Supporting Information for

The Achilles Heel of Batteries with Alkali Metal Electrodes

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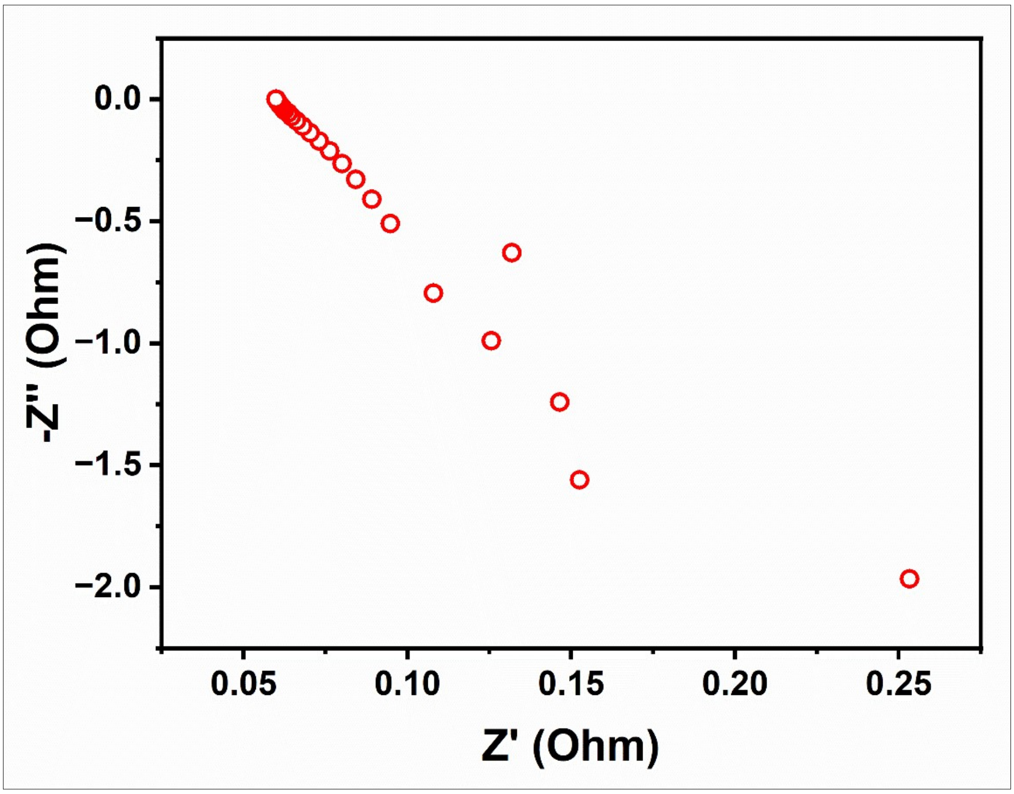

Figure S1 Impedance spectra of 30 mΩ shunt resistor.

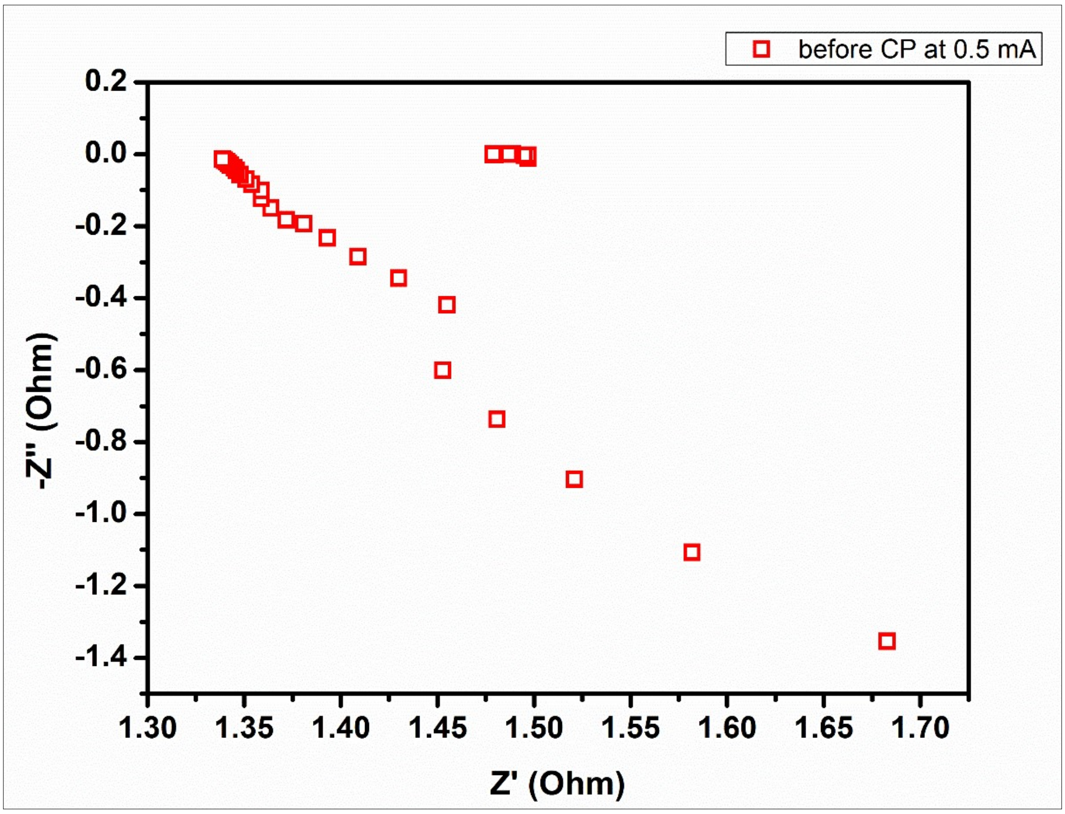

Figure S2 Impedance spectra of Al-Na/BASE/Na-Al cell values recorded after depositing and stripping Na at 0.4 mA.

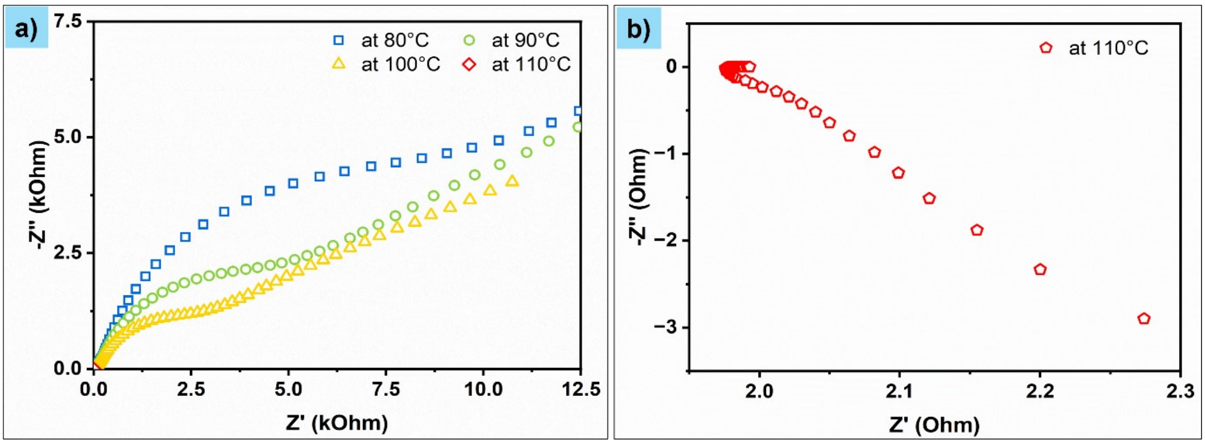

Figure S3a Impedance spectra of Al-NMO/BASE/Na-Al cell in the temperature range of 80 °C to 110 °C with increments of +10 °C; b) Impedance spectra of Al-NMO/BASE/Na-Al cell at 110 °C.

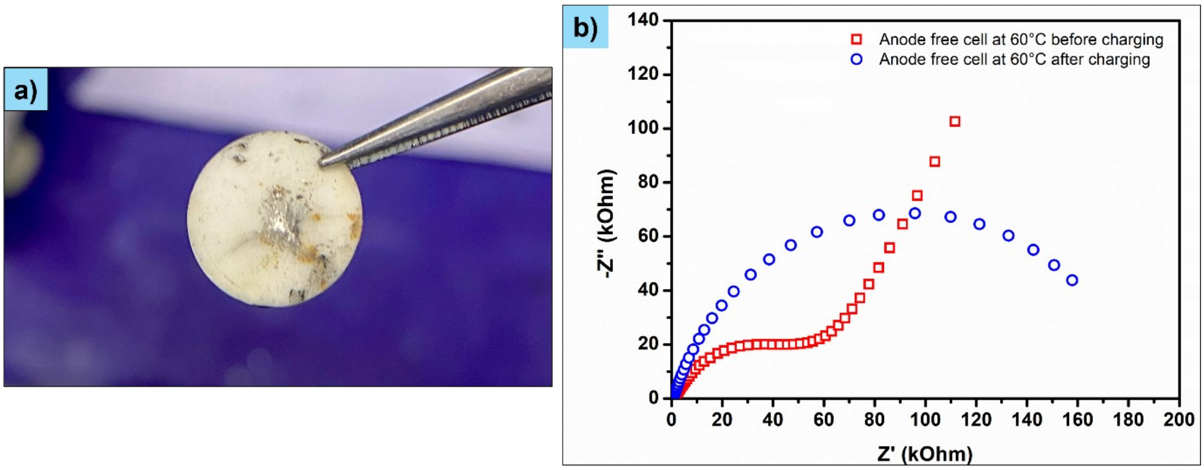

Figure S4a digital image of the anode side of the NGS disc from the cell Al-NMO/NGS/Al after the first charge. b) impedance spectra of the same cell before and after charge at 60 °C.

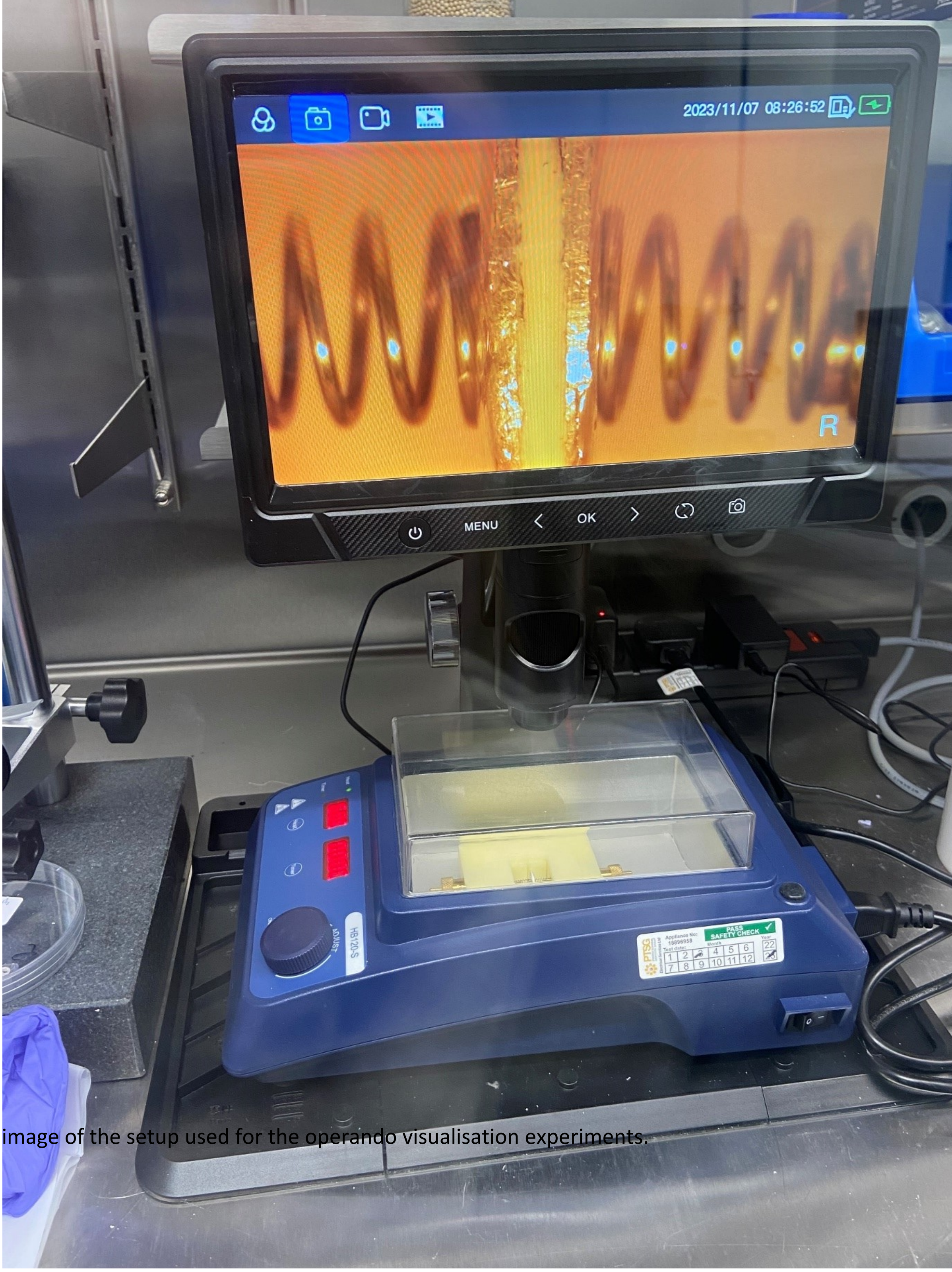

Figure S5 Digital image of the setup used for the operando visualisation experiments.

Figure S6 The video of the cell (Al-Na/NGS/Na-Al) was recorded at 110 °C (changes are evident after the 7th minute). Link to video

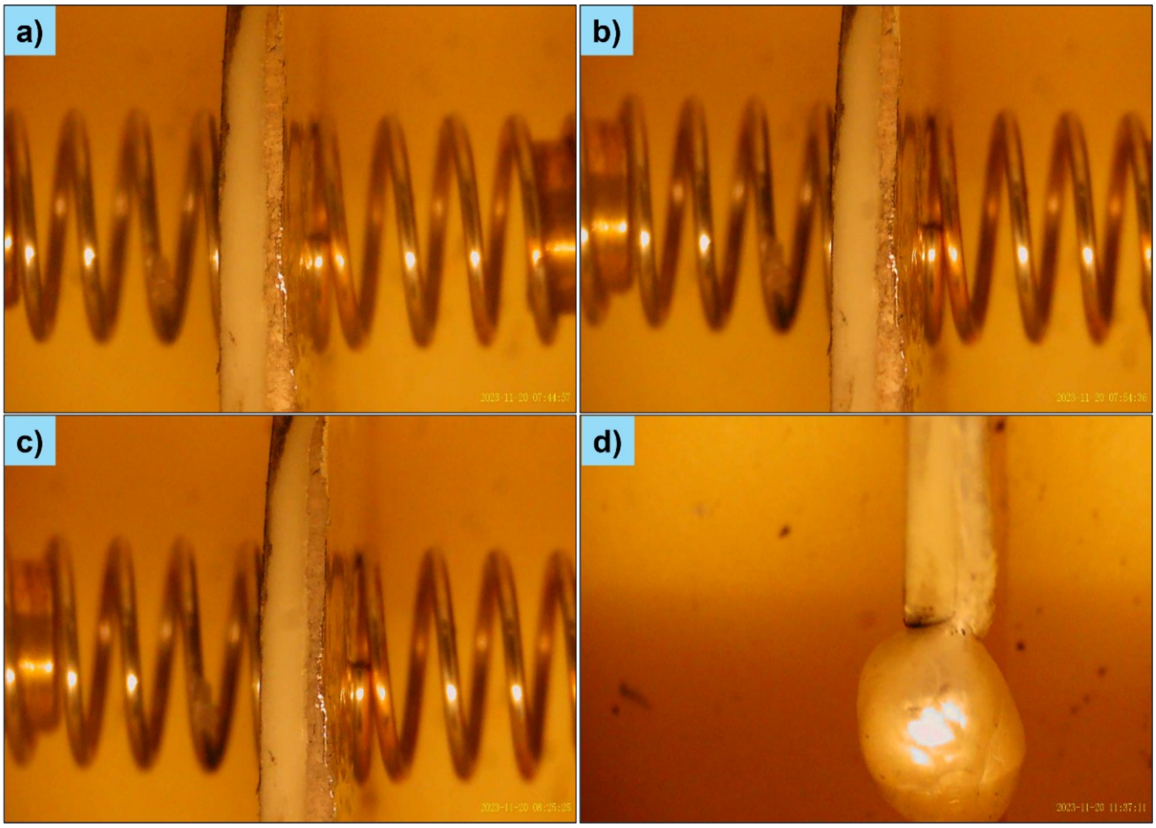

Figure S7 *Optical images of the half cell (Al-NMO/NGS/Na-Al) at various temperatures: a) at 80 °C, b) at 110 °C, and c) at 120 °C. d) digital image of the solid electrolyte taken at RT after cooling down the cell after heating to 120 °C.*

Temperature Rising Mechanisms in Batteries

The temperature rise in a battery can occur either by heating, overcharging, external or internal short-circuiting, or fast charging. Heating a battery to a specific temperature (generally between 80 °C and 120 °C) triggers a cascade of reactions in batteries. This raises the battery's temperature quickly, leading to a thermal runaway and potential explosion. LIBs are charged beyond the allowed voltage or state of charge (SoC) when overcharging. Overcharging LIBs can lead to the deposition of Li metal on the anode, which can create an internal short circuit. Overcharging can also decompose liquid electrolytes, forming toxic and combustible gases. Oxygen evolution under overcharging conditions is another major issue with certain metal oxide cathodes. The presence of oxygen and flammable gases creates excessive gas pressure inside the cells that can result in venting with flames. Heating and overcharging often lead to TR (Table S3 and S4).

Internal short circuits (ISC) in batteries can occur in many ways. ISC enables direct exothermic chemical reactions, quickly raising the temperature of the battery, triggering chain reactions, and leading to TR and potential explosion. Table S5 summarises some ISC results. Like ISC, external short circuits (ESC) can occur in many ways, even daily (by wrongly connecting the batteries to electronic devices). When the battery is externally short-circuited, current is passed through it heavily. This raises the temperature of the battery due to the resistance of the battery components (Joule heating) (Table S6).

There is a strong intention to charge batteries at a higher rate. We speculate that charging batteries at a higher rate is potentially equal to ESC and should be avoided. For example, the 1C charge rate (60 minutes) of an NMC battery with a 2Ah capacity is 2A. Passing a 60A of current (30C rate; 2 minutes) through this cell can raise the battery's surface temperature to 97 °C (the internal temperature could be higher). This can melt the Na metal anode. Charging the battery at a 2C rate raised its temperature to 50 °C. Fast charging can also enable the deposition of Li and Na metals on the carbon anodes. Beyond melting, this metal deposition could lead to dendrite growth upon repeated cycling and leading to ISC.

Internal short circuits with Lithium and Sodium metals

The rise of the battery's temperature under ESC conditions is higher when low-resistance wires are used for ESC (Table S5). For example, in a 15 Ah pouch cell, the temperature rises to 113 °C in 18s when 0.562 mΩ short was used. At the same time, it increased to 90 °C (in 50s) and to 68 °C (in 500s) when 0.778 mΩ and 24.0 mΩ were used for ESC. The lower the shorting resistance, the higher the rate of temperature rise. On the other hand, the surface temperature of the battery was raised to 126 °C when the copper nails were used to induce internal short circuits through nail tests. The temperature rose between 100-110 °C when the steel nails were used and mostly unchanged when the plastic nails were used. The battery's surface temperature increased with the nail's electrical conductivity. Considering the high electrical conductivity of alkali metals (1.1×10^7 S/m for Li and 2.1×10^7 S/m for Na and low resistivity $9.4\text{x}10^{-8}$ mΩ for Li and $4.69\text{x}10^{-8}$ mΩ for Na) and their liquid state when melted (enable the high contact with cathode when short-circuited internally), might lead to a disastrous situation when short-circuited.

Table S1 Impedance values of Cu-Li/LLZO/Li-Cu and Cu-Li/LBASE/Li-Cu cells.

Temperature (°C)	Cu-Li/LLZO/Li-Cu (Ω)	Cu-Li/LBASE/Li-Cu (Ω)
100	298	495
110	192	267
120	132	153
130	92	89
140	67	52
150	51	30
160	39	19
170	31	6
180	25	4
190	0.694	2
200	-	0.001

Table S2 Impedance values of Al-Na/BASE/Na-Al and Al-Na/NGS/Na-Al cells.

Temperature (°C)	Al-Na/BASE/Na-Al (Ω)	Al-Na/NGS/Na-Al (Ω)
40	76	108
50	56	75
60	43	52
70	33	37
80	26	28
90	20	21
100	0.583	16
110	-	0.787

Table S3 The effect of external heating on various batteries. LFP - $LiFePO_4$; LMO - $LiMn_2O_4$; LCO - $LiCoO_2$; NCA - $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$; NMC - $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. NA- not available.

Battery type	Capacity (Ah)	Cathode	TR Initial T in °C	TR Final T in °C	Ref
18650	1.1	LFP	220	(404 ± 23)	[1]
18650	1.5	NMC	220	(678 ± 13)	[1]
18650	2.6	NMC+LCO	220	(853 ± 24)	[1]
18650	2.6	LCO	198 to 236	290 to 511	[2]
18650	2.95	NA	103.8 to 117.6	325.3 to 462.7	[3]
18650	2.9	NMC	160.09	641.41 (surface) 1117.8 (internal)	[4]
18650	3.1	NMC	Induction heating	734/741/830	[5]
Pouch	39	NMC	Induction heating	400/420	[5]
Prismatic	94	NMC	Induction heating	550	[5]
18650	2.6	NMC	Heating to 133.9	681.9	[6]
	60	NMC	189.4	1149.5	[7]
	150	NMC	191.5	988	[7]
	180	NMC	202.2	889.1	[7]

Table S4 The effect of overcharging on various batteries. LFP - $LiFePO_4$; LMO - $LiMn_2O_4$; LCO - $LiCoO_2$; NCA - $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$; NMC - $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. NA- not available.

Battery Type	Capacity (Ah)	Cathode	Overcharging Conditions	Testing T in °C	Max T in °C	TR	Ref
18560	2.6	LCO	1C, 2C and 3C until	35	62.6,	N	[8]

			5V		66.4,72.1		
18560	2.6	LCO	1C, 2C and 3C until 5V	50	67.4,74.6,77.5	N	[8]
18560	2.6	LCO	1C, 2C and 3C until 5V	60	78.9, 83.5, 86.6	N	[8]

Table S5 The internal short circuit (ISC) effect on various batteries. Nail penetration test (NPT); LFP - $LiFePO_4$; LMO - $LiMn_2O_4$; LCO - $LiCoO_2$; NCA - $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$; NMC -$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$; NA - not available.

Battery Type	**Capacity (Ah)**	**Cathode**	**ISC method**	**Max T in °C**	**Ref**
Pouch	15	LMO+NMC	NPT with Cu (10x50) mm at 10 c S^{-1}	126	[9]
18650	NA	NA	Bending and deformation (indenter force - 2.98kN)	107	[10]
Pouch	10	NMC	Needle penetration		[8]

Table S6 The external short circuit (ESC) effect on various batteries. LFP - $LiFePO_4$; LMO - $LiMn_2O_4$; LCO - $LiCoO_2$; NCA - $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$; NMC - $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. NA- not available.

Battery Type	**Capacity (Ah)**	**Cathode /Chemistry**	**ESC method**	**Max peak Current in A**	**Max peak T in °C**	**Ref**
18650	2.6	LCO	4.39mΩ	NA	110	[5]
18650	2	NMC	NA	Over 60A	97	[11]
Coin cell	0.075	LCO/NMC	50mΩ	Over 10C	85	[12]
Pouch	9.6	NMC	1.1mΩ	1415	107	[13]
Pouch	9.7	NCA	1.3mΩ	1342	121	[13]
Pouch	7	LFP	Cu cable	900	100	[14]
Pouch	45	LFP	Cu cable	1084	NA	[14]
Prismatic	NA	NCA	NA		120	[15]
Pouch	NA	NMC	5mΩ	1220	90	[16]
Prismatic	NA	NMC	5mΩ	1492	271	[16]
18650	2.45	NMC	NA	Over 75	97	[17]
18650	2.75	NCA	4/8/15/30mΩ	90	123	[18]
Prismatic	1.15	LCO	5mΩ	40	115	[19]
18650	2	NMC	25mΩ	74	120	[20]
18650	1.35	LFP	NA	Over 65	110	[21]
Prismatic	1.5	LCO	5mΩ	36	94/109	[22]
Laminated	0.75	LCO	<30mΩ	25	110	[23]
Prismatic	160	LFP	NA	1075	190	[24]
Prismatic	8	LFP	NA	82	95	[24]
Cylindrical	13	$SOCl_2$	NA	51	550	[24]
Pouch	15	LMO-NMC	0.562mΩ	1850	113	[9]

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