

Improving Lithium-ion Cells by Replacing Polyethylene Terephthalate Jellyroll Tape

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1 **Improving Lithium-ion Cells by Replacing Polyethylene Terephthalate Jellyroll Tape**

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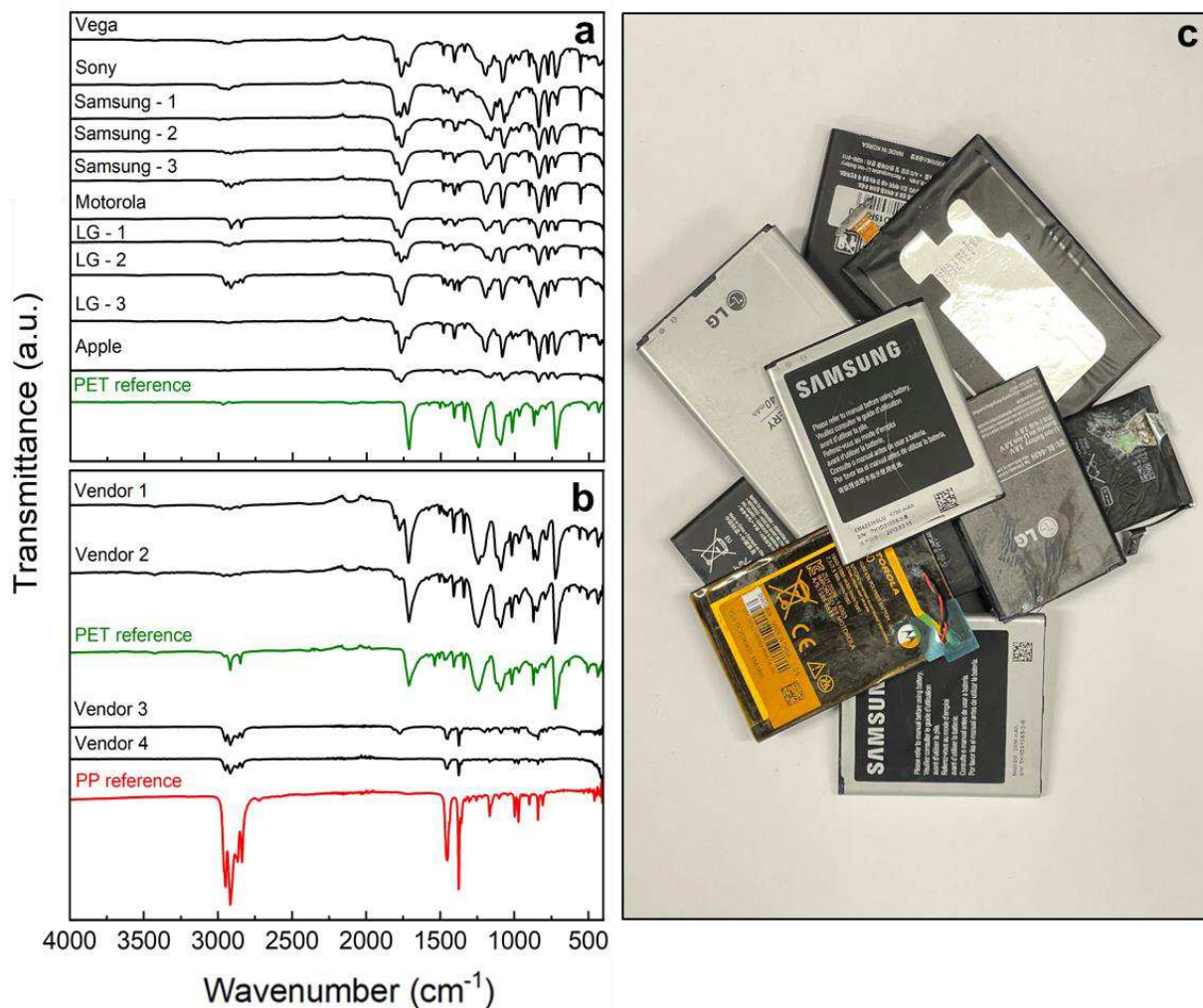
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12 **Polyethylene terephthalate (PET) tape is widely used by well-known lithium-ion battery**
13 **manufacturers to prevent electrode stacks from unwinding during assembly. PET tape is**
14 **selected since it has suitable mechanical and electrical properties, but its chemical stability**
15 **has been largely overlooked. In the absence of effective electrolyte additives, PET can**
16 **depolymerize into its monomer dimethyl terephthalate (DMT), which is an unwanted redox**
17 **shuttle that induces significant self-discharge in a lithium-ion cell. This study presents a**
18 **chemical screening experiment to probe the PET decomposition mechanism involving *in situ***
19 **generated methanol and lithium methoxide from dimethyl carbonate, one of the most**
20 **common electrolyte solvents in lithium-ion cells. By screening other polymers, it is found that**
21 **polypropylene (PP) and polyimide (Kapton) are stable in the electrolyte. Finally, it is**
22 **demonstrated that reversible self-discharge of LiFePO₄/graphite cells can be virtually**
23 **eliminated by replacing PET jellyroll tape with chemically stable PP tape.**

24

25 Every commercial lithium-ion battery (LIB) made by stacking or winding the electrode sheets
26 contains tape. This tape holds the assembled cell stack or jellyroll together, before it is inserted
27 into the cylindrical, prismatic or pouch cell casing during manufacturing. Typically, thin tapes are
28 used to avoid wasting valuable space or adding unnecessary weight that would lower the energy
29 density of the cell. After manufacturing, the tape does not serve a function and is generally
30 regarded as an inactive cell component.

31 Fig. 1 shows that many well-known battery manufacturers use PET tape in their cells. Fourier
32 transform infrared spectroscopy (FTIR) of tapes extracted from discarded smartphone batteries
33 show the characteristic absorption bands of PET (Figs. 1a,c). Out of ten randomly selected cells
34 from major smartphone OEMs (Fig. 1a) and four 18650-sized cylindrical cells from reputable
35 suppliers (Fig. 1b), only two cells did not contain PET tape. Apart from its use as tape, PET has
36 been proposed by various companies, such as Soteria¹, DuPont², and Meta³, as a substrate for
37 lighter and safer metal-coated aluminum and copper current collectors. PET is also used as
38 separator material, electrode coating, and organic electrode material in the academic literature.⁴
39 For all these applications, the chemical stability of PET plays an important role, but has not been
40 investigated.



41

42 **Figure 1.** FTIR spectra of jellyroll closure tapes found in commercial cellphone batteries (a) and
 43 cylindrical 18650 cells from reputable vendors (b). Cellphone batteries from which the tapes were
 44 obtained are shown in (c).

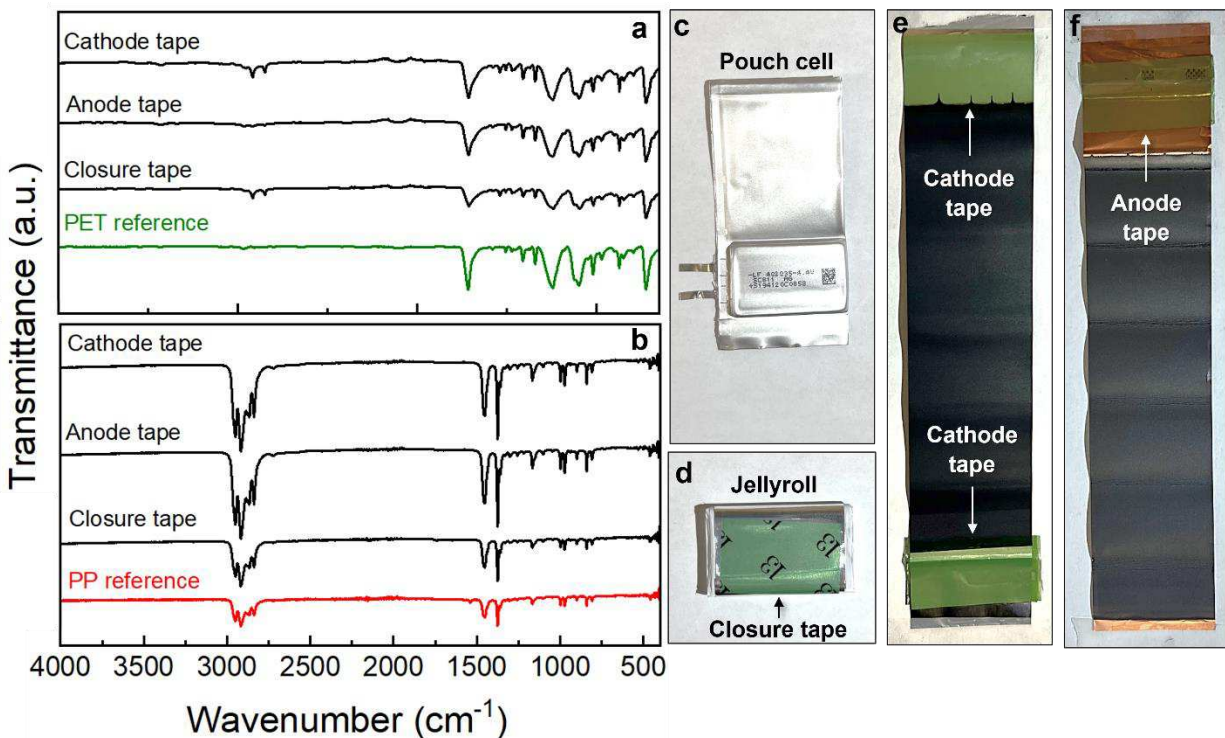
45 Recently, Logan et al.⁵ and Büchele et al.⁶ showed that lithium-ion batteries with LiFePO₄ (LFP)
 46 or LiNi_{1-x-y}Mn_xCo_yO₂ (NMC) positive electrodes and graphite negative electrodes are prone to
 47 rapid self-discharge at elevated temperature unless effective electrolyte additives are used. The
 48 LFP/graphite cells lost ~30% of their charge over 500 h of storage at 40°C, and self-discharged
 49 completely when stored at 60°C for 500 h.⁶ Büchele et al. found an unwanted redox shuttle
 50 molecule that is generated *in situ* during formation, cycling or storage of some battery cells at
 51 elevated temperature.⁷ A redox shuttle can diffuse between the positive and negative electrode of

52 a battery and transport electrons from one side to the other through a reversible redox reaction,
53 accepting an electron from the negative electrode, and donating it to the positive electrode. This
54 results in lithium ions being transferred from the negative to the positive electrode without charge
55 being drawn from the cell to power a device in the external circuit. This self-discharge reaction is
56 (in principle) non-damaging and reversible since the lithium inventory is unaffected, but it is of
57 concern in many applications, e.g., consumer electronics. In addition, it is of great concern for
58 cells that are connected in series in a battery module. If the self-discharge rates of such cells differ,
59 the cell balancing algorithm of the battery management system may fail to safely charge the
60 module. Büchele et al. identified the shuttle molecule as dimethyl terephthalate (DMT).⁷ This
61 study will demonstrate that DMT is the product of PET depolymerization with methanol and
62 lithium methoxide⁸, two reactants that can be generated in lithium-ion cells from dimethyl
63 carbonate (DMC), a ubiquitous electrolyte solvent. In addition, this study will show how reversible
64 self-discharge of lithium-ion batteries can be virtually eliminated by replacing PET tape with
65 polypropylene (PP), an alternative polymer with far superior chemical stability.

66

67 *Decomposition of PET tape in lithium-ion cells*

68 Fig. 2 shows FTIR spectra of the cathode, anode and jellyroll closure tapes of wound LFP/graphite
69 pouch cells either made with PET (a) or PP tapes (b). To indicate the location of the tapes in the
70 cells, Fig. 2c shows a dissection of one of the 402035-sized pouch cells used in this study. The
71 closure tape is on the outside of the jellyroll (Fig. 2d) and the cathode and anode tapes are on the
72 unrolled electrodes (Figs. 2e,f).



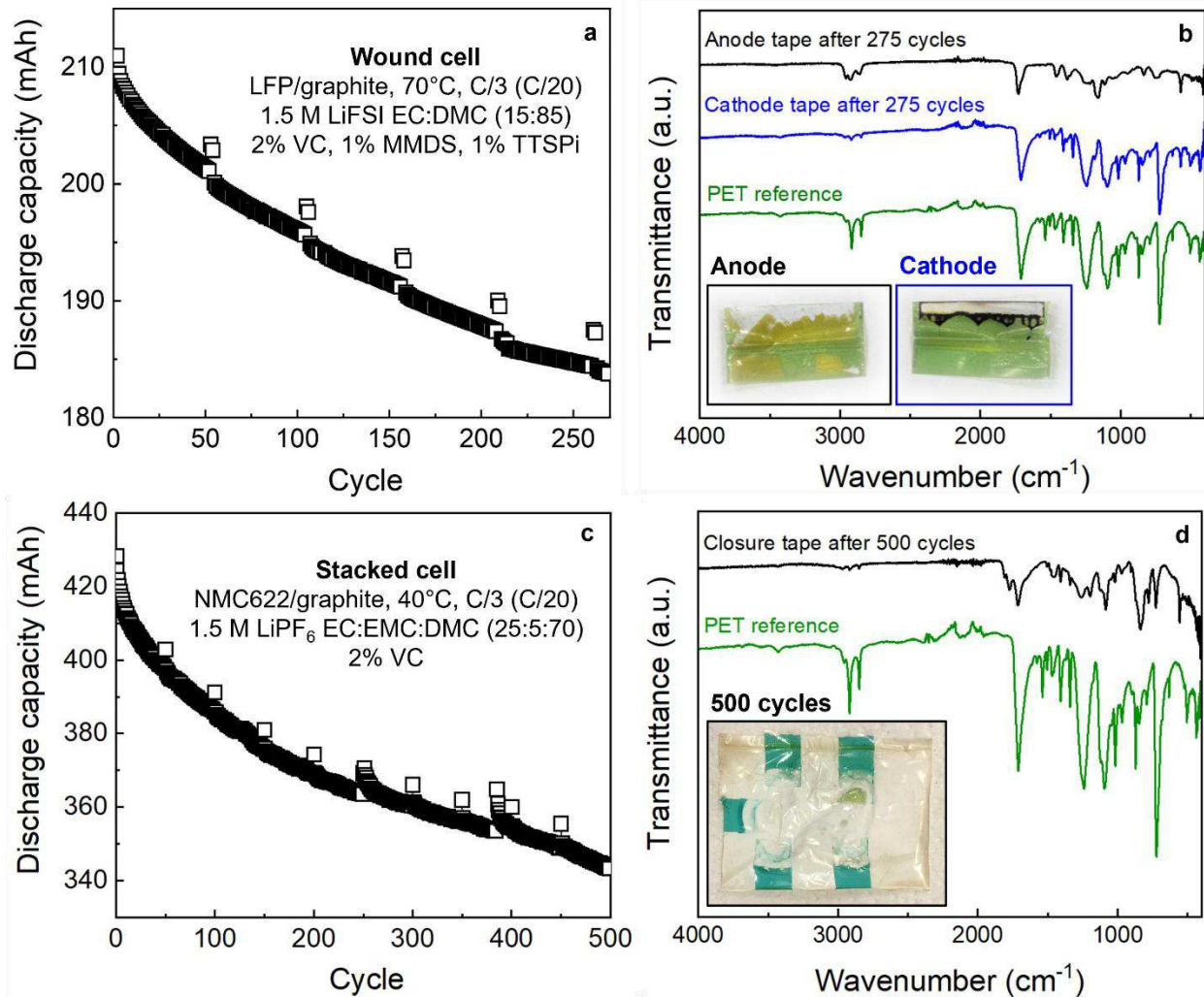
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74 **Figure 2.** FTIR spectra of cathode tape, anode tape, and closure tape extracted from PET (a) and
 75 PP cells (b). This study uses 402035-sized pouch cells (c); the closure tape can be seen on the
 76 outside of the jellyroll (d); cathode and anode tapes can be seen on the unrolled electrodes (d and
 77 e). Reference spectra of polyethylene terephthalate (PET) and polypropylene (PP) are added to
 78 panel a in green and red, respectively.

79

80 Fig. 3 shows two cells with different formats, cell chemistry and testing conditions cycled for
 81 several months. The first cell is a wound LFP/graphite pouch cell, cycled for 275 charge-discharge
 82 cycles at 70 °C (Fig. 3a), and the other is a stacked NMC622/graphite cell cycled for 500 charge-
 83 discharge cycles at 40 °C (Fig. 3c). The LFP/graphite cell used 1.5M LiFSI EC:DMC (15:85) with
 84 2% VC, 1% MMDS, and 1% TTSPi additives as the electrolyte (see Methods). The
 85 NMC622/graphite cell used 1.5M LiPF₆ EC:EMC:DMC (25:5:70) with 2% VC and 1% DTD
 86 additives as the electrolyte. After cycling, both cells were opened, and their PET jellyroll tapes
 87 were examined. The insets of Figs. 3b and d show that the PET tapes have severely corroded in
 88 both cells, and even fully dissolved in some locations. The FTIR spectra in Fig. 3b show that the

89 anode tape has lost some of its characteristic absorption bands, while the cathode tape still
90 resembles the PET reference spectrum. The closure tape of the stacked cell (Fig. 3d) also shows a
91 substantially altered FTIR absorption spectrum, which indicates PET decomposition.



92

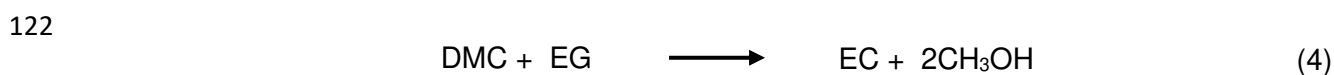
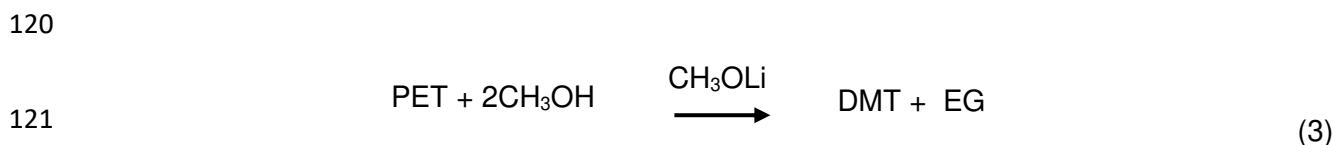
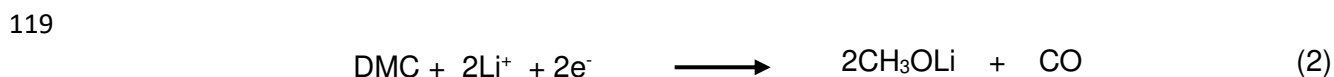
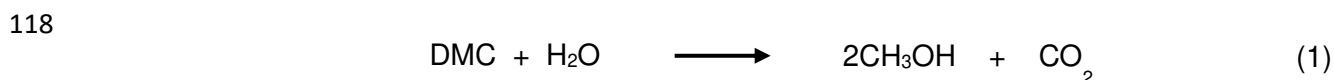
93 **Figure 3.** (a) Capacity retention of LFP/graphite pouch cell cycling at 70 °C and C/3 (C/20 check-
94 up cycles every 50 cycles) with 1.5M LiFSI EC:DMC (15:85) electrolyte plus 2% VC, 1% MMDS,
95 and 1% TTSPi additives. (b) FTIR spectra of PET tapes extracted from the pouch cell after 275
96 cycles show that the tape on the anode side is visually discolored, and many of the FTIR peaks
97 have either split or disappeared, indicating the decomposition of PET. On the other hand, the tape
98 on the cathode side looks like the pristine cathode tape shown in Fig. 2d, and the FTIR spectrum
99 matches well with the reference spectrum. Capacity retention of NMC622/graphite pouch cell
100 cycling at 40 °C and C/3 (C/20 check-up cycles every 50 cycles) with 1.5M LiPF₆ EC:EMC:DMC
101 (25:5:70) electrolyte plus 2% VC and 1% DTD additives. (d) FTIR spectrum of PET tape extracted

102 after 500 cycles shows that it is severely degraded after cycling, and much of it has visually
103 dissolved in the middle of the cell, whereas the tape on the edges is fully intact after cycling.

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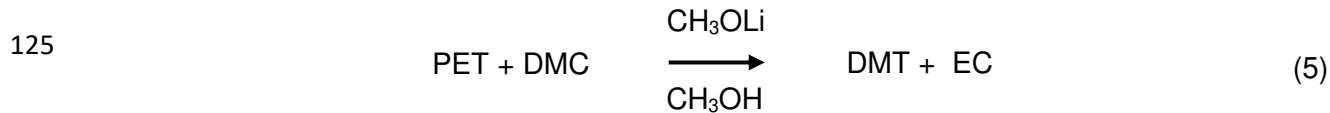
105 *The reaction path of PET decomposition*

106 Tanaka et al.⁸ have demonstrated in the context of waste recycling that PET can be depolymerized
107 with methanol and lithium methoxide. In lithium-ion cells, both methanol and lithium methoxide
108 can be generated *in situ* from DMC (Scheme S1). Methanol is a product of DMC hydrolysis (1),
109 and a common manufacturing impurity⁹; lithium methoxide can be formed by DMC reduction at
110 the unpassivated negative electrode (2).^{10,11} When reacting with PET, methanol dissociates into a
111 proton and a methoxide anion, which attacks the electrophilic reaction center of PET (Scheme S2).
112 This cleaves the ester bonds of the PET polymer, creating the DMT monomer and ethylene glycol
113 (EG) from reaction with the adjoining proton, thus effectively depolymerizing PET (3). Ethylene
114 glycol then reacts with DMC, producing ethylene carbonate (EC) with a stable cyclic structure,
115 making the reaction path virtually irreversible (4). The sum reaction shows that methanol and
116 lithium methoxide are not consumed, and only catalytic quantities are needed to induce the reaction
117 of PET and DMC to DMT and EC (5).



123

124 **Sum reaction:**

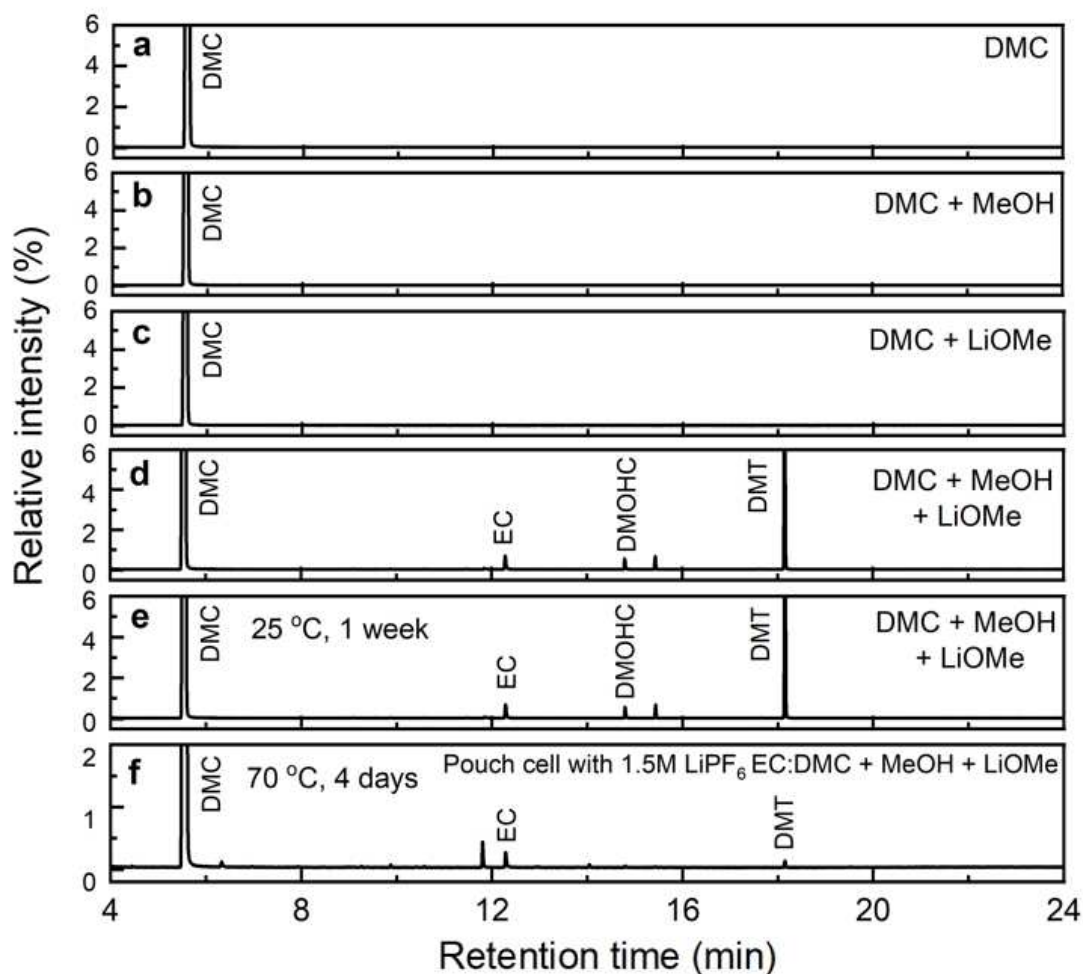


127 *Chemical stability screening of jellyroll tapes*

128 To test the proposed PET decomposition mechanism, PET tape was placed in a pouch bag with
129 mixtures of DMC, 2 wt% lithium methoxide, and 10 wt% methanol, sealed and kept at 70 °C for
130 5 h (Fig. S1). Subsequently, the liquid mixture was extracted and analyzed by GC-MS (Fig. 4).
131 Figs. 4a-c show that DMC alone and single combinations of DMC with lithium methoxide or
132 methanol do not depolymerize PET and the only component found by GC-MS is DMC (note that
133 lithium methoxide is extracted with the aqueous phase, and methanol is either all consumed in the
134 reaction or not visible in the retention time range used in this study, see Methods). Fig. 4d shows
135 that PET tape dissolves and DMT is created when DMC, lithium methoxide, and methanol are
136 added. In addition to DMT, EC is generated, further confirming the proposed reaction path shown
137 above. Interestingly, ethylene glycol bis-(methyl carbonate) (DMOHC) is produced from the *in*
138 *situ* generated EC reacting with DMC (Scheme S3).¹² Like the PET depolymerization, this
139 dimerization reaction is also catalyzed by lithium methoxide. DMOHC formation consumes EC,
140 which explains why there is less EC than DMT in Fig. 4d, even though they should be produced
141 in equal amounts according to the proposed PET depolymerization mechanism (3). Fig. 4e shows
142 that PET also depolymerizes at room temperature when DMC, lithium methoxide, and methanol
143 are added, and the pouch bag is stored for 1 week. Similar amounts of DMT, EC and DMOHC are
144 formed as in the experiment at 70 °C, thus PET depolymerization does not need elevated
145 temperature. Note that the analogous depolymerization reaction of PET with ethanol and lithium

146 ethoxide from diethyl carbonate (DEC) produces diethyl terephthalate (DET), which is another
147 proof that the proposed mechanism is accurate (Fig. S2 and Scheme S4).

148 Fig. 4f shows an analogous experiment with an LFP/graphite pouch cell that contained PET
149 jellyroll tape (Fig. 2). The cell was filled with 2 mL of 1.5M LiPF₆ in DMC electrolyte, 0.5 wt%
150 of lithium methoxide and 0.5 wt% of methanol, which are closer (but still very much in excess) to
151 the concentrations of these species in real lithium-ion cells.¹¹ The pouch cell was kept at 70 °C for
152 four days – the time of a standard formation protocol (see Methods, note that the temperature is
153 higher than typical formation temperatures). Afterwards, the cell was opened, and the electrolyte
154 was analyzed by GC-MS. The obtained spectrum (Fig. 4f) shows the same compounds as the
155 corresponding pouch bag test (Fig. 4d), but in smaller concentrations. A clear signal is obtained
156 for the DMT redox shuttle confirming its *in situ* generation from PET tape decomposition. This
157 simple screening experiment unambiguously proves that PET depolymerization is a chemical
158 rather than an electrochemical reaction and elevated temperature or voltage are not needed for the
159 reaction to occur (Fig. 4e). Note, however, that methanol generation from DMC hydrolysis (1)
160 does require elevated temperature >40 °C to proceed at significant rates⁹, and lithium methoxide
161 generation from DMC reduction (2) is an electrochemical process that can only happen when the
162 negative electrode is not passivated with a well-insulating SEI layer.¹³



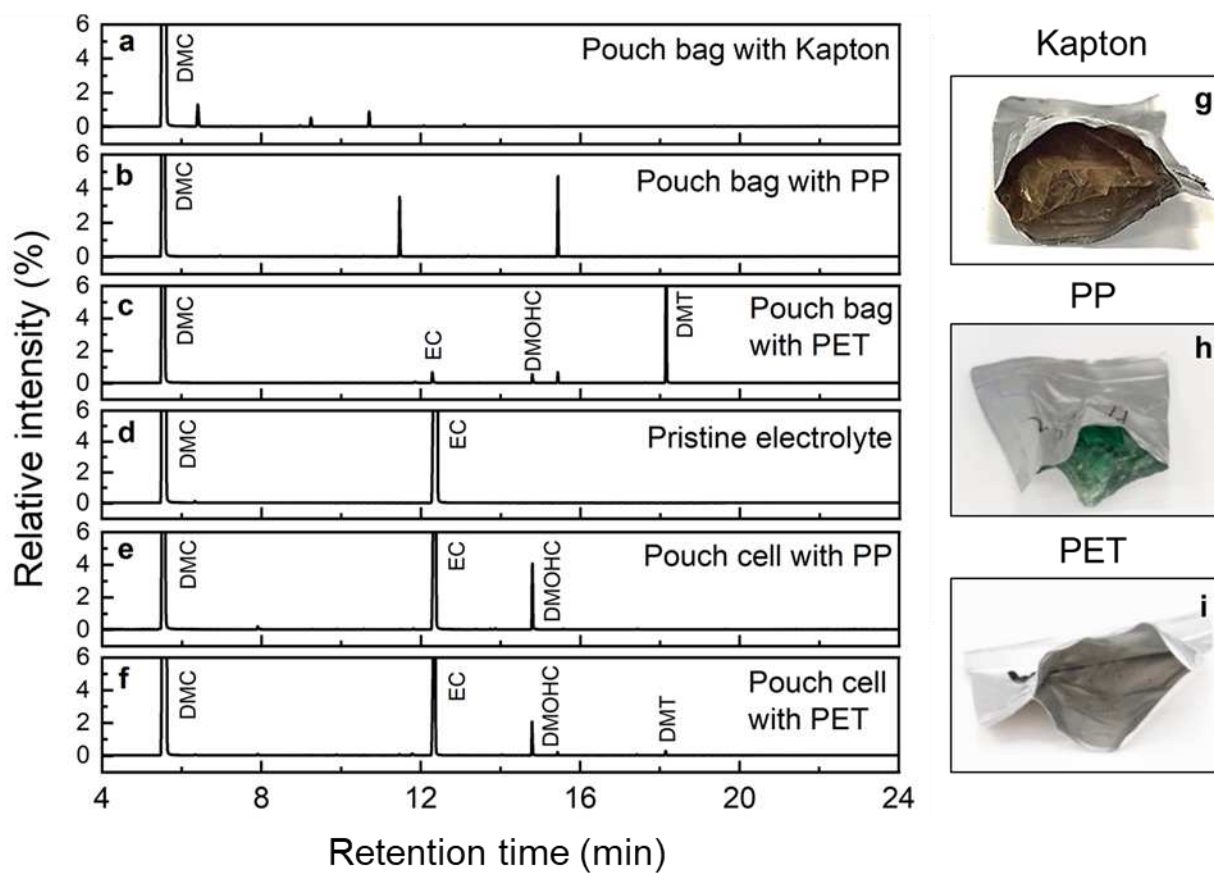
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164 **Figure 4.** GC-MS spectra of liquid mixtures extracted from pouch bags with PET tape and
 165 combinations of DMC, 2 wt% MeOH, and 10 wt% LiOMe (0.5 wt% MeOH and LiOMe for pouch
 166 cell in panel f). The pouch bags were kept at 70 °C for 5 h, unless otherwise specified. All three
 167 reactants, i.e., DMC, MeOH and LiOMe, are needed, to depolymerize PET into DMT.

168

169 Next, the chemical screening method is used to find alternative polymers that do not dissolve in
 170 lithium-ion cells. Scheme S5 shows that neither polypropylene (PP) nor polyimide (Kapton) has
 171 ester bonds that could be cleaved by lithium methoxide or methanol. Therefore, tapes made from
 172 these polymers should be immune to the depolymerization mechanism described above. To
 173 confirm this hypothesis, PP and Kapton tapes were tested in pouch bags with DMC, lithium

174 methoxide, and methanol at 70 °C for 5 h, followed by GC-MS analysis of the liquid mixtures.
175 Figs. 5a-c show no DMT redox shuttle in pouch bags with Kapton and PP, but a clear DMT signal
176 with PET. Other peaks in the GC-MS spectra correspond mainly to acrylics or silicon compounds,
177 often used as tape adhesives.¹⁴ Figs. 5g-i show that PP and Kapton tapes are intact, whereas PET
178 tape has fully dissolved after 5 h at 70 °C. Kapton has a significantly higher cost than PP,¹⁵ and its
179 polyimide group has been found to cause a notable increase in irreversible capacity loss when in
180 contact with the negative electrode¹⁶. PP is already common in many battery separators, hence, PP
181 tape is used in the following to replace PET tape in custom LFP/graphite pouch cells. Figs. 5e and
182 f show GC-MS spectra of electrolytes extracted from LFP/graphite pouch cells with PP and PET
183 jellyroll tape, respectively, after formation at 70 °C with 1.5M LiPF₆ in EC:DMC (3:7) electrolyte
184 (CTRL). The DMT redox shuttle was only produced when PET tape was used (Fig. 5f), not when
185 PP tape was used (Fig. 5f).⁷ Interestingly, DMOHC is found regardless of the jellyroll tape, which
186 implies that lithium methoxide is generated in both cases, but only in the presence of PET can it
187 yield the DMT redox shuttle. The higher chemical stability of PP tape in lithium-ion cells should
188 lead to lower self-discharge rates and higher coulombic efficiency especially in the absence of
189 additives.



190

191 **Figure 5.** GC-MS spectra of liquid mixtures extracted from pouch bags with Kapton (a), PP (b)
 192 and PET tape (c) in DMC, 10 wt% MeOH and 2 wt% LiOMe. After 5 h at 70 °C PET tape has
 193 fully dissolved (i), whereas PP (h) and Kapton tapes are intact (g). Also, GC-MS spectra of pristine
 194 1.5M LiPF₆ EC:DMC (3:7) electrolyte (d), extracted electrolyte from LFP/graphite pouch cell with
 195 PET tape (e) and PP tape (f). The cells were formed at 70 °C and kept at room temperature for 1
 196 week before extracting the electrolyte.

197

198 *Improving lithium-ion cells by replacing PET with PP tape*

199 Figs. 6a-c show the voltage vs time curves of fully charged LFP/graphite cells with PET or PP
 200 jellyroll tape during 500 h of storage at 40 °C or 60 °C after formation at 40 °C or 70 °C. The self-
 201 discharge rates of these cells can be inferred from the decay in open circuit voltage (OCV).¹⁷ In
 202 the absence of electrolyte additives, cells with PP jellyroll tape (Fig. 6c) show significantly slower

203 self-discharge than cells with PET tape (Figs. 6a,b). When 2% VC is added all cells show very
204 slow self-discharge (dashed lines in Figs. 6a-c).

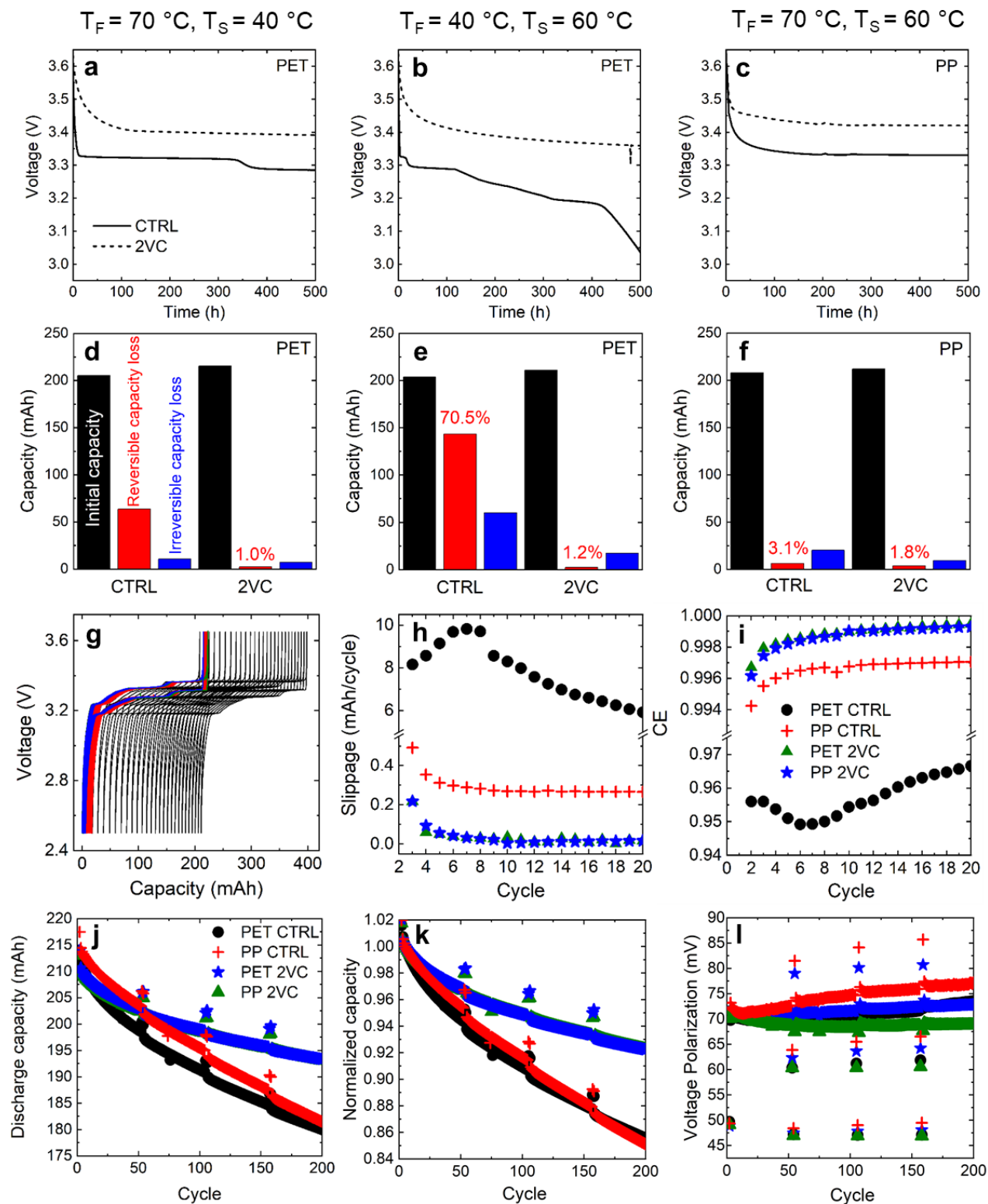
205 Figs. 6d-f show the reversible (red) and irreversible storage losses (blue) obtained by recharging
206 the cells and comparing the discharge capacity after storage to the initial discharge capacity
207 (black). Cells with CTRL electrolyte and PET tape formed at 70 °C and stored at 40 °C lost one
208 third of their capacity, and the majority of the storage losses are reversible since they originate
209 from the *in situ* generation of the DMT redox shuttle from PET tape. After 40 °C formation and
210 60 °C storage the PET CTRL cells have completely self-discharged and 70% of the storage losses
211 are reversible. In contrast, cells with CTRL electrolyte and PP tape formed at 70 °C and stored at
212 60 °C (i.e., a combination of the harshest conditions) still retained ~90% of their initial capacity.
213 Interestingly, the reversible capacity loss is almost completely eliminated in cells with PP tape
214 (only 3%), even without electrolyte additives (Fig. 6f), which underlines the stability of the PP
215 polymer and the absence of a redox shuttle. When 2% VC is added, both, reversible and
216 irreversible losses become very small for all cells, since the well-insulating VC-derived SEI
217 prevents the formation of lithium methoxide and thus the decomposition of PET tape as well as
218 other parasitic reactions.⁷

219 Figs. 6g-i show ultra-high precision coulometry results for LFP/graphite pouch cells with PET and
220 PP tapes formed at 70 °C and cycled 40 °C. Cells with CTRL electrolyte and PET tape (black)
221 show a clear slippage of the voltage curves of up to 10 mAh per cycle (Figs. 6g,h), due to the
222 DMT-induced self-discharge during cycling. In cells with PP tape (red) this parasitic reaction is
223 absent, thus there is virtually no charge endpoint capacity slippage and an overall higher coulombic
224 efficiency during cycling (Fig. 6i). Cells with 2% VC (blue and green) show even less slippage

225 and higher coulombic efficiency due to an improved passivation of the negative electrode. The
226 well-insulating VC-derived SEI has also been shown to prevent DMT from shuttling.¹⁹

227 Figs. 6j-l show corresponding long-term cycling tests at C/3 and 70 °C. In the absence of additives,
228 cells with PP jellyroll tape show similar capacity retention to cells with PET tape, confirming that
229 the use of PP does not induce new unwanted side reactions. Cells with 2% VC outperform the
230 additive-free cells due to a superior passivation of the negative electrode, which prevents lithium
231 loss – the major aging mechanism in high temperature LFP/graphite cells as shown by Logan et
232 al.¹⁸ Since most commercial cells use SEI-forming additives like VC, one could infer that the use
233 of PET is unproblematic, even if it depolymerizes into the DMT redox shuttle. However, previous
234 studies have shown that VC and other SEI forming additives can be consumed during cycling.^{20,21}

235 It is likely that additive consumption in heavily cycled cells would correlate with a deterioration
236 of the SEI layer, the formation of alkoxides from reduction of linear carbonates, and subsequent
237 decomposition of PET tape (Fig. 3). **In order to eliminate the root cause of redox shuttle**
238 **generation from tape decomposition, it is recommended that lithium-ion cell producers**
239 **replace PET jellyroll tape with chemically stable PP tape.**



240

241 **Figure 6.** Voltage vs time profiles of LFP/graphite pouch cells with PET tape formed at $T_F = 70$
 242 $^\circ\text{C}$ and stored at $T_S = 40\text{ }^\circ\text{C}$ (a), with PET tape formed at $40\text{ }^\circ\text{C}$ and stored at $60\text{ }^\circ\text{C}$ (b), and with

243 PP tape formed at 70 °C and stored at 60 °C (c). The corresponding bar graphs (d-e) show initial
244 capacity, reversible capacity loss and irreversible capacity loss. UHPC cycling profiles (g), charge
245 endpoint capacity slippage (h), and Coulombic efficiency (CE) (i) for LFP/graphite cells with
246 either PET or PP tape. Cells were formed at 70 °C and transferred to the UHPC system at 50%
247 SOC. All UHPC data was recorded at C/20 and 40 °C from 2.5 to 3.65 V. The CTRL electrolyte
248 was 1.5M LiPF₆ in EC:DMC (3:7). CTRL electrolyte with 2% VC is marked as 2VC. Discharge
249 capacity (j), normalized capacity (k), and the voltage polarization (l) of LFP/graphite pouch cells
250 with either PP or PET tape, formed at 40 °C and cycled at 70 °C with a current of C/3. The CTRL
251 electrolyte was 1.5M LiFSI in EC:DMC (15:85). CTRL electrolyte with 2% VC is abbreviated as
252 2VC.

253

254 *Outlook*

255 This study has shown the generation of the unwanted DMT redox shuttle from the chemical
256 decomposition of PET jellyroll tape, which is used by many well-known lithium-ion cell
257 manufacturers. DMT is responsible for significant reversible self-discharge of additive-free
258 LFP/graphite cells. Replacing PET with PP jellyroll tape resulted in slightly better capacity
259 retention, higher Coulombic efficiency and almost a complete elimination of reversible self-
260 discharge, even in additive-free cells. Cell manufacturers should replace PET tape with PP tape in
261 order to eliminate any parasitic reactions from this long overlooked, supposedly inactive cell
262 component.

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318 **Methods**

319 *Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)*

320 All FTIR spectra were collected in an Ar-filled glovebox using a Cary 630 FTIR spectrometer
321 equipped with a Ge crystal ATR accessory. MicroLab PC software was used to collect the data
322 with a resolution of 4 cm⁻¹. The polymer films used in this study were cleaned with dry antistatic
323 tissue to remove any impurities before the measurement.

324 *Pouch bag experiments*

325 Small pockets containing either PET or PP tape were prepared from battery-grade pouch foil with
326 a heat sealer. The pouch bags were filled with 2-3 mL dimethyl carbonate (DMC) containing 10%
327 methanol (MeOH) and 2% lithium methoxide (LiOMe) in an Ar-filled glovebox, heat-sealed, and
328 placed into a 70 °C temperature box for 5 h. Pouch bags with pure DMC or DMC with just MeOH
329 or LiOMe were also tested, so were full lithium-ion pouch cells with these reactants. Some pouch
330 bags were not heated but stored at room temperature for one week. All pouch bags were opened,
331 the liquid mixture was extracted, and analyzed in a gas chromatograph connected to a mass
332 spectrometer.

333 *Electrolyte preparation*

334 The control electrolyte (CTRL) in this study was 1.5M lithium hexafluorophosphate (LiPF₆) in a
335 3:7 (w/w) ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC). Other electrolyte
336 formulations contained lithium bis(fluorosulfonyl)imide (LiFSI), ethyl methyl carbonate (EMC),
337 vinylene carbonate (VC), 1,3,2-Dioxathiolane 2,2-Dioxide (DTD), methylene methane disulfonate
338 (MMDS, >98.7% Tinci Materials Technology) or tris(trimethylsilyl) phosphite (TTSPi, >95%
339 Sigma-Aldrich). All solvents and salts had <20 ppm water, were used as-received from Shenzhen
340 Capchem (China) unless specified otherwise and were mixed in an Ar-filled glovebox.

341 *Pouch cells*

342 402035-sized 220 mAh LiFePO₄/graphite pouch cells with PET and PP jellyroll tapes were
343 obtained vacuum sealed without electrolyte from LiFUN Technologies (China). The cells were cut
344 open in an Ar-filled glovebox, dried at 140 °C under vacuum for 14 h, filled with 1 mL of
345 electrolyte, and re-sealed under vacuum at -90 kPa gauge pressure. The stacked NMC622/graphite
346 cell shown in Fig. 3c,d was obtained from a reputable cell manufacturer.

347 *Formation protocol*

348 All cells were charged to 1.5 V and then underwent a 16 h voltage hold to ensure wetting of the
349 electrode pores with electrolyte while avoiding dissolution of the copper current collector. Then
350 the cells completed a single C/20 formation cycle between 2.5 and 3.65 V and a C/10 recharge to
351 50% SOC on a Maccor 4000 series charger at 40 or 70°C.

352 *Gas chromatography-mass spectrometry (GC-MS)*

353 GC-MS protocol and instrumentation was the same as described by Petibon et al.¹¹ Pouch cells
354 were filled with 1 mL of methyl acetate (MA), resealed, and kept at room temperature for 1 week
355 to ensure full equilibration of electrolyte components, MA, and any reaction products in the

356 jellyroll. Similar to Petibon et al.¹¹ 0.2 mL of water was added to the mixture of CH₂Cl₂ and
357 electrolyte for salt removal. After shaking and resting for 5 min, the aqueous layer was removed
358 with a syringe, MgSO₄ was added to bind residual water, and the organic layer consisting of
359 organic electrolyte components in CH₂Cl₂ was injected into the GC-MS.

360 *Long-term cycling protocols*

361 After formation, the cells were cut open in an Ar-filled glovebox for degassing, resealed under
362 vacuum, and brought to a Neware (China) or Novonix (Canada) system for cycling at 40 or 70 °C
363 in constant current constant voltage mode with a C/3 rate for charge and discharge as well as a
364 C/20 “check-up cycle” every 50 cycles. Pair cells were made for every test condition.

365 *Self-discharge experiments*

366 To characterize the rate of self-discharge, open circuit voltage (OCV) storage experiments were
367 conducted at 40 and 60 °C as described by Sinha et al.¹⁶ After formation, the cells completed two
368 full charge/discharge cycles at C/10 to precisely determine the initial discharge capacity (D₀),
369 followed by a full charge to the upper cut-off potential of 3.65 V and a constant voltage hold for
370 10 h and a 500 h OCV storage period. Subsequently, the cells were discharged (D₁), charged, and
371 discharged again (D₂) at C/10 rate to determine the irreversible (D₀-D₂) and reversible capacity
372 loss (D₂-D₁) during storage.

373 *Ultra-high precision coulometry (UHPC)*

374 Charge endpoint capacity slippage and coulombic efficiency (CE) were measured on the UHPC
375 system at Dalhousie University described by Bond et al.²² The cells were cycled at 40 °C and C/20
376 from 2.5 to 3.65 V. Pair cells were made for every test condition.

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384 **Author contributions**

385 A.A. designed and carried out experiments, analyzed the data, conceived the PET
386 depolymerization mechanism in cells, and wrote the paper. K.T. assisted with all UHPC and
387 storage measurements and data analysis. T.B. co-designed and carried out the pouch bag
388 experiments. S. A. performed long cycling on cells with PET tape and developed the method for
389 electrolyte extraction used in the study. M.D.L.G. performed long cycling on cells with PET tape.
390 M.M. provided supervision and guidance and edited the manuscript.

391 **Competing Interests Declaration**

392 The authors declare no following competing interests.

393 **Additional Information**

394 Supplementary Information is available for this paper.

395 Correspondence and requests for materials should be addressed to michael.metzger@dal.ca.

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