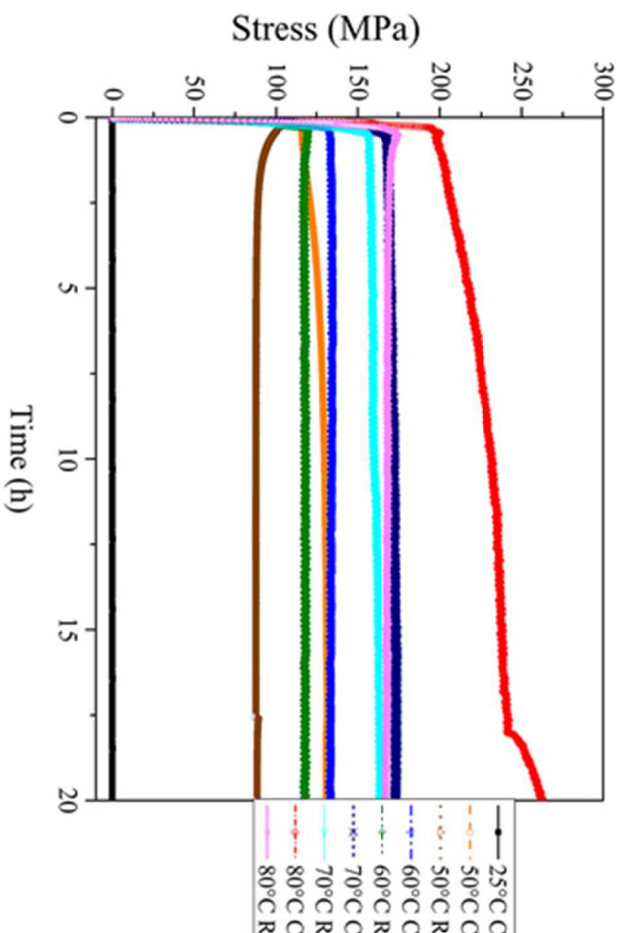


figure 5  
44x31mm (300 x 300 DPI)

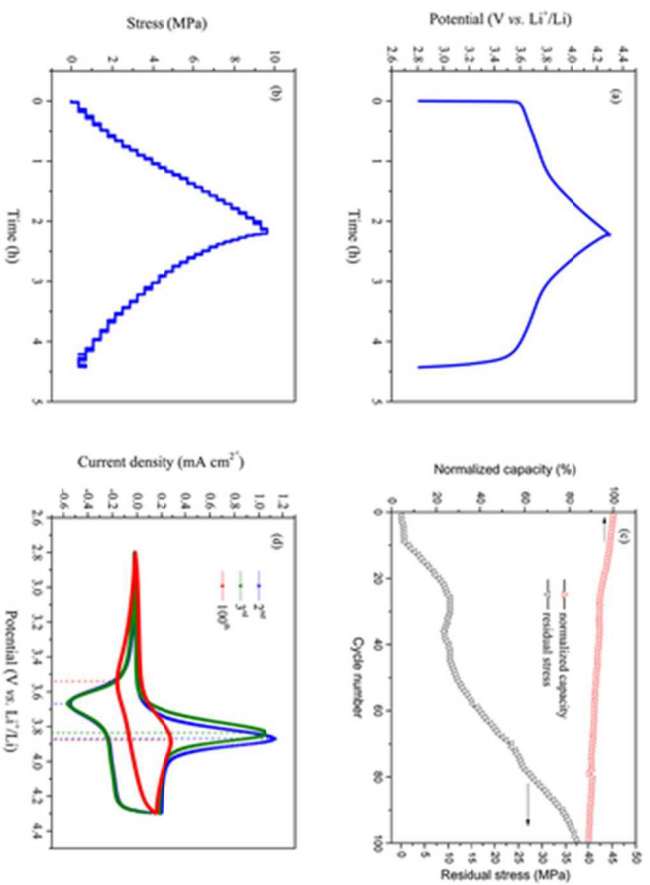


figure 6  
45x32mm (300 x 300 DPI)

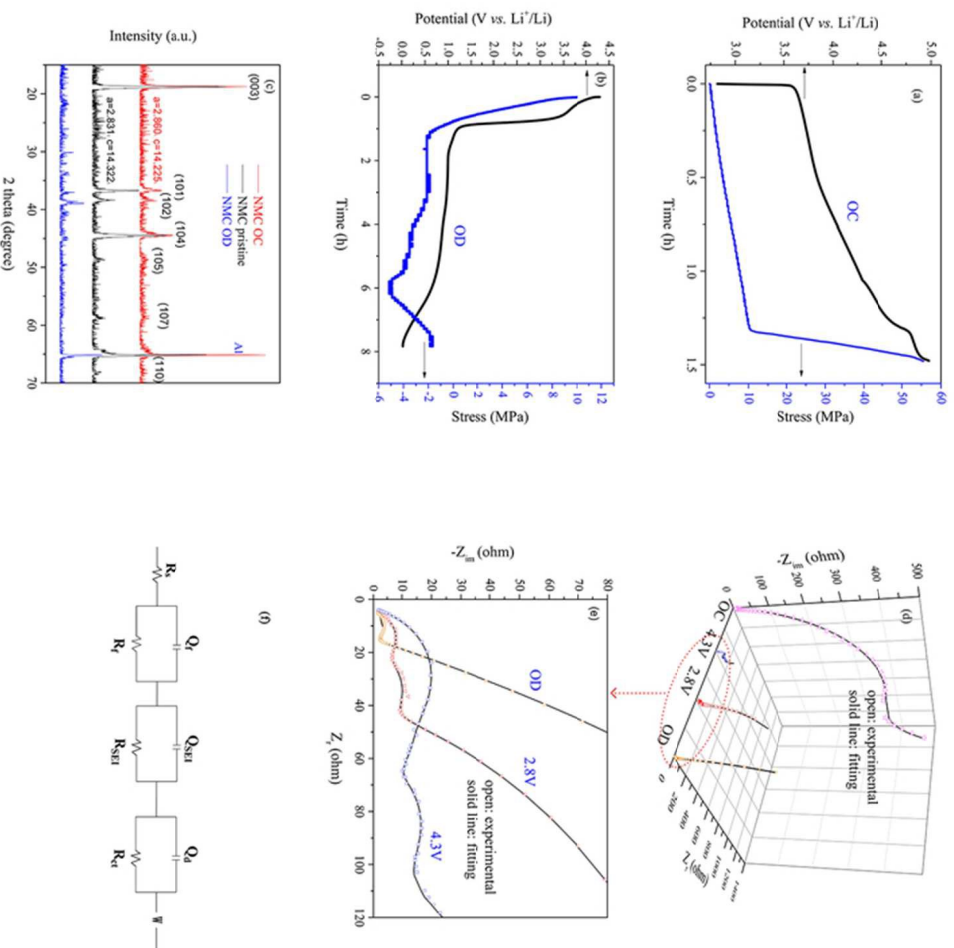


figure 7  
63x64mm (300 x 300 DPI)

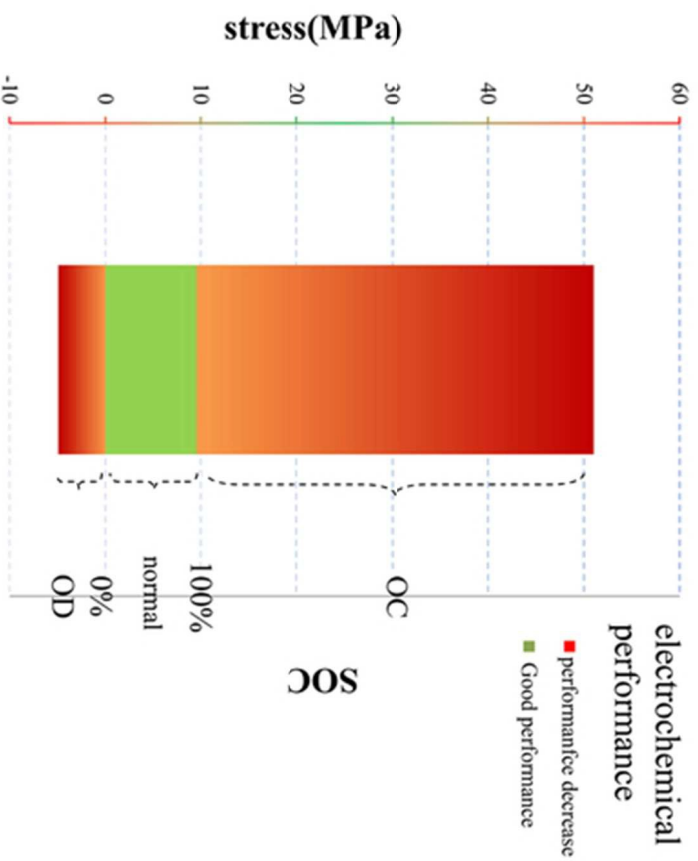


figure 8  
47x35mm (300 x 300 DPI)

**Graphical abstract:**

The stresses in lithium cells are real-time monitored without destruction, and the relationship between stress and electrochemical performance is discussed.

