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Electrolyte oxidation pathways in lithium-ion batteries

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Abstract

The mitigation of decomposition reactions of lithium-ion battery electrolyte solutions is of critical importance in controlling device lifetime and performance. However, due to the complexity of the system, exacerbated by the diverse set of electrolyte compositions, electrode materials, and operating parameters, a clear understanding of the key chemical mechanisms remains elusive. In this work, operando pressure measurements, solution NMR, and electrochemical methods were combined to study electrolyte oxidation and reduction at multiple cell voltages. Two-compartment LiCoO₂/Li cells were cycled with a lithium-ion conducting glass-ceramic separator so that the species formed at each electrode could be identified separately and further reactions of these species at the opposite electrode prevented. One principal finding is that chemical oxidation (with an onset voltage of ~4.7 V vs Li/Li⁺ for LiCoO₂), rather than electrochemical reaction, is the dominant decomposition process at the positive electrode surface in this system. This is ascribed to the well-known release of reactive oxygen at higher states-of-charge, indicating that reactions of the electrolyte at the positive electrode are intrinsically linked to surface reactivity of the active material. Soluble electrolyte decomposition products formed at both electrodes are characterised, and a detailed reaction scheme is constructed to rationalise the formation of the observed species. The insights on electrolyte decomposition through reactions with reactive oxygen species identified through this work have direct impact on understanding and mitigating degradation in high voltage/higher energy density LiCoO₂-based cells, and more generally for cells containing nickel-containing cathode materials (e.g. LiNi_xMn_yCo_zO₂; NMCs), as they lose oxygen at lower operating voltages.

Introduction

A major challenge in lithium-ion battery (LIB) research is to find ways to improve energy density without compromising cell lifetime or safety. Many improvements have been made through optimisations of cell manufacturing and geometry,¹ although for further improvements as design limits are approached it becomes necessary to alter the cell chemistry or operating parameters. Two strategies that attract considerable industry and academic interest involve raising the upper cut-off voltage of the cell and increasing the nickel content in the positive electrode material (usually a layered transition metal oxide, *e.g.* LiCoO₂; LCO or LiNi_xMn_yCo_zO₂; NMC). A higher cut-off voltage allows for more Li⁺-ions to be extracted from the same mass of active material, due to the sloping voltage profile of these materials, and a higher nickel content allows for more Li⁺-ions to be extracted at a given voltage compared to NMC electrode with a lower nickel content.² However, going to a higher voltage, and thus to a higher state-of-charge (SOC), leads to rapid capacity fading, which limits the cycle life of the cell.^{3,4} This is often ascribed to degradation at the positive electrode, including reconstruction of the surface layers and concomitant loss of lattice oxygen and transition metal dissolution, and decomposition of the electrolyte.⁵⁻⁸

LiCoO₂ remains the highest energy density cathode material and a commercially relevant cathode material for portable electronic devices, particularly mobile phones where energy density (rather than cost) is paramount. There is considerable industry and academic desire to increase the operational voltages to improve energy density for the development of so-called 'HV-LCO' cells (*i.e.* > 4.6 V vs. Li/Li⁺).⁹ For example, a ~40% increase in energy density can be achieved by simply charging a LiCoO₂ cathode to 4.6 V vs Li/Li⁺ rather than 4.3 V vs Li/Li⁺.¹⁰ A major research focus involves modifying the cathode-electrolyte interface, for example with surface coatings and electrolyte additives.^{11,12} Nonetheless, the chemical reactions and mechanisms at this interface are not well understood, posing a major hurdle for research efforts and for the rational design of electrolytes and electrolyte additives.

The direct and indirect consequences of electrolyte oxidation can negatively impact cell behaviour and lifetime in a variety of ways. The evolution of gaseous decomposition products can cause swelling or rupture of cell casings. Consumption of those evolved gases, deposition or further decomposition of the electrolyte decomposition products on either or both electrodes, as well as reactions of those species with the protective solid-electrolyte interphases (SEIs), and enhanced rates of transition metal dissolution can all lead to further irreversible capacity losses (as measured by electrode slippage) and slower interfacial kinetics (as measured by impedance).^{8,13-18} These and other processes related to electrolyte oxidation lead to decreased cell performance and lifetime.

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3 The observed decomposition of the electrolyte solution at high voltages is generally believed to
4 proceed via oxidation of the organic carbonate solvent at the positive electrode. This has
5 experimentally been shown to lead to the formation of CO₂, CO, and H₂O,^{3,19–21} from *operando*
6 measurements including differential electrochemical mass spectrometry (DEMS)²⁰ and online
7 electrochemical mass spectrometry (OEMS).^{3,19,21–24} Other studies have used *ex situ* measurements,
8 such as analysing the electrolyte by gas chromatography mass spectrometry (GC-MS)²⁵ or nuclear
9 magnetic resonance (NMR) spectroscopy²⁶ of the electrolyte, or X-ray photoelectron spectroscopy
10 (XPS) of the electrodes^{27–30} following cycling. There are also a variety of *in situ* and *operando*
11 techniques that examine changes at the full cell level, for example isothermal microcalorimetry has
12 been used to measure parasitic reaction rates and enthalpies^{2,31,32} and differential thermal analysis
13 (DTA) has been used to examine changes in salt concentration following cycling.³³ Finally, many
14 additional decomposition reactions and products have been proposed based on *ab initio*
15 calculations.^{34–36} These studies provide valuable information about electrolyte decomposition, but it
16 is difficult to conclusively identify individual reactions and chemical mechanisms.

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18 It has been widely reported that electrolyte oxidation occurs electrochemically at the surface of both
19 the active material and the conductive carbon particles.^{20,22} There is evidence that the onset of
20 Faradaic oxidation reactions only occurs at electrode potentials greater than ~4.8 vs Li/Li⁺, which is
21 higher than to those expected in normal lithium-ion cell operation.^{37,38} However, a wide range of
22 electrode potentials for electrolyte decomposition have been reported in the literature.³⁹ It has also
23 been suggested that electrolyte decomposition is related to the release of reactive oxygen species
24 from the transition metal oxide lattice.^{40–44} Recent work by Gasteiger and co-workers suggests that
25 highly reactive lattice oxygen species are released as singlet oxygen into the electrolyte at high SOC
26 that *chemically* oxidise the electrolyte.^{3,8,21,23} This oxygen release occurs at lower electrode potentials
27 than are required for Faradaic oxidation to occur and, thus, are suggested to be the dominant pathway
28 for electrolyte oxidation in most lithium-ion cell designs. It is noteworthy that electrolyte oxidation
29 and decomposition of the cathode material are intrinsically linked processes in this proposed
30 mechanism. However, challenges remain to fully understand the chemical reactions that occur within
31 cells. It would be valuable to develop a deeper understanding of chemical and electrochemical
32 oxidation, for example by measuring their relative rates in a variety of cell chemistries or at different
33 voltages. Furthermore, there is relatively limited understanding of the soluble decomposition
34 products that are produced under various cell operating conditions.

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36 A principal goal of the present work is to prepare a simplified, yet detailed summary of the myriad of
37 processes that occur in support of a deeper understanding of how degradation occurs in a variety of
38 cell designs and usage scenarios. The approach here adopted is to examine the wealth of published
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3 results that have been reported in conjunction with a series of new experiments to bridge gaps and
4 to answer specific questions in the literature. Generally, the chemical processes occurring at the SEI
5 and in the electrolyte at the anode surface are better understood and have been reviewed,⁴⁵ whereas
6 considerably less is known about the reactions at the cathode and the interplay between electrodes.
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8 In this work, the electrolyte decomposition products formed at each electrode individually were
9 characterised by solution NMR spectroscopy and then used to infer the primary reactions that take
10 place at each electrode. Separation of the electrolyte was achieved by using a lithium-ion conducting
11 glass-ceramic separator, which prevents the migration of decomposition products in the electrolyte
12 to the opposite electrode. This approach has been used previously by Gasteiger and colleagues to
13 study gas-phase decomposition products, and it has been shown that with careful construction, the
14 glass-ceramic is an effective barrier for cross-migration.^{19,22,23,46}

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22 First, the onset potential for electrolyte oxidation at the positive electrode was determined via
23 operando pressure measurements. In situ gas volume measurements using polymer laminate pouch
24 cells have shown that gas produced at low cell voltages is primarily due to SEI formation and reactions
25 at the negative electrode, whereas the evolution of gas at high cell voltage correlates to electrolyte
26 oxidation at the positive electrode.⁴⁷

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28 Subsequently, two LiCoO₂/Li cells with a lithium-ion glass ceramic were cycled to below and above the
29 onset potential for electrolyte oxidation, as determined from the operando gas experiment, and the
30 electrolytes from both sides of the cell were analysed by solution NMR to identify any decomposition
31 products that formed. Solution NMR spectroscopy was chosen as the main analytical method in this
32 work because it provides considerable chemical and bonding information for several prominent
33 elements in electrolyte solutions (H, C, F, P) and, although data interpretation is nuanced and often
34 challenging, NMR is often suitable for the study of complex mixtures with low concentration
35 components. The decomposition products observed in the LiCoO₂/Li cells were compared with those
36 formed through electrolysis of electrolyte, to gain insights into the oxidation mechanism
37 (electrochemical or chemical oxidation). Finally, a unified reaction scheme is presented that considers
38 primary processes at each electrode and secondary reactions that incorporate 'cross-talk' resulting
39 from movement of gaseous products between electrodes.
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Experimental

Electrodes and electrolytes

LiCoO₂ electrodes were prepared by grinding LiCoO₂ powder (Alfa Aesar, 99.5%, ~5 μm), Super P carbon nanoparticles (Timcal) and Kynar polyvinylidene difluoride (PVDF, Arkerma) in an 8:1:1 mass ratio with an agate mortar and pestle. *N*-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, 99.5%, anhydrous) was added to form a slurry, which was blade-coated at a wet film thickness of 300 μm on an aluminium foil current collector. The films were dried at 65 °C in ambient atmosphere for 12 hours. Disks of the desired size were cut (active material loading of ~1 mg cm⁻²), dried further at 100 °C under vacuum for 24 hours, and then transferred to an argon-filled glovebox (MBraun, Germany; O₂ and H₂O < 0.1 ppm). In all experiments, a 1.0 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) electrolyte (LP30; EC:DMC=50:50 (v/v), Sigma-Aldrich, battery grade) was used.

Two-compartment cells

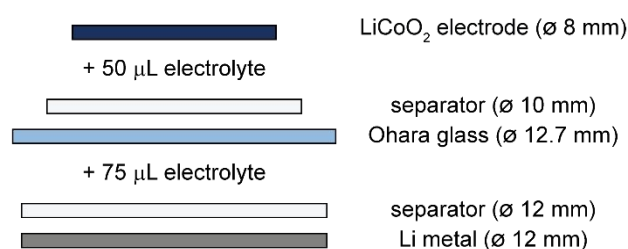
LiCoO₂/Li cells were assembled in a two-compartment half-inch inner-diameter Swagelok cell as shown in Figure 1a. Lithium metal was chosen as the negative electrode instead of graphite, as it provides a more stable reference potential for studying oxidation reactions at the positive electrode. A lithium-ion conducting glass-ceramic (Ohara, Japan) was placed between two borosilicate glass fibre separators (Whatmann, GF/B, 0.68 mm thick, 1.0 μm pore size), so that the species formed at each electrode could be identified separately and so further reactions of these species at the opposite electrode are prevented. A borosilicate glass fibre separator was used instead of a polymer separator, as it is able to hold more electrolyte solution, providing enough sample for further analysis. Furthermore, this type of separator provides some cushioning and protects the lithium-ion conducting glass-ceramic from breaking, avoiding electrolyte leakages between the two compartments. To further prevent mixing of the electrolytes, the electrodes and separators were punched to smaller diameters than the glass-ceramic, the separators were wetted with only the minimal amount of electrolyte, and the cells were kept upright to prevent leakage of the electrolyte around the edges of the glass-ceramic. The LiCoO₂/Li cells were assembled as follows: a lithium metal foil disk (Ø 12 mm; Aldrich, 99%) was placed on the anode current collector at the base of the cell, covered with a borosilicate glass fibre separator (Ø 12 mm) and wetted with 75 μL of electrolyte. The glass-ceramic (Ø 12.7 mm) was then carefully placed and gently pressed onto the separator, to ensure good contact between with the glass fibre separator and the ceramic. Another, slightly smaller, glass fibre separator (Ø 10 mm) was placed in the centre of the glass-ceramic and wetted with 50 μL of electrolyte and a LiCoO₂ electrode (Ø 8 mm) was placed on top. A cathode current collector/plunger was added to seal

the cell, which was then gently tightened to avoid breaking the brittle glass-ceramic. All cell assembly was performed in an argon-filled glovebox.

Electrochemical measurements

Electrochemical measurements were performed using a Biologic MPG2 potentiostat/galvanostat instrument running EC-lab software. The LiCoO_2/Li cells were galvanostatically charged and discharged at C/5 (based on the practical capacity of $\text{LiCoO}_2 = 140 \text{ mAh g}^{-1}$) between 3.0–4.6 V or 3.0–4.9 V (vs Li/Li^+) for 10 cycles. A modest cycling rate was chosen to avoid experimental complications that can occur at higher cycling rates, such as ionic concentration gradients and large overpotentials.

a) half-inch Swagelok cell



b) one-inch Swagelok cell

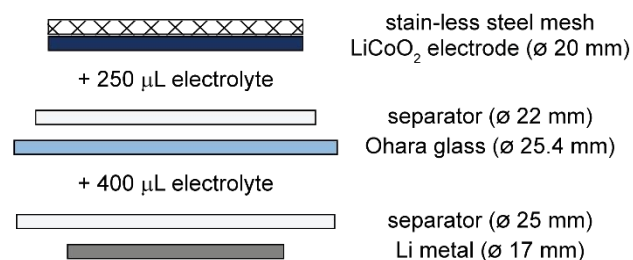


Figure 1. Schematic illustration of the assembly of the a) half-inch and b) one-inch two-compartment electrochemical cells with a lithium-ion conducting glass ceramic (Ohara glass) between two porous borosilicate glass fibre separators.

Operando pressure measurements

The onset potential for gas evolution at the cathode was determined by measuring the internal cell pressure as a function of the voltage. A two-compartment setup with a lithium-ion conducting glass-ceramic was used to inhibit cross-migration of species between the electrode compartments. LiCoO_2/Li cells were assembled in a two-compartment one-inch Swagelok cell, in a similar way as described above, except larger electrodes (\varnothing 17 mm lithium metal foil disk and \varnothing 20 mm LiCoO_2 electrode), separators (\varnothing 25 and 20 mm) and more electrolyte (400 μL for the anode and 250 μL for the cathode) were used in the one-inch Swagelok setup (Figure 1b). A stainless-steel mesh was placed on top of the LiCoO_2 electrode to ensure electrical contact between the cathode and lithium metal anode, while simultaneously allowing for any formed gases to diffuse into the headspace.

The Swagelok cell was connected to an Omega (PX309-030A5V) pressure sensor to measure changes in the internal pressure of the cell. After a 12-hour rest at open circuit voltage (OCV) to allow the baseline pressure to stabilise, the cell was charged to a series of target voltages in steps of 0.1 V and ranging from 4.2 V to 5.0 V. For each cut-off voltage, the cell was first charged at C/5, held at the target voltage for 10 hours, and then allowed to rest at open circuit for one hour. This series was then

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3 repeated for each target voltage in the series. The measurements were performed at 25 °C in a
4 temperature-controlled environment.
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6 7 *Electrolysis of electrolyte (H-cell experiments)* 8

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10 An H-cell was used to electrolyse the electrolyte, so that the species formed through electrochemical
11 oxidation could be compared to the degradation products formed inside the LiCoO₂/Li cells. A glass H-
12 cell with two compartments separated by three separators (Celgard 2400), in order to limit convective
13 mixing between the two halves, was filled with 6 mL of electrolyte (LP30; 1 M LiPF₆ in EC:DMC=50:50
14 (v/v) in each compartment. A Pt wire (working electrode, 5 cm) and a Ag/AgCl (saturated KCl in
15 acetonitrile) electrode (reference electrode) were placed in one half and a stainless-steel mesh
16 (counter electrode, approx. 2 cm × 6 cm) was placed in the other (Figure S 1). The H-cell components
17 were dried for several hours at 60 °C and transferred while still hot into an argon-filled glovebox,
18 where all assembly and electrochemical measurements were performed. Each compartment was
19 covered with parafilm to prevent evaporation of the electrolyte. Electrochemical measurements were
20 conducted using a Biologic SP-150 potentiostat/galvanostat. A current of 10 mA was applied for 30
21 minutes (i.e., 5 mAh), after which 0.1 mL of electrolyte was taken from each side to be analysed by
22 solution NMR.
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24
25 After 30 min electrolysis, the level of fluid in the positive electrode compartment was observed to
26 have decreased by about a third (~2 mL) while the level of fluid in the negative electrode compartment
27 was observed to have risen by the same amount.
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29 30 *Electrolyte hydrolysis* 31

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33 To understand what electrolyte decomposition products form through the hydrolysis of the
34 electrolyte solution, LP30 electrolyte (1 M LiPF₆ in EC:DMC =50:50 v/v) was prepared with 10% water
35 (v/v %) and stored for 2 months in an air-tight polypropylene container. A control electrolyte was
36 stored under the same conditions and 0.1 mL was taken from each electrolyte solution for
37 characterisation by solution NMR.
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39 40 *Solution NMR* 41

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43 After cycling the LiCoO₂/Li cells, the cells were disassembled in an argon-filled glovebox and the glass
44 fibre separator was soaked in 0.7 mL of DMSO-d₆ (Aldrich, 99.9 atom % D, 99% CP) for 5 minutes. The
45 solution was transferred to an airtight NMR tube fitted with a Young's tap.
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47
48 One-dimensional ¹H, ¹⁹F{¹H}, ³¹P{¹H} NMR spectra and two-dimensional ¹H–¹H correlation
49 spectroscopy (COSY) and ¹H–¹³C heteronuclear single quantum coherence (HSQC) NMR spectra were
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3 recorded on a Bruker AVANCE III HD 11.7 T ($\omega_{1H} = 500$ MHz) spectrometer using a BBO probe. 1H and
4 ^{13}C spectra were internally referenced to DMSO- d_6 at 2.50 ppm (δ 1H) and 39.5 ppm (δ ^{13}C), ^{19}F and ^{31}P
5 spectra were internally referenced to $LiPF_6$ at -74.5 ppm (δ ^{19}F) and -145.0 ppm (δ ^{31}P).
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Results

Two-compartment cells:

Operando pressure measurement (1st charge):

A LiCoO₂/Li half-cell was charged while measuring the internal pressure of the cell, Figure 2 showing the time-dependent *operando* pressure data overlaid with the cell voltage. The cell pressure decreases slightly as the cell was charged up to 4.6 V, but between 4.6 – 4.7 V the pressure starts to rise noticeably, and keeps increasing as the cell was charged up to 4.9 V. The increase in cell pressure at high voltages (> 4.6 V) is attributed to the evolution of gaseous decomposition products at the positive electrode, which increases at higher voltages. The small decrease in cell pressure at low voltages is most likely due to a slow leakage of gases from the cell. The gas evolution from electrolyte decomposition at the negative (Li) electrode is assumed to be similar throughout the experiment and therefore does not explain the increase in cell pressure at the end of charge: Initially, the lithium metal surface becomes passivated with an SEI through the reduction of electrolyte when the cell is assembled, leading to gas evolution that is expected to decrease rapidly as the SEI is formed. As the cell is charged, lithium ions are extracted from the positive electrode and plated (*i.e.*, reduced) at the negative electrode. The deposition of lithium ions can cause surface roughening and can include lithium metal microstructures; both can crack or penetrate the anode SEI, continuously providing small areas of fresh surface for electrolyte reduction and thus giving a constant evolution of gases throughout the experiment. Conversely, the reduction of any CO₂ that is formed may cause a slow decrease in pressure.¹⁷ The two-compartment setup in this work should inhibit any migration of non-gaseous electrolyte oxidation species to the negative electrode.

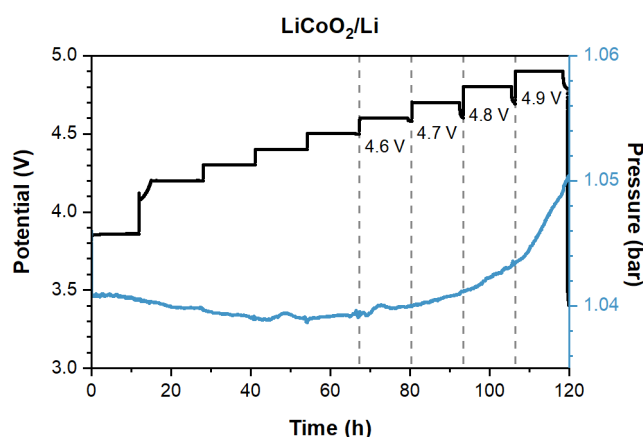


Figure 2. Operando pressure measurement of a LiCoO₂/Li cell charged in 0.1 V steps from OCV to 5.0 V (for detailed charging protocol, see Methods section). The internal cell pressure and voltage-time data are shown in blue and black, respectively. The electrolyte was a 1M LiPF₆ solution in 1:1 EC:DMC (LP30). The electrodes were separated by a lithium-conducting glass-ceramic to prevent migration of any decomposition species across the cell.

Electrochemistry (cycling data):

Two LiCoO₂/Li cells were constructed and cycled to just below (4.6 V) or well above (4.9 V) the onset voltage for electrolyte oxidation as determined by the *operando* pressure measurement. Similar to the setup used for the *operando* pressure measurement, a lithium-conducting glass-ceramic was used to separate the cell compartments to allow for the separate identification of the electrolyte decomposition products formed at each electrode. This had the further effect of preventing any ‘cross-talk’ reactions by preventing migration of the dissolved species in the electrolyte to the opposite electrode. Two LiCoO₂/Li cells were cycled between 3.0 – 4.6 or 3.0 – 4.9 V at a C/5 rate for 10 cycles (electrochemical data is shown in the Supplementary Information; Figure S 2). The cell cycled to 4.6 V showed some capacity loss (17%) over the 10 cycles (Figure S 2a), which is attributed degradation processes at the positive electrode, including reconstruction of the surface layers and concomitant loss of lattice oxygen, and decomposition of the electrolyte as well as phase transformations involving a change in the stacking sequence of the material⁴⁸, all resulting in impedance growth at the surface of the LiCoO₂ particles.⁴⁹ The cell cycled to 4.9 V suffered from a far more dramatic decrease in capacity (99% capacity loss; Figure S 2b), which may correspond to an enhanced rate of degradation processes at higher voltages. After cycling, the two LiCoO₂/Li cells were disassembled, and the glass fibre separators were soaked in deuterated DMSO to extract the electrolyte and its decomposition products for analysis by solution NMR.

Solution-state NMR:

Each of the four extracted samples (electrolytes from the positive and negative electrode, cycled from 3.0 V to 4.6 or 4.9 V), as well as a pristine reference sample, was characterised using ¹H, ¹⁹F, and ³¹P one and two-dimensional homo and heteronuclear NMR spectroscopies. A list of the observed signals in the ¹H, ¹⁹F and ³¹P NMR spectra (Table S 3) as well as a detailed discussion of their assignments are given in the SI. Briefly, the assignments of the NMR signals are supported by complementary and detailed NMR measurements such as two-dimensional experiments (COSY and HSQC) and J-coupling analysis, measurements of reference compounds reference compound measurements, and literature examples. An overview of the assignments of the observed chemical shifts is given in Table 1 and summarised below.

¹H NMR

Figure 3 shows the ¹H NMR spectra of the pristine electrolyte (bottom) and the electrolyte extracted from the cells cycled from 3.0 V to 4.6 V (middle) and 4.9 V (top). The ¹H NMR spectra over the full shift range (12 – 0 ppm) are given in the supplementary information (Figure S 3). It is immediately observed that the spectra contain several differences in the weak signals arising from minor

components between the two sides of each cell, suggesting that the glass-ceramic successfully inhibited cross-migration of species other than lithium ions.

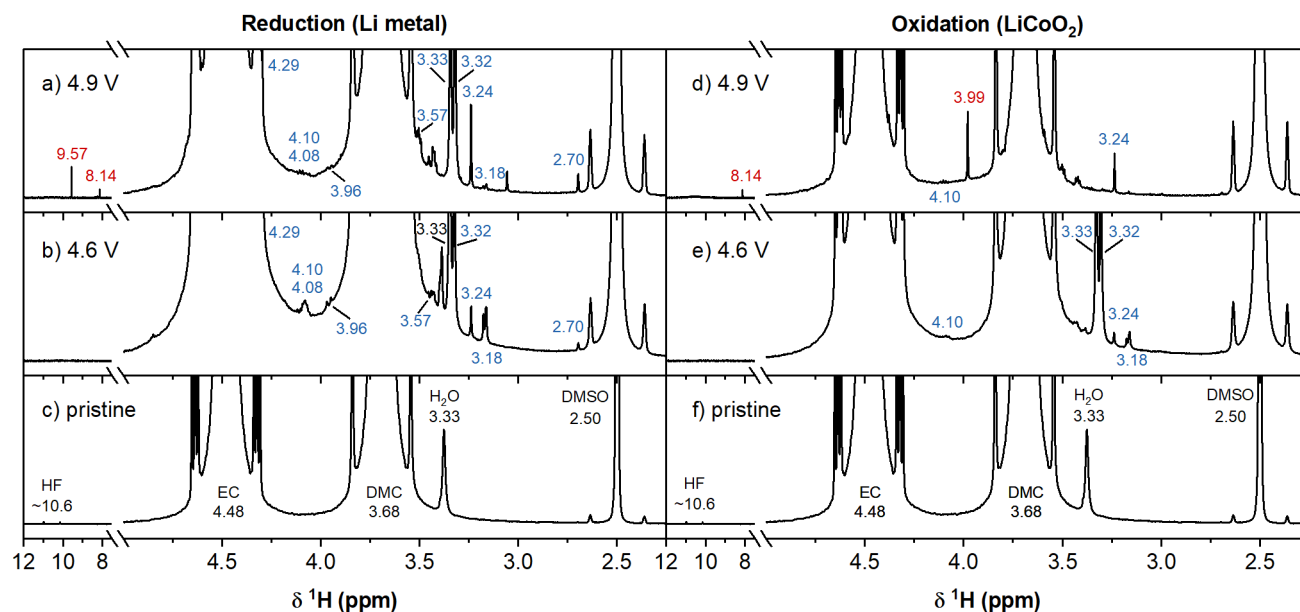


Figure 3. ^1H solution NMR spectra of LP30 electrolyte extracted from the two-compartment LiCoO_2/Li cells after 10 cycles between 3.0 – 4.9 V (top; a, d) and 3.0 – 4.6 V (middle; b, e) and pristine electrolyte (bottom; c, f). The spectra on the left are of electrolyte from the lithium metal side (a, b), the spectra on the right are of electrolyte from the LiCoO_2 side of the cell (d, e). The signals of ethylene carbonate (EC; 4.48 ppm), dimethyl carbonate (DMC; 3.68 ppm) and dimethyl sulfoxide (DMSO; 2.50 ppm) are annotated in black on the bottom spectra. The chemical shifts in blue and red correspond to signals that appeared after cycling to 4.6 V and 4.9 V, respectively.

Pristine electrolyte: The ^1H NMR spectrum of the pristine electrolyte (Figure 3c and f) shows two main signals of ethylene carbonate (EC; 4.48 ppm) and dimethyl carbonate (DMC; 3.68 ppm).^{50,51} As expected, these solvent peaks are present in all of the spectra in Figure 3. Traces of hydrofluoric acid (HF) and water are also detected by the appearance of signals at 10.6 ppm (HF) and 3.33 ppm (H_2O).^{52–54} The signal at 2.50 ppm is assigned to non-deuterated DMSO impurities in the DMSO-d_6 solvent.⁵²

4.6 V: After cycling to 4.6 V, several new signals appear between 2.5 – 5 ppm in the ^1H NMR spectrum of the electrolytes from both the positive and negative electrolyte, indicating the formation of electrolyte decomposition products. At the LiCoO_2 side (Figure 3d), the electrolyte contains methanol (4.10, 3.18 ppm),⁵² lithium methoxide (3.32 ppm) and lithium methyl carbonate (LMC; 3.24 ppm).⁵⁵ At the lithium metal side (Figure 3c), the ^1H NMR spectrum of the electrolyte also shows the species observed at the positive electrode, but additionally contains, lithium ethylene dicarbonate (LEDC; 4.29 ppm),⁵⁶ lithium ethylene monocarbonate (LEMC; 4.08 and 3.55 ppm), the difluorophosphate ester, $\text{OPF}_2(\text{OCH}_3)$ (3.96 ppm) and a signal tentatively ascribed lithium succinate (2.70 ppm).

4.9 V: After cycling to 4.9 V, additional signals between 8 – 11 ppm appear in the electrolytes of both electrodes. The ^1H spectrum of the electrolyte from the LiCoO_2 side cycled to 4.9 V (Figure 3b) shows the additional presence of formic acid (8.14 ppm),⁵⁷ HF and other H-bonded protons (broad signal at

10.6 ppm; Figure S 11) and lithium glycolate or glycolic acid (3.99 ppm). No trace moisture remains in the electrolyte, as the signal at 3.33 ppm is no longer observed. The ^1H spectrum of the electrolyte from the lithium metal side of the cell cycled to 4.9 V (Figure 3a) shows two additional signals compared to the ^1H NMR spectrum of the 4.6 V cell, assigned to formaldehyde (9.57 ppm) and lithium formate (8.14 ppm).⁵⁷

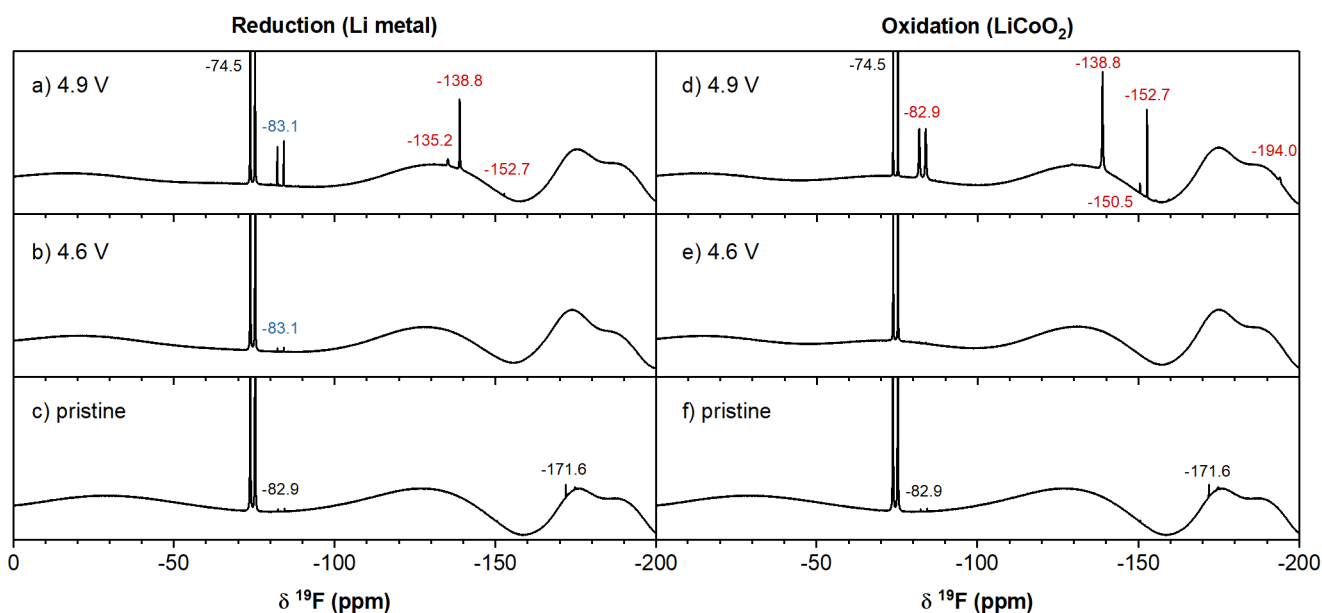


Figure 4. $^{19}\text{F}\{^1\text{H}\}$ solution NMR spectra of LP30 electrolyte extracted from the two-compartment LiCoO_2/Li cells after 10 cycles between 3.0–4.9 V (top; a, d) and 3.0–4.6 V (middle; b, e) and pristine electrolyte (bottom; c, f). The spectra on the left are of electrolyte from the lithium metal side (a, b), the spectra on the right are of electrolyte from the LiCoO_2 side of the cell (d, e). The chemical shifts of the signals found in the pristine electrolyte are given in black, those of signals that appeared after cycling to 4.6 and 4.9 V are given in blue and red, respectively. The extremely broad features at approximately -130 ppm and -175 and -190 ppm arise from a combination of probe background and ringing effects and are not due to additional electrolyte species.

^{19}F NMR

Pristine electrolyte: The $^{19}\text{F}\{^1\text{H}\}$ spectrum measured from the pristine electrolyte (Figure 4c and f) shows a major signal from LiPF_6 (–74.5 ppm, $d, {}^1J_{\text{p-F}} = 710$ Hz, see Figure S11 for the ^{31}P NMR spectrum), and minor signals from LiPO_2F_2 (–82.9 ppm, $d, {}^1J_{\text{p-F}} = 955$ Hz) and HF (–171.6 ppm) impurities.^{51,53,54}

4.6 V: The ^{19}F NMR spectrum of the electrolyte from the LiCoO_2 side (Figure 4e) reveals no detectable fluorine-based decomposition products. The electrolyte take from the lithium metal side after cycling to 4.6 V (Figure 4b), however, shows the presence of $\text{OPF}_2(\text{OCH}_3)$ (–83.1, $d, {}^1J_{\text{p-F}} = 947$ Hz).

4.9 V: After cycling to the higher cut-off voltage of 4.9 V, several new signals are observed in the spectra measured from the electrolytes from both sides of the cell. At the LiCoO_2 side (Figure 4d), the presence of $\text{OPF}_2(\text{OH})/\text{PO}_2\text{F}_2^-$ (–82.9 ppm, see Figure S 10 for the ^{31}P NMR spectrum), silicon fluorides (SiF_x , $x = 4-6$; –138.8),⁵⁸ lithium fluoroborate ($\text{LiBF}_4/\text{BF}_4^-$; –152.7 ppm; Figure S 14)⁵⁹ and HF (–194.0 ppm)^{53,54} are observed. A signal at -150.5 ppm is tentatively assigned to $\text{OPF}_2(\text{OH})\text{-BF}_3$.⁶⁰ In the lithium

metal electrolyte (Figure 4a), a higher concentration of $\text{OPF}_2(\text{OCH}_3)$ is seen, as well as signals from silicon fluoride species (-135.2 and -138.8 ppm)⁵⁸ and LiBF_4 or BF_4^- (-152.7 ppm).

Table 1. Summary of observed chemical shifts and the corresponding species assignments in this work. It is noted that not all species in this table are expected in commercial lithium-ion cells, which may use different separators and additives.

Nucleus	Chemical shift (ppm)	Assignment	
^1H	4.48 (s)	Ethylene carbonate (EC)	
	3.69 (s)	Dimethyl carbonate (DMC)	
	~ 10.6 (d, $^1J_{\text{F-H}} = 410$ Hz; broad)	Hydrofluoric acid (HF)	
	9.61 (s)	Glyoxal	
	9.57 (s)	Formaldehyde	
	8.14 (s)	Formic acid	
	7.71 (s)	Vinylene carbonate (VC)	
	6.55 (ddd, $^2J_{\text{F-H}} = 60.7$ Hz; $^3J_{\text{H-H}} = 4.1, 0.7$ Hz); 4.73 (ddd, $^2J_{\text{F-H}} = 36.3$ Hz; $^3J_{\text{H-H}} = 11.0, 4.2$ Hz); 4.64 (ddd, $^2J_{\text{F-H}} = 21.3$ Hz; $^3J_{\text{H-H}} = 11.0, 0.7$ Hz)	Fluoroethylene carbonate (FEC)	
	5.79 (s) 5.70 (s) 5.69 (s)	Acetal; $\text{RCH}(\text{OR})_2$ (e.g. methanediol, methoxymethanol)	
	4.29 (s)	Lithium ethylene dicarbonate (LEDC)	
	4.10 (q, $^3J_{\text{H-H}} = 5.5$ Hz); 3.18 (d, $^3J_{\text{H-H}} = 5.5$ Hz)	Methanol	
	4.08 (t, $^3J_{\text{H-H}} = 4.7$ Hz); 3.55 (t, $^3J_{\text{H-H}} = 4.7$ Hz)	Lithium ethylene monocarbonate (LEMC)	
	3.99 (s)	Glycolic acid or lithium glycolate	
	3.96 (d, $^3J_{\text{P-H}} = 10.0$ Hz)	$\text{OPF}_2(\text{OCH}_3)$	
	3.34 (s)	H_2O	
	3.32 (s)	Lithium methoxide (LiOCH_3)	
	3.24 (s)	Lithium methyl carbonate (LMC)	
	2.70 (s)	Lithium succinate	
	$^{19}\text{F}\{^1\text{H}\}$	-65.9 (dd, $^1J_{\text{P-F}} = 762$ Hz, $^2J_{\text{F-F}} = 56$ Hz); -81.0 (dt, $^1J_{\text{P-F}} = 740$ Hz, $^2J_{\text{F-F}} = 60$ Hz)	Trifluorooxalatophosphate ($\text{PF}_3(\text{C}_2\text{O}_4)$)
		-74.5 (d, $^1J_{\text{P-F}} = 710$ Hz)	LiPF_6
		-82.9 (d, $^1J_{\text{P-F}} = 955$ Hz)	$\text{OPF}_2(\text{OH})$
-83.1 (d, $^1J_{\text{P-F}} = 947$ Hz)		$\text{OPF}_2(\text{OCH}_3)$	
-126.3 (s)		Fluoroethylene carbonate (FEC)	
-135.2 (s) -138.8 (s)		Silicon fluorides (SiF_x)	
-150.5 (s)		$\text{OPF}_2(\text{OH})\text{-BF}_3$	
-152.7 (s)		BF_4^-	
-171.6 (s) -194.0 (s)		HF (in various coordinations and complexations, e.g. FHF^- , $\text{F}(\text{HF})_2$, $\text{F}(\text{HF})_3$ or $\text{F}(\text{HF})_4$)	
^{31}P		-145.0 (septet, $^1J_{\text{F-P}} = 711$ Hz)	LiPF_6
	-16.6 (t, $^1J_{\text{F-P}} = 947$ Hz)	$\text{OPF}_2(\text{OCH}_3)$	
	-15.5 (t, $^1J_{\text{F-P}} = 955$ Hz)	$\text{OPF}_2(\text{OH})$	

Electrochemical oxidation of electrolyte (Electrolytic H-cell experiments)

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3 To consider whether any of the electrolyte decomposition products identified in the LiCoO₂/Li cells
4 formed via *electrochemical* oxidation, a conventional 2-compartment electrolysis H-cell was
5 constructed. Three separators were used to partition the cell in order to limit convective mixing
6 between the two halves. A noticeable volume displacement from the positive electrode compartment
7 to the negative electrode compartment was observed: after 30 min electrolysis, the level of fluid in
8 the positive electrode compartment was observed to have decreased by about a third (~2 mL) while
9 the level of fluid in the negative electrode compartment was observed to have risen by the same
10 amount. This net movement of the solution ascribed to the establishment of an electro-osmotic flow,
11 generally defined as the motion of a fluid in response to an external electric field across a porous
12 material, capillary tube, membrane, or other fluid conduit.^{61,62} The phenomenon is well-known for
13 aqueous systems, for example across ion-exchange membranes in fuel cells and electrolyzers,⁶³
14 through plant phloem and across membranes in vascular biology,⁶⁴ and through silica capillaries in
15 capillary electrophoresis separations.⁶⁵ However, the authors are not aware of any rigorous treatment
16 of electro-osmosis of non-aqueous electrolyte solutions across nonpolar, porous polymer battery
17 separators. We therefore suggest this phenomenon may have significance for the operation of high
18 power and fast-charging batteries that merits its own investigation. With regards to the present work,
19 the practical result of the observed volume displacement is that it will have prevented the migration
20 of any reduction species from the negative electrode to the positive electrode compartment of the H-
21 cell.
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36 Figure 5 shows the ¹H NMR spectrum measured from the electrochemically oxidised electrolyte (d).
37 For comparison, the results from the two-compartment LiCoO₂/Li cells cycled to 4.9 V (e) and pristine
38 electrolyte (f) are also shown. A peak corresponding to acetonitrile (δ ¹H = 2.07 ppm) is not observed
39 for any of the spectra, indicating that there was no leakage from the reference electrode into the cell.
40 Electrochemical oxidation of the electrolyte leads to a large range of new signals, but most of the
41 carbonate solvent remains intact. By repeating the experiment using an electrolyte without EC (*i.e.*
42 1M LiPF₆ in DMC), the signals corresponding to the electrolyte decomposition products originating
43 from EC and DMC can be separated (Figure S 15). A list of the observed signals in the ¹H, ¹⁹F and ³¹P
44 NMR spectra (Table S 3) as well as a detailed discussion of their assignments are given in the SI.
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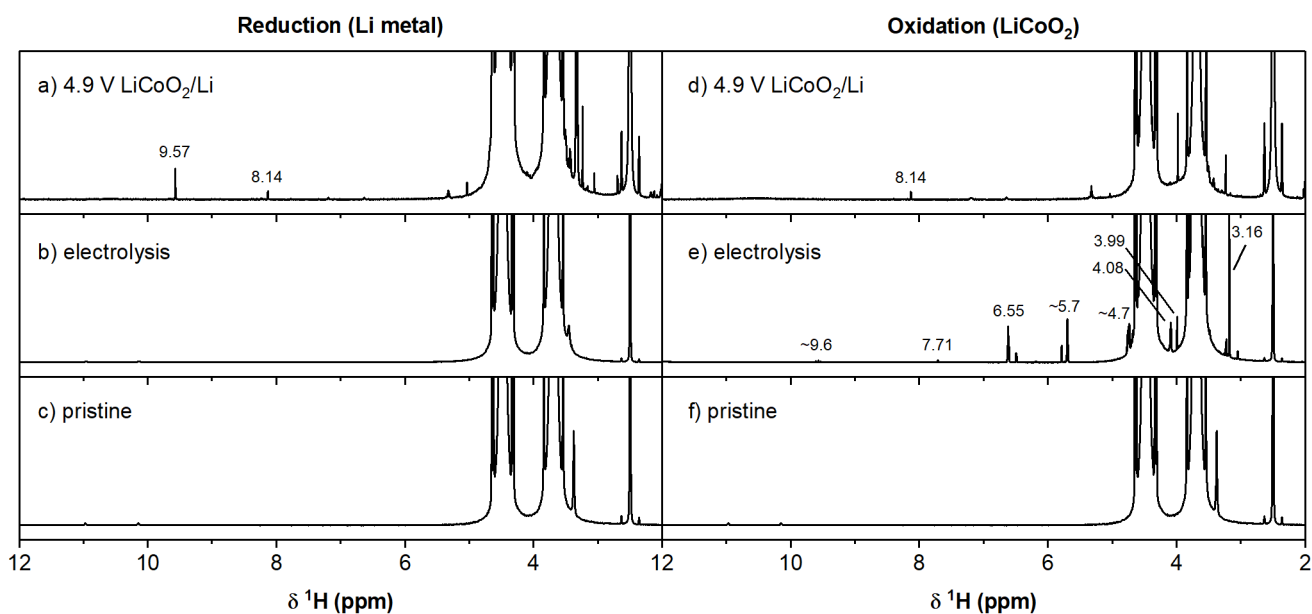


Figure 5. ^1H solution NMR spectra of LP30 electrolyte extracted from the two-compartment LiCoO_2/Li cells after 10 cycles between 3.0 – 4.9 V (top; a, d) and the conventional 2-compartment electrolysis H-cell after applying a current of 10 mA for 30 min (middle; b, e) and pristine electrolyte (bottom; c, f).

^1H NMR: The signals attributed to EC decomposition products are assigned to vinylene carbonate (VC; 7.71 ppm),⁶⁶ a small symmetrical molecule with an aldehyde-functionality, such as glyoxal, $\text{H}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{H}$ (9.61 ppm) and fluoroethylene carbonate (FEC; 6.55, 4.73, 4.64 ppm, see Figure S 16). The signals originating from the decomposition products of DMC are attributed to formaldehyde (9.57 ppm), glycolic acid or lithium glycolate (3.99 ppm) various simple acetal species, $\text{RCH}(\text{OR})_2$, such as methanediol and methoxymethanol (5.79 ppm, s; 5.70 ppm, s; 5.69 ppm, s). Finally, a broad signal at ~ 12.4 ppm is observed and assigned to H-bonded protons in the electrolyte.

^{19}F NMR: The ^{19}F NMR spectrum of the electrochemically oxidised electrolyte (Figure S 17) is dominated by the signal from the LiPF_6 salt (-74.5 ppm), but reveals new signals from $\text{OPF}_2\text{OH}/\text{PO}_2\text{F}_2^-$ (-83.6 ppm), FEC (-126.3 ppm, Figure S 18), $\text{LiBF}_4/\text{BF}_4^-$ (-153.0 ppm) and HF (-172.8 ppm). The multiplets at -65.9 and -81.0 ppm are tentatively assigned to trifluorooxalatophosphate ($\text{PF}_3\text{C}_2\text{O}_4$).

The electrolyte decomposition products identified in the various experiments in this work are summarised in Table 2.

Table 2. Summary of electrolyte decomposition products observed in this work, as identified by solution NMR, and the conditions under which they are formed. A 'x' indicates the species was present under that condition, whereas a '-' indicates the species was not.

Species	Pristine electrolyte	Lithium metal		LiCoO ₂ electrode		Electrochemical electrolyte oxidation
		4.6 V	4.9 V	4.6 V	4.9 V	
H ₂ O	x	x	x	x	-	-
HF	x	-	-	-	x	x
Lithium ethylene dicarbonate (LEDC)	-	x	x	-	-	-

Lithium methyl carbonate (LMC)	-	x	x	x	x	x
Lithium methoxide	-	x	x	x	-	-
Lithium succinate	-	x	x	-	-	-
Methanol	-	x	x	x	x	x
Formic acid	-	-	x	-	x	-
Formaldehyde	-	-	x	-	-	x
Glycolic acid/lithium glycolate	-	-	-	-	x	x
Glyoxal	-	-	-	-	-	x
Vinylene carbonate (VC)	-	-	-	-	-	x
Fluoroethylene carbonate (FEC)	-	-	-	-	-	x
Acetals	-	-	-	-	-	x
OPF ₂ (OH)	-	-	-	-	x	x
OPF ₂ (OCH ₃)	-	x	x	-	-	-
PF ₃ (C ₂ O ₄)	-	-	-	-	-	x
SiF _x	-	-	x	-	x	-
BF ₄ ⁻	-	-	x	-	x	x
OPF ₂ OH-BF ₃	-	-	-	-	x	-

Discussion

The results of this work were used to construct a detailed scheme showing the various electrolyte decomposition reactions that occur at high voltages/SOC, which are summarised here to put the following discussion in context (Figure 6). The scheme is based on both a careful analysis of the NMR spectra collected in this work and from a review of the wealth of proposed reactions in the extensive published literature. Electrolyte decomposition pathways were categorised into three types of reactions:

- 1) Chemical reduction and oxidation
- 2) Faradaic reduction and oxidation
- 3) Non-redox reactions

We were careful to adhere to the fundamentals of organic and inorganic chemical reaction mechanisms,^{67,68} and to be consistent with known data. The following discussion walks through the logic and organic reactions used to construct Figure 6. We then summarise the reactions and discuss the broader implications of the proposed mechanisms.

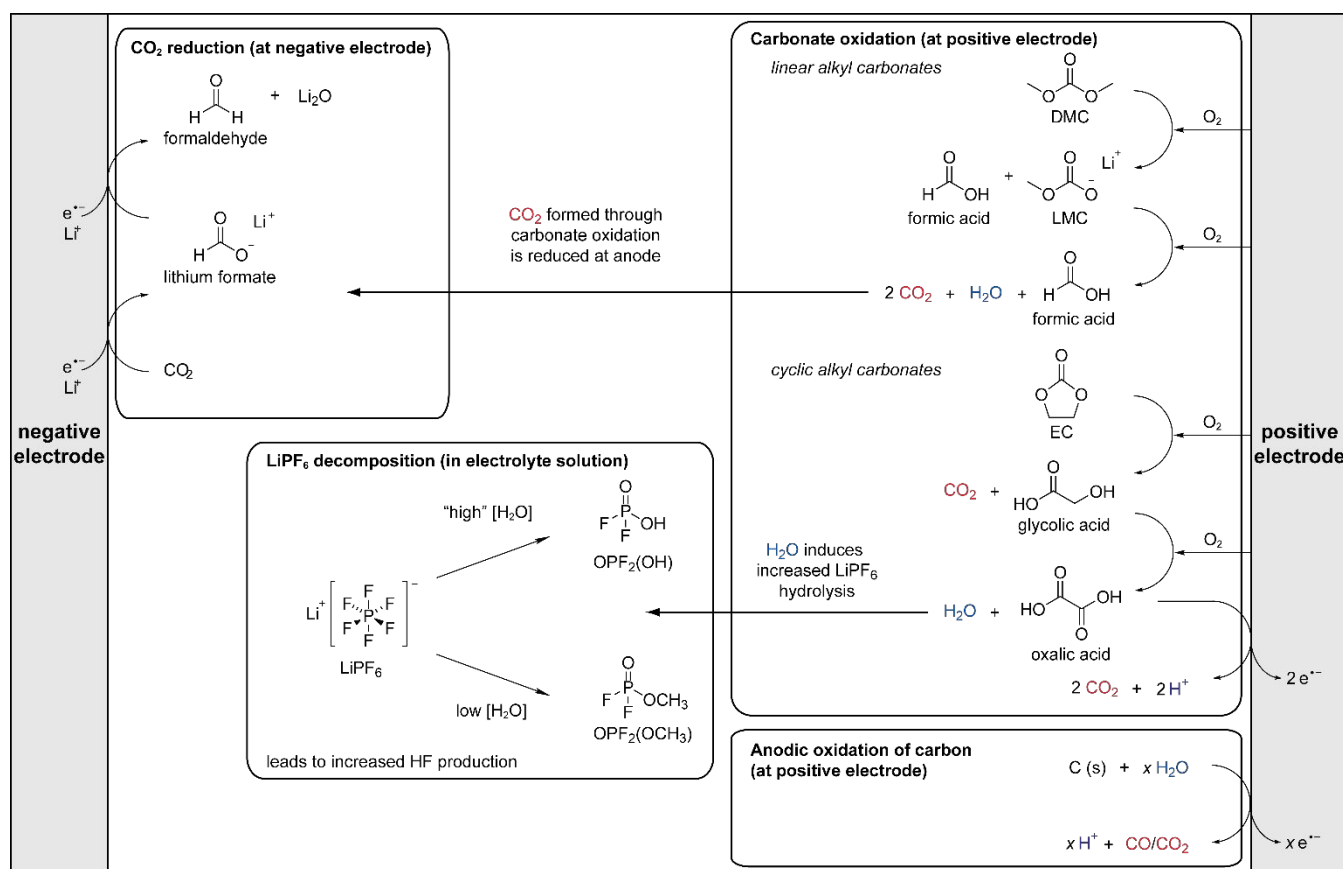


Figure 6. Overview of electrolyte decomposition reactions that occur at high voltages (or high SOC) initiated at the positive electrode.

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3 In the electrolyte solution, any protic species formed (*e.g.*, methanol or hydrogen methyl carbonate;
4 HMC) may exist as the protic acid, as the lithium conjugate base complex (in this case, lithium
5 methoxide and LMC; Scheme 1, step II) or as the uncoordinated conjugate base. The preferred “state”
6 or the equilibrium between these states is complex to predict and will probably involve such factors
7 as the stability of the conjugate base, the solubility of the formed lithium-conjugate base salt, the
8 coordination of the proton in the electrolyte solution (*e.g.*, H-F hydrogen bonded network) and the
9 consumption of protons by other reactions in the cell – including that ultimately may occur via
10 crossover reactions on anode (in the absence of the glass-ceramic separator). It is challenging to
11 determine the “state” of these species from solution NMR spectra, as the effect of the coordinating
12 ion (H^+ vs Li^+) on the chemical shift is not always known and may not have a detectable effect (N.B.
13 the chemical shift difference is noticeable for lithium methoxide and methanol). In the reaction
14 schemes proposed in this work, the H^+ - or Li^+ -equivalent are used as based on the assignments of the
15 chemical shifts and keeping in mind that H^+ ions are generated at the positive electrode, whereas OH^-
16 /LiOH is generated and H^+ are consumed via reduction to H_2 at the negative electrode. As a result, the
17 proposed reaction schemes may not always be balanced in terms of Li/H; (we have however tried to
18 ensure they are balanced in terms of carbon and O content and formal (carbon) oxidation state).

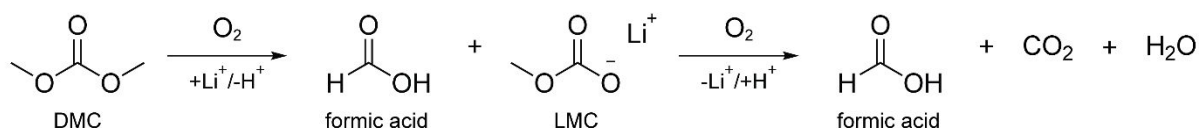
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21 From the $LiCoO_2/Li$ cell cycled to 4.9 V, *i.e.*, above the gas evolution onset potential, the main
22 decomposition products that were observed on the $LiCoO_2$ side were formic acid, LMC and glycolic
23 acid/lithium glycolate (Table 2), as well as an increase in the HF/H-bonded proton concentration. The
24 dominant oxidation pathway of the carbonate solvent was determined to proceed via non-Faradaic
25 oxidation. The reactions all involve the addition of oxygen, which strongly supports the proposal that
26 they are associated with or driven by the release of reactive oxygen species at the $LiCoO_2$ surface; this
27 was the starting point for proposing formation reaction pathways for these decomposition products.
28 Note that the evolution of singlet oxygen (1O_2) from layered transition metal oxides at high electrode
29 potentials has been observed previously by photon emission spectroscopy.⁸ Singlet oxygen is an
30 excited state of oxygen that is far more reactive than the triplet ground state (3O_2) and it has been
31 identified as an important cause of degradation in $Li-O_2$ chemistry⁶⁹ and in biological systems.⁷⁰ We
32 note, however, that the decomposition reactions may not necessarily involve dissolved 1O_2 but may
33 be coupled with the cathode surface reconstruction process that leads to the oxygen release.

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36 In general, carbon-carbon bonds are very difficult to break (unless extremely reactive radicals are
37 present), because they are strong and not easily polarised. Note that singlet oxygen, while highly
38 reactive, is not a radical but is rather a strong electrophile. Formic acid and LMC do not contain any
39 carbon-carbon bonds, so they are, therefore, presumed to originate from DMC, rather than EC. A
40 possible reaction scheme to form formic acid and LMC via chemical oxidation of DMC is proposed and
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outlined in (Scheme 2). Firstly, DMC is chemically oxidised with a reactive oxygen species, *e.g.* singlet O_2 , to produce formic acid and LMC. The formation of the semi-carbonate LMC at the positive electrode may seem surprising, since semi-carbonates are conventionally thought to only form at the negative electrode through the reduction of DMC (Scheme 9b). LMC has previously been observed as an anode SEI component, proposed to form via reduction of DMC (or EMC).⁷¹ However, the oxidation reactions of DMC at the positive electrode have not been studied independently of those at the negative electrode, hence it could not be concluded that LMC does not also form at the positive electrode. The results in this work suggest that LMC can be formed at both electrodes. It is then proposed that LMC could be chemically oxidised again to release more formic acid, as well as CO_2 and water. Alternatively, LMC can react further via hydrolysis, thermal decomposition, reaction with PF_5 , or migrate to the negative electrode where it may be reduced to CO_2^* and lithium methoxide.^{55,72}

Scheme 2. Proposed reaction scheme for the chemical oxidation of dimethyl carbonate (DMC) to formic acid, CO_2 and water. Lithium methyl carbonate (LMC) (identified here by NMR) is a proposed intermediate.

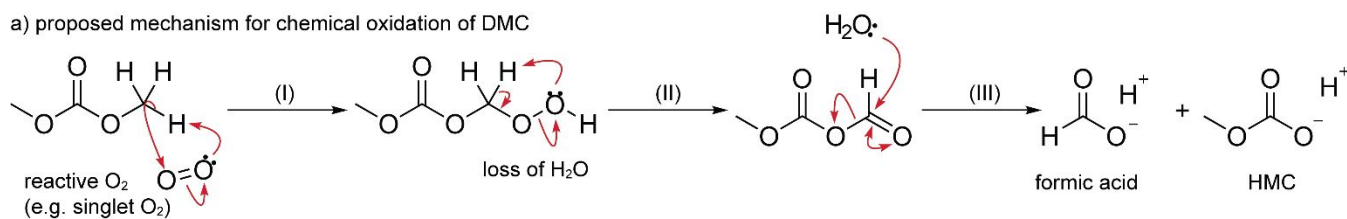
chemical oxidation of DMC



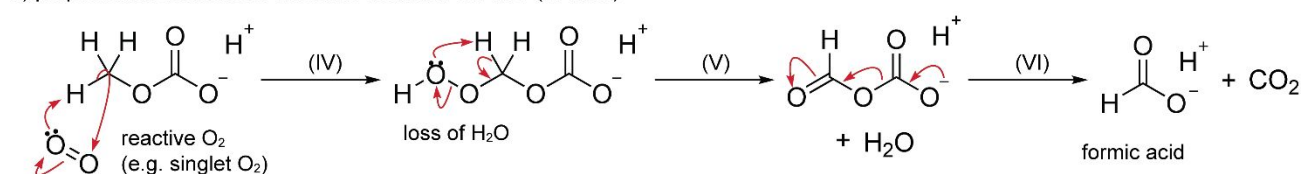
The proposed mechanism for the chemical oxidation of DMC and LMC is given in Scheme 3. A reactive oxygen species deprotonates the methyl group on DMC, followed by nucleophilic attack of the deprotonated carbon onto the second oxygen to form a new carbon-oxygen bond (Scheme 3a, step I). The first oxygen deprotonates the same carbon on DMC again to form an aldehyde unit and release water (step II). The water molecule can attack back into the carbonyl group of the aldehyde to produce formic acid (or lithium formate) and LMC (step III). LMC can be oxidised in a similar way to DMC (Scheme 3b). The main difference is that after forming the aldehyde moiety (step V), the water that is lost does not reattack and the resulting species decomposes to form lithium formate and CO_2 .

Scheme 3. Proposed mechanism for the chemical oxidation of (a) dimethyl carbonate; DMC and (b) lithium methyl carbonate (LMC).

a) proposed mechanism for chemical oxidation of DMC



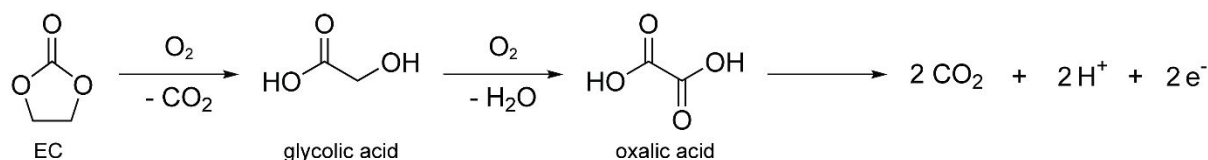
b) proposed mechanism for chemical oxidation of HMC (or LMC)



The observed glycolic acid or lithium glycolate is assumed to be a decomposition product of EC and not DMC, on the basis of its two connected carbon atoms; the formation of carbon-carbon bonds at the positive electrode is unlikely, as no reagents or functional groups are present that could facilitate the formation of such bonds. A possible reaction scheme for the chemical oxidation of EC to glycolic acid and CO₂ is proposed and outlined in Scheme 6. First, EC is chemically oxidised to CO₂ and glycolic acid, which can then be chemically oxidised again to form water and oxalic acid. At this cell potential (4.9 V vs Li/Li⁺), oxalic acid is rapidly oxidised (electrochemically) to CO₂ and H⁺.⁷³ Thus, the overall reaction equation for the proposed complete chemical oxidation of EC would be EC + 4 O_{lattice} → 3 CO₂ + H₂O + 2 H⁺. Even though the presence of oxalic acid (or lithium oxalate) in the electrolyte could not be determined due to the technique used (¹H NMR), its low solubility in both the electrolyte and NMR solvent suggests that oxalic acid is more likely found precipitated out on the electrode surface, rather than in the electrolyte. The rapid oxidation of oxalic acid above 4.5 V (vs Li/Li⁺),⁷³ also suggests that the presence of oxalic acid in the electrolyte is unlikely. The increased proton concentration in the electrolyte provides evidence for the oxidation of oxalic acid but could also be due to the oxidation of water that is formed through carbonate oxidation.

Scheme 4. Proposed reaction scheme for the chemical oxidation of ethylene carbonate (EC) to 3 CO₂, H₂O and 2 H⁺. Glycolic acid and oxalic acid are thought to be intermediates in this reaction. The electrochemical oxidation of oxalic acid is also shown.

chemical oxidation of EC

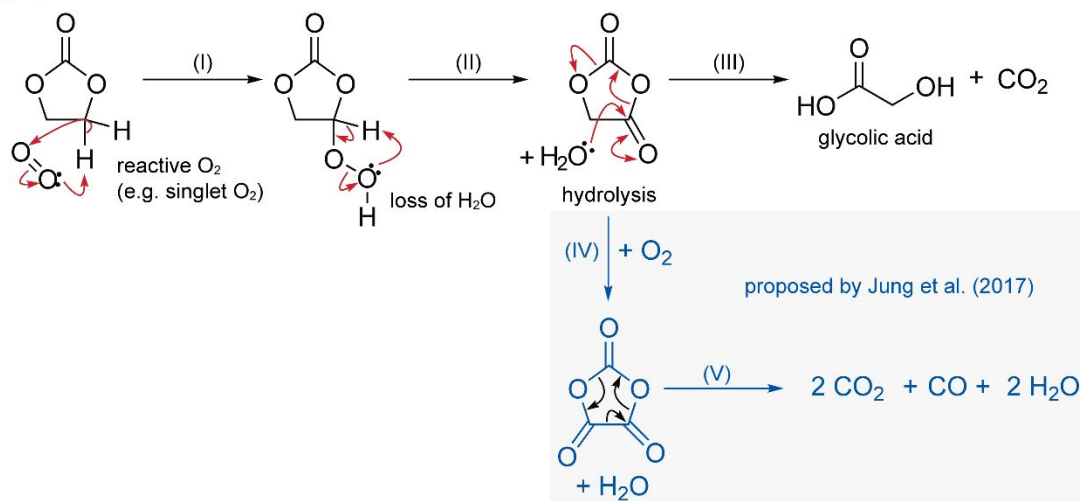


Scheme 5a shows the proposed mechanism for the chemical oxidation of EC and formation of glycolic acid. Steps (I) and (II) are identical to the mechanism proposed for DMC and are not discussed further.

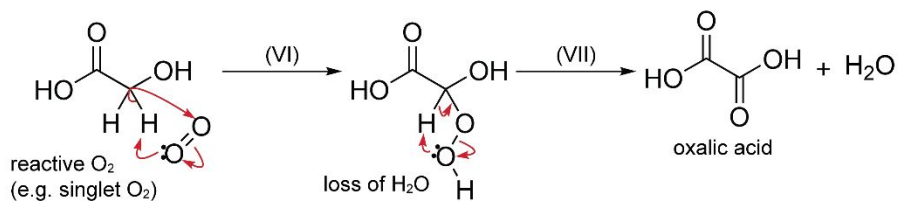
The intermediate formed after step (II) can be hydrolysed by the water that is released in the previous step, after which the molecule decarboxylates to form glycolic acid and CO₂ (step III). Nucleophilic attack of water will preferentially occur at the carbonyl group of the ester unit, rather than at the carbonate group, as the ester is more reactive towards nucleophilic attack. Glycolic acid can be chemically oxidised in a similar way to produce oxalic acid and water (Scheme 5b).

Scheme 5. Proposed mechanism for the chemical oxidation of (a) ethylene carbonate (EC) and (b) glycolic acid.

a) proposed mechanism for chemical oxidation of EC



b) proposed mechanism for chemical oxidation of glycolic acid



Gasteiger and co-workers³ previously proposed that the overall reaction equation for the chemical oxidation of EC at an NMC electrode surface is $\text{EC} + 4 \text{O}_{\text{lattice}} \rightarrow 2 \text{CO}_2 + \text{CO} + 2 \text{H}_2\text{O}$, based on OEMS measurements that showed a CO₂ to CO ratio of 2:1. They suggested a similar mechanism as discussed above (steps I and II), however, they argued that the molecule formed after step II must be oxidised further (step IV), instead of decomposing into formaldehyde, CO₂ and CO, as no formaldehyde was detected and a higher CO₂ to CO ratio was observed. However, we suggest that the intermediate formed after step II is highly reactive and could quickly hydrolyse to form glycolic acid, before a second oxidation step occurs. This reaction scheme would also be consistent with the reaction mechanism proposed for the oxidation of DMC. Alternative explanations for the observation of CO by Jung et al.³ were therefore considered. Oxidation of water at the conductive carbon would produce CO and 2 H⁺, however, they demonstrated this was not the case using ¹³C-labelled conductive carbon for OEMS measurements.²² The CO production in their NMC/graphite cells was coupled to O₂ release from the

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3 transition metal oxide, thus also excluding reduction reactions at the negative electrode. It is therefore
4 proposed that the reaction pathways III and IV in Scheme 5a are competitive with those suggested by
5 Jung et al.,²² with relative reactions rates that are likely determined by the material- and voltage-
6 dependent kinetics of oxygen loss and mass transport rate of the intermediate. Additional NMR
7 studies using the methods outlined in the present work are suggested to look for glycolic acid or
8 lithium glycolate reaction products at NMC electrodes.
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14 Finally, no evidence for dehydrogenation of EC at the positive electrode to form VC, hydrolysis of EC,
15 nor transesterification of EC or DMC were observed in this work.
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17 *CO₂ reduction at the negative electrode*

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20 Chemical oxidation of the carbonate solvent at the positive electrode results in the production of H₂O
21 and CO₂. Even though a lithium-ion conducting ceramic is used to inhibit migration of electrolyte
22 decomposition species between the electrodes, CO₂ formed at the positive electrode can pass around
23 the edges of the ceramic and diffuse to the surface of the negative electrode. At the lithium metal
24 surface, CO₂ that is dissolved in the electrolyte, is reduced to a CO₂ radical anion. This radical anion
25 rapidly abstracts a proton from other species in the electrolyte, *e.g.* H₂O, to form lithium formate,
26 which can be reduced further in a similar way to generate formaldehyde (Scheme 6a). This proposed
27 pathway also produces Li₂O, a known component in the 'mature' negative electrode SEI.⁴⁵
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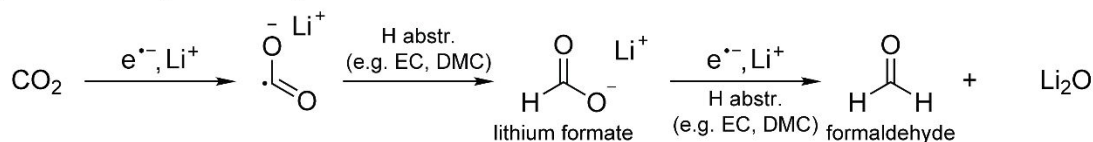
34 Other pathways for the reduction of CO₂ that have been reported in the literature include the
35 formation of lithium oxalate (Scheme 6b) and lithium carbonate (Scheme 6c).⁷³ Neither species
36 contains protons, so they cannot be detected with ¹H NMR, but due to their low solubility in both the
37 electrolyte and the NMR solvent, they are again most likely present on the electrode surface rather
38 than and not in the electrolyte solution. Moreover, Li₂CO₃ can react with HF formed in the cell via an
39 acid-base reaction to form lithium fluoride (LiF), H₂O and CO₂, and may therefore be challenging to
40 detect;⁷⁴ it is also known to be removed electrochemically at above 4.2 V.^{74,75}
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47 CO₂ can also be produced in cells with lower cut-off voltages via the decomposition of the DMC-
48 reduction product, LMC, or via the decarboxylation of EC-reduction products, *e.g.* lithium alkyl
49 carbonate radicals or polycarbonate oligomers at the negative electrode.¹⁹ However, these reactions
50 are negligible compared to the generation of CO₂ at the positive electrode at high cell voltages,^{3,23} and
51 explains why formaldehyde and lithium formation are not observed at lower cell voltages.
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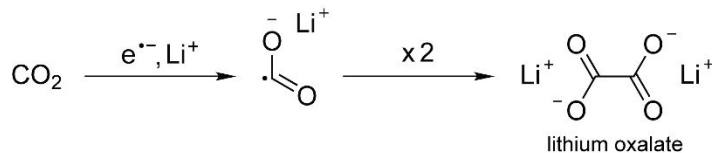
55 *Scheme 6. Reaction schemes for the reduction of CO₂ to (a) lithium formate and formaldehyde, (b) lithium oxalate and (c)*
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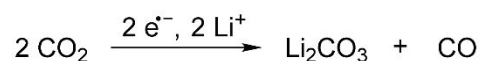
a) reduction of CO₂ to formaldehyde



b) reduction of CO₂ to lithium oxalate



c) reduction of CO₂ to lithium carbonate



LiPF₆ decomposition

The non-Faradaic oxidation of organic carbonates at the positive electrode at high cell voltages also results in an increased water concentration in the electrolyte. This leads to enhanced decomposition (hydrolysis) of the LiPF₆ salt, as is observed by the formation of OPF₂(OH) and HF in the electrolyte. The formation of these species has been reported before and is shown in Scheme 7a.^{51,76} The HF that is generated from increased LiPF₆ decomposition can react with the borosilicate glass fibre separator to produce boron and silicon fluorides (Scheme 7b and c). Whereas borosilicate glass fibre separators are relatively common in academic research, it is noted that these reactions would not be observed in cells employing a polymer-only separator. Moreover, many commercial cells will actually use ceramic-coated polymer separator designs (e.g., with Al₂O₃ particles on one or both sides), which would have different reactivity than was observed in the present work. We therefore suggest that separator components must be taken into account when one is proposing cross-talk processes, especially those involving HF, moisture, and acidic or basic species. No LiPF₆ decomposition products could be detected in the electrolyte from the LiCoO₂ side from the LiCoO₂/Li cell cycled to 4.6 V, suggesting that little LiPF₆ decomposition had occurred.

The electrolyte from the Li metal side shows the formation of a different difluorophosphate ester, OPF₂(OCH₃), and again enhanced LiPF₆ decomposition is seen for the cell with the higher cut-off voltage. The formation of this difluorophosphate ester is usually ascribed to the reaction of OPF₃ has been with DMC, which produces fluoromethane and CO₂ as side products.^{51,60} An additional route is proposed where OPF₃ reacts with methanol to give the OPF₂(OCH₃) species and HF as a side product (Scheme 7a bottom), in a similar way to the reaction with trace moisture (Scheme 7a top). OPF₃ has previously been observed at high cell voltages via OEMS measurements,²⁴ but since this species is gaseous, it would not have been directly detect in the present work. Even though HF is produced as a side product in the LiPF₆ decomposition pathways, no HF is detected in the electrolyte from the

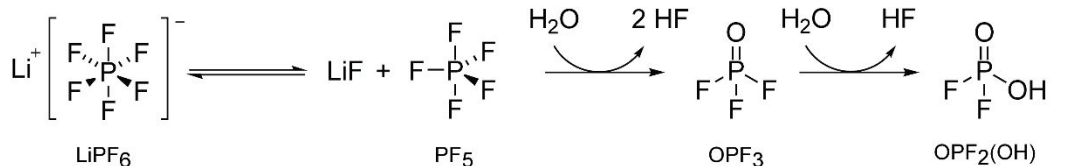
negative electrode, as lithium metal can remove HF by reducing it to LiF and H₂ gas. The increased LiPF₆ decomposition at higher cell voltages implies that more water and/or alcohol and alkoxides species are formed at the negative electrode under these conditions. The quantity and morphology of the lithium plated at the negative electrode during the first charging step differs for the two cut-off voltages, so the amount of electrolyte decomposed to form the SEI layer will be different, which could explain the increased formation of alkoxide/alcohol species in the cell cycled to 4.9 V.

The electrolyte from the lithium metal side also contains silicon fluorides, but only small amounts of BF₄⁻, whereas the electrolyte from the LiCoO₂ side has approximately equal quantities of silicon and boron fluorides, both originating from the borosilicate glass fibre separator. The reactivity of silicon oxide is higher than that of boron oxide, hence more silicon fluoride is seen if on the lithium metal side. However, if enough HF is present, as is the case on the LiCoO₂ side, it can also react with the boron oxide to form BF₄⁻.

The pristine electrolyte contains LiPO₂F₂ (or Li⁺OPF₂(O⁻)) and HF impurities, which form through reaction of the LiPF₆ salt with trace moisture present in the electrolyte (Scheme 7a top).^{51,76}

Scheme 7. (a) LiPF₆ decomposition pathways,^{51,76} and reactions of hydrofluoric acid (HF) with the borosilicate glass fibre separator: (b) reaction between boron oxide (B₂O₃) and (c) reaction between silicon oxide (SiO₂).

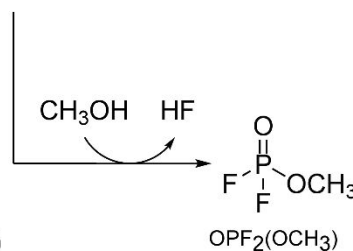
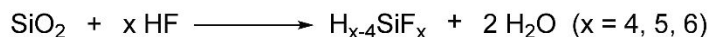
a) LiPF₆ degradation pathways



b) Reaction of HF with B₂O₃



c) Reaction of HF with SiO₂



The preferential formation of OH-based fluorophosphates at the positive electrode and OCH₃-based fluorophosphates at the negative electrode is rationalised by the relative concentrations of water and methanol present at each side. At the negative electrode, the water concentration is presumed to be low, since trace moisture is partially removed at the lithium metal surface by reducing it to LiOH and H₂ gas. Due to DMC reduction at the lithium metal surface, the methanol concentration is most likely higher than that of water, explaining the formation of OCH₃-based difluorophosphate species. On the positive electrode side, however, oxidation of the carbonate solvent leads to high water concentrations, therefore the formation of OH-based difluorophosphate species are preferred.

H₂O at high cell voltages

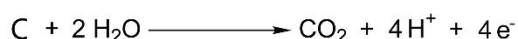
Water was not observed in the electrolyte from the LiCoO₂ half of the cell cycled to 4.9 V, even though it is a proposed product of solvent oxidation. OEMS measurements have shown that water enhances the anodic oxidation of conductive carbon particles and that this reaction proceeds at 4.8 V vs Li/Li⁺, but can occur at slightly lower potentials if the water concentration is high (4.7 V vs Li/Li⁺ for 4000 ppm H₂O).²² The water-enhanced corrosion reaction of carbon consumes water and produces CO₂ or CO and protons (Scheme 8a).²² The resulting protons can form ion pairs with PF₆⁻ and decompose the anion to PF₅ and HF (Scheme 8b).⁷⁷

The reactions in Scheme 8a and b are consistent with the appearance of a broad signal in the ¹H NMR spectrum (Figure 3b), which is ascribed to HF and other H-bonded proton species. It has also previously been proposed that protons can intercalate into the partially delithiated transition metal oxide, leading to a loss of active material at the positive electrode (Scheme 8c).⁴⁸

The absence of water in the electrolyte is not attributed to the consumption of water via hydrolysis of the LiPF₆ salt or the carbonate solvent. Increased LiPF₆ decomposition due to the reaction with water is observed, however, this reaction is relatively slow, supported by the presence of some water in other electrolytes in this work. Furthermore, only trace quantities of methanol (a hydrolysis product of DMC) and no observable amounts of LEMC or EG (hydrolysis products of EC) are observed. Therefore, hydrolysis of the salt and the solvent only represent minor processes for the consumption of water.

Scheme 8. Reaction schemes for (a) the water-enhanced anodic oxidation of carbon,²² (b) the acid-catalysed decomposition of PF₆⁻⁷⁷ and (c) the intercalation of H⁺ into the (partially) delithiated transition metal oxide.⁴⁸

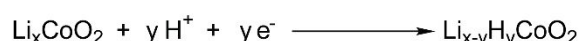
a) water-enhanced anodic oxidation of carbon



b) acid-catalysed decomposition of PF₆⁻



c) intercalation of H⁺ into delithiated LiCoO₂



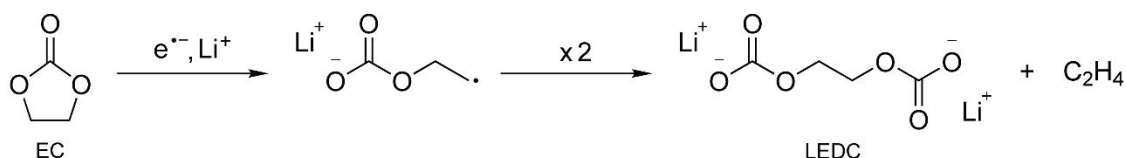
Reduction of the carbonate solvent at the negative electrode

The reduction products and pathways of EC and DMC have previously been studied extensively and reviewed.^{45,78} The electrolyte decomposition products observed at the lithium metal side of the LiCoO₂/Li cells in the present work include LEDC and LEMC, consistent with previous literature. Both

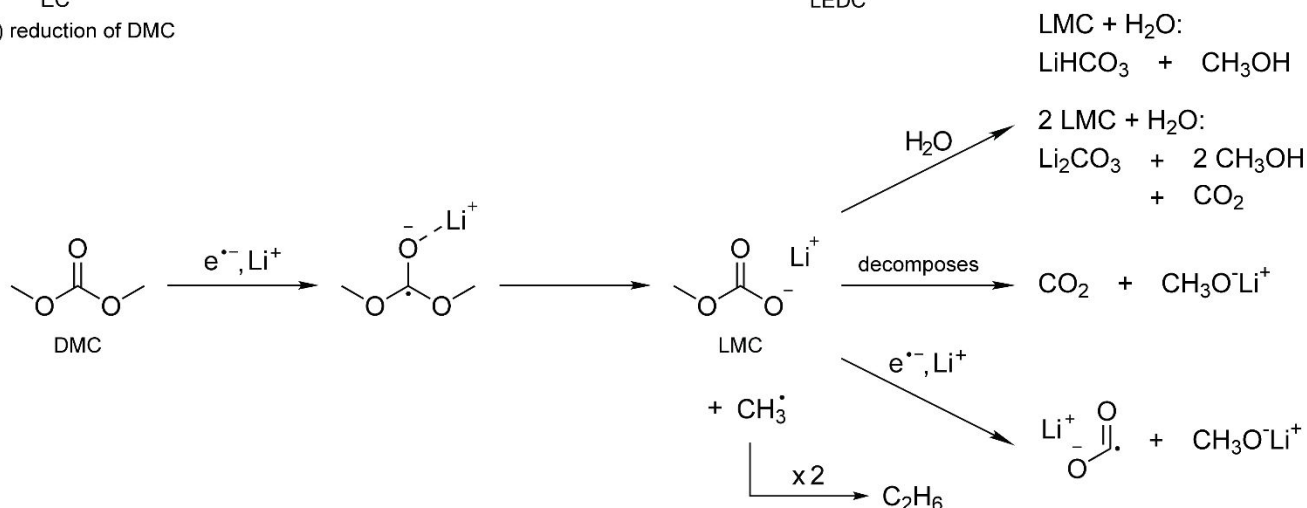
are proposed to originate from EC, and the remaining observed products, LMC, lithium methoxide, lithium succinate and methanol were also observed to originate from the DMC.^{27,79} Scheme 9a shows the reduction of EC to LEDC; EC is reduced via a one-electron ring-opening reaction, forming a lithium alkyl carbonate radical, which dimerises to form LEDC and release ethene gas.^{55,79,80} The reduction of DMC (Scheme 9b) also proceeds via a one-electron reaction forming a lithium alkyl carbonate radical that decomposes into lithium methyl carbonate (LMC) and a CH_3^\bullet radical.^{27,79} This CH_3^\bullet radical dimerises to form ethane gas. LMC can react further in several ways: it can decompose to release CO_2 gas and to form lithium methoxide, it can react with water to form a mixture of carbonates, methanol and CO_2 , or it can be reduced further to generate lithium methoxide and a CO_2^\bullet radical.^{27,79} This radical, can also be formed through the reduction of CO_2 and results in the formation of various products, one of which is lithium succinate (Scheme 9c).⁸¹ This mechanism is proposed based on previous literature and is consistent with the signatures of lithium succinate in the ^1H NMR spectra (Figure 3a and b).

Scheme 9. Summary of reduction reactions at the negative electrode consistent with the chemical signatures detected by solution NMR. a) The reduction of ethylene carbonate (EC) to lithium ethylene dicarbonate (LEDC).^{55,79,80} b) The reduction of dimethyl carbonate (DMC) to lithium methyl carbonate (LMC) and further reactions of LMC.^{27,79} c) The formation of lithium succinate.⁸¹

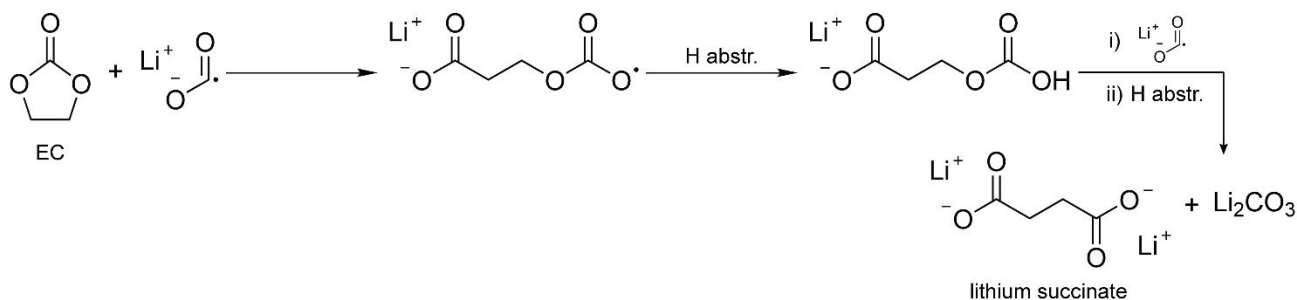
a) reduction of EC to lithium ethylene dicarbonate (LEDC)



b) reduction of DMC



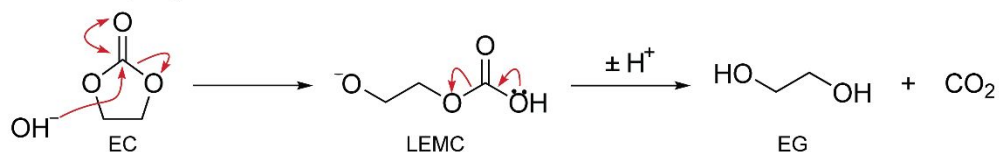
c) formation of lithium succinate



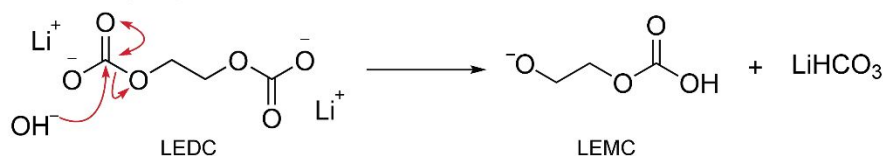
Not all electrolyte decomposition reactions are electrochemical in nature or even involve a reduction or oxidation step; some decomposition proceeds via non-redox reactions. For example, LEMC can form either through the hydrolysis of EC (purely chemical; Scheme 10a) or from the hydrolysis of LEDC (Scheme 10b). Even though the H₂O-driven hydrolysis of EC does not proceed at appreciable rates at room temperature, the OH⁻ driven (*i.e.*, base-catalysed) hydrolysis of EC is appreciable at room temperature, as OH⁻ is a stronger nucleophile.⁴⁷ Sources of OH⁻ in the electrolyte include the reduction of trace moisture at the negative electrode to form LiOH or OH⁻ and H₂ gas, the reduced anode representing a highly basic environment (noting of course the difficulty in defining basicity in non-aqueous solvents). LEMC could decompose further to ethylene glycol (EG) and CO₂, but no evidence for EG (δ ¹H = 3.40 ppm; s)⁵² is observed in our ¹H NMR spectra. Other proposed decomposition pathways for LEMC include reactions with the carbonate solvent to form carbonate ether oligomers and reactions with fluorophosphate esters to produce phosphate carbonate oligomers,⁸² but no evidence for these species was seen in our ¹H NMR spectra of the electrolyte solution. The formation of LMC, lithium methoxide and methanol could similarly be explained via the hydrolysis of DMC (Scheme 10c), in addition to the electrochemically-induced pathways described in Scheme 9b. Evidence that these species can form through hydrolysis is provided by the ¹H NMR spectrum of electrolyte deliberately spiked with 100,000 ppm water after storage for 2 months (Figure S 20), which shows the presence of LEMC, LMC, lithium methoxide and methanol (see SI for more details).

Scheme 10. The base-driven hydrolysis reactions of (a) ethylene carbonate (EC) to lithium ethylene monocarbonate (LEMC), which can decompose to ethylene glycol (EG) and CO₂, (b) lithium ethylene dicarbonate (LEDC) to LEMC and lithium hydrogen carbonate, and (c) dimethyl carbonate (DMC) to lithium methyl carbonate (LMC) and methoxide.

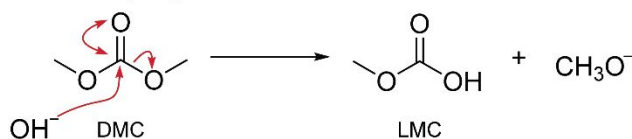
a) base-driven hydrolysis of EC



b) base-driven hydrolysis of LEDC



c) base-driven hydrolysis of DMC



Summary of electrolyte decomposition at high voltages

An overview of the electrolyte decomposition reactions that occur at high voltages (high SOC) was given in Figure 6, and can now be discussed in the context of the various mechanistic schemes proposed above. Reactive oxygen species released from the transition metal oxide particles chemically oxidise the carbonate solvent, producing carboxylic acids and semi-carbonates and releasing CO₂ and water (Scheme 2 and Scheme 4). The CO₂ that is produced migrates to the negative electrode, where it is first reduced to lithium formate and then formaldehyde, but other reduction products (lithium carbonate, lithium oxalate) could be formed too (Scheme 6). The water that is formed hydrolyses the LiPF₆ salt, producing fluorophosphate species and HF, which in turn can attack various components of the cell (*e.g.* separator, active material at positive electrode; Scheme 7). Water also enhances the anodic oxidation of the conductive carbon particles, raising the concentration of protic species in the electrolyte (Scheme 8). An overview of the electrolyte decomposition reactions that occur including those at the negative electrode is given in Figure S 21.

The scheme of electrolyte decomposition reactions in a cell without a lithium-ion conducting ceramic will be inherently more complex as it will involve electrode cross-talk (*i.e.*, the migration of species formed at one electrode to the other electrode, where they may react further). This process, well-known for gases, may lead to the consumption of the species in Figure 6 (or Figure S 21) or the generation of additional species, other than those identified in this work.

Implications of decomposition products and mechanisms

It is noted that oxygen loss is less documented in LiCoO₂ than in higher nickel content materials, especially the NMCs, in part because LiCoO₂ is not generally operated at such high potentials; the upper cell voltage limit for cycling LCO/graphite full cells with practical lifetime is conventionally ~4.25 V, above which material-level decomposition leads to capacity loss over time and thermal instabilities poses safety risks. Modern LCO materials that have been surface-coated, doped or otherwise treated can be cycled with good lifetime as high as ~4.5 V, corresponding to ~4.6 V vs Li/Li⁺ at the LCO electrode.^{9,49,83} Although it is desirable to cycle at even higher potentials, the results of the present work (Figure 2) indicate that electrolyte oxidation becomes significant at full cell voltages >4.5 V, which correlates well with the reported upper limit. The chemical oxidation of electrolyte at the positive electrode, especially at higher states of charge, directly leads to increased gas evolution in the cell and impedance growth at the positive electrode, due to the deposition of decomposition species on the surface. This process is expected to proceed independently of the negative electrode chemistry (*i.e.*,

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3 Li, graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, etc.). The production of dissolved protons (water oxidation) and HF (LiPF_6
4 hydrolysis), can lead to intercalation of H^+ into the positive electrode and lead to enhanced transition
5 metal dissolution rates from the active material; both processes will lead to a loss of the available
6 active material, in addition to the O loss that causes this in the first place. The dissolved transition
7 metals ions can then migrate to the anode surface and reductively deposit, where they can disrupt
8 the SEI and catalyse electrolyte reduction, leading to irreversible loss of active Li^+ -ions and impedance
9 growth.¹⁵ Electrolyte oxidation products formed at the cathode can also migrate to the anode, where
10 they will could be reduced and deposited on the surface, further increasing the cell impedance.^{16,17}
11 Over several charge-discharge cycles, this layer will build up and can limit ion transport to the bulk of
12 the anode (interfacial kinetic hinderance), which can make significant contribution to the capacity fade
13 (especially at high rates).^{84,85} Recently, it has been suggested that the acidic species generated at the
14 positive electrode are also involved in the degradation of the SEI layer, via acid-base reactions with
15 the basic species in the SEI.⁸⁶ We therefore encourage that future work should consider relative
16 acidity/alkalinity effects in the context of cross-talk. The loss of active material and the various
17 reactions of the decomposition products at both electrodes can also cause cell slippage (*i.e.*, a
18 mismatch of the relative capacity-voltage curves for each electrode) and a further decrease in the
19 available capacity.

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Decomposition of the electrolyte will not only affect the electrodes, but also the physical chemical
properties of the electrolyte itself. For example, decomposition of the LiPF_6 will lead to a decrease in
the lithium salt concentration in the electrolyte. If an asymmetrical alkyl carbonate solvent such as
ethyl methyl carbonate, EMC, is used, then trans-esterification can affect the relative concentrations
of the solvent components. Both of these changes can have significant effects on the solution
properties, such as melting point, conductivity, and viscosity. These changes may have importance for
cell performance in low-temperature and high-rate applications.

Future studies will examine chemical reactivity with singlet oxygen generated directly and the role
that catalysis of these reactions by the transition metal oxide surfaces, or coupled metal-ion reduction,
oxygen loss, and electrolyte degradation mechanisms^{40–44,87} - proposed to be important in Ni-
containing systems – play in controlling the potentials of both electrolyte degradation and oxygen loss.

Conclusions

This work has utilised specially designed LiCoO_2/Li cells in which the anode and cathode compartments were separated by a lithium-ion conducting glass-ceramic to examine electrolyte degradation of a standard lithium-ion battery electrolyte. The benefit of this approach is that electrolyte decomposition products formed under different cycling conditions could be independently identified at each electrode, without the complication of “cross-talk” or shuttling effects. The oxidation products resulting from electrochemical oxidation of electrolyte solution was studied in an H-cell. Of note, significant electro-osmotic flow was detected in the H-cell experiments, and the role that this has on battery performance particularly at high rates merits further investigation.

The analysis of the decomposition products detected by NMR spectroscopy was used to construct a detailed reaction scheme which accounts for all the observed decomposition products and attempts to rationalise the formation of products proposed in prior studies that were detected via complementary analytical techniques (Figure 6). One principal finding is that chemical oxidation driven by oxygen loss, rather than electrochemical oxidation, is the dominant driver for electrolyte decomposition at the positive electrode surface at high voltages. It is emphasised that the oxidative decomposition of the electrolyte at the positive electrode is intrinsically linked to surface reactivity of the active material. It is therefore suggested that an understanding the electrode-electrolyte interfacial chemistry will benefit research into improving cell lifetime at higher upper cut-off voltages. It is hoped that the present work will assist future studies to consider the underlying chemical mechanisms and kinetics for controlling oxygen loss when, for example, designing surface coatings, doping of the cathodes to increase stability, and electrolyte additives.

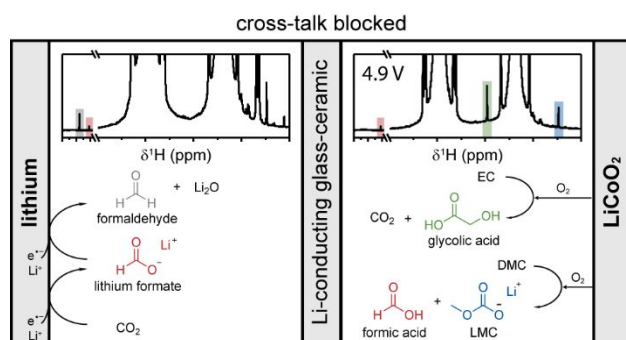
Supporting Information

Experimental setup; electrochemical data; additional ^1H , ^{19}F and ^{31}P NMR spectra and assignments; overview of electrolyte decomposition reactions discussed in this work.

Acknowledgements

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Table of content figure



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