Topical Review

Review: mechanisms and consequences of chemical cross-talk in advanced Li-ion batteries

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Abstract

Electrode cross-talk in Li-ion batteries refers to side reactions in which soluble products are generated at one electrode and consumed or further reacted at the other electrode. While these reactions impact battery lifetime directly, they perhaps have even greater consequence for battery management systems and state-of-health prediction. In this work, we review the current literature on cross-talk mechanisms, classify various reactions as firmly detrimental or beneficial to cell lifetime, and identify future scientific challenges in the area.

1. Introduction

Li-ion batteries have already established market dominance in consumer electronics and are rapidly increasing their penetration into electric vehicles. While a battery lifetime of less than five years is acceptable for consumer electronics, large-scale vehicle batteries cannot be so economically replaced. This need motivates improved lifetime and, just as importantly, improved monitoring and prediction of battery lifetime and state of health.

Electrode cross-talk refers to processes in which chemical or electrochemical side reactions at one electrode of a battery produce compounds that react chemically or electrochemically at the other electrode. Cross-talk is important to cell lifetime for three reasons. First, any side reaction has the potential to cause capacity fade. Capacity fade in advanced batteries is caused by a combination of loss of cyclable Li, loss of active material, and increased impedance. Numerous cell cycling analyses and post-mortem studies have concluded that in both mature and emerging chemistries, cell failure is dominated by loss of cyclable Li (LCL) at the anode [1–12]. LCL occurs when side reactions disturb the stoichiometric balance between electrodes, resulting in incomplete charge and discharge. Because LCL is caused by imbalance between electrodes, it cannot be observed in Li-metal ‘half-cells’, but only in ‘full cells’ with two intercalation electrodes. Although many side reactions can lead to LCL, the dominant source is the growth of the solid–electrolyte interphase (SEI) on the anode [1–12].

Second, cross-talk has amplified impacts on measurements of coulombic efficiency (CE), or the ratio of discharge : charge capacity. This metric remains the best single predictor of battery lifetime. If measured with extreme accuracy, CE can be used to screen formulations in weeks instead of months [5–7, 13]. However, it cannot distinguish between competing reactions, and therefore does not scale universally with lifetime. Several groups have hypothesized that the electrolyte can decompose into soluble products that reversibly shuttle between electrodes [14–19]. Such redox shuttles would decrease CE without affecting lifetime, because the current balances between electrodes without trapping Li.

Finally, the physical and chemical nuances of cross-talk greatly increase the complexity of battery reaction networks, which in turn forces a highly empirical paradigm for testing cell lifetime. Cells are cycled or stored at various temperatures and potentials, after which the remaining cell capacity is measured and fed to a statistical model [20–22]. Despite advances in artificial intelligence and machine learning, acquiring this performance data is still extremely time- and capital-intensive. Cross-talk reactions are naturally dependent on both the anode and cathode material; this interdependence requires that data-driven lifetime models...
must be trained and validated separately for every electrode combination. Electrochemical models can reduce the number of experiments necessary to predict lifetime [23–30], but rate constants are treated as more fitting parameters for capacity fade data [20]. In contrast to batteries, fuel cell controls predict the rates of individual failure mechanisms such as carbon corrosion, catalyst deactivation, and peroxide formation [31–33]. These comparatively well-understood mechanisms can be measured directly ex situ in order to provide transport and kinetic data to cell-stack management systems. Developing physics-based predictive models of device lifetime is far more challenging for nonaqueous Li-ion batteries than for aqueous fuel cells. However, such a model would be a ‘holy grail’ for battery engineers because it would allow more efficient cell utilization while drastically improving the speed of market deployment.

To this end, we survey the current literature for cross-talk mechanisms to identify areas of critical importance to cell lifetime and reaction network complexity. In this work, cross-talk refers specifically to physical exchange of molecules across a separator. Phenomena where mismatched electrodes or side reactions cause ‘marching’ or ‘slippage’ to undesirable potentials [13, 34] are not considered cross-talk by our nomenclature; nor are purely physical phenomena based on pressure changes from gassing [35]. We also exclude reactions of soluble polysulfides in Li–S and Na–S batteries, as these have been reviewed extensively elsewhere.

In this review, we first summarize the dominant techniques that can be used to observe the effects of cross-talk. Selected studies that use coulombic efficiency (2.1), chemical analysis (2.2) and four-electrode measurements (2.3) to conclusively demonstrate the presence of cross-talk reactions are highlighted. Phenomena are then classified by their origin at the positive or negative electrode. At the positive electrode, the major sources of cross-talk are transition metal dissolution (3.1), CO2/CO generation (3.2), and formation of reactive oxygen species (3.3). Cross-talk species that originate at the negative electrode include both gases (4.1) and higher–molecular–weight products such as oligomers (4.2). Throughout the review, reactions are identified as firmly beneficial, detrimental, or benign to cell lifetime, where possible.

2. Evidence of cross-talk and methods of quantifying its effects

2.1. Coulombic efficiency

While high CE is generally considered to be necessary for long battery lifetimes, side reactions are not intrinsically detrimental to battery lifetime. Christensen et al developed a framework to analyze the effects of cathode and anode CE on capacity fade and showed that perfectly balanced oxidation and reduction side reactions have no effect on lifetime [36]. However, a higher rate of reduction side reaction at the anode causes the discharge cutoff potential to be reached before Li has been completely removed from the cathode. The resulting LCL is the dominant cause of capacity fade under mild conditions. Similarly, byproducts of electrolyte oxidation at Li4Ni0.3Mn1.3O4 (LNMO) cathodes can migrate to Li2TiO3 (LTO) anodes and affect the cycle behavior, by causing accelerated capacity marching of the anode relative to the cathode [37, 38]. The implications of marching across cases depend on a number of factors including if the cell is anode- or cathode-limited. In an anode-limited cell, cross-talk may result in improved capacity retention, while a cathode-limited cell sees rapid capacity fade. The relative kinetics of electrolyte degradation and cross-talk reactions can vary with temperature [37]. When decay rates are matched, the cell will maintain a constant capacity with a decreased CE, but at elevated temperatures, anode side reactions can accelerate capacity loss. In contrast, balanced side reactions are naturally present in aqueous lead–acid and nickel–metal hydride batteries, where a small amount of water is split into H2 and O2 at a high state of charge. Because the H2 and O2 cross over and are reacted back to water at the cathode and anode, respectively, the only effect of the side reaction is reduced energy efficiency. A similar process has been proposed to provide overcharge protection in Li-ion batteries by intentionally adding molecular redox shuttles [39–43].

The presence of a naturally occurring shuttle reaction is not intuitive for organic carbonate electrolytes, where reversible solvent decomposition seems very unlikely, but it is still supported by some experimental evidence (figure 1). Deshpande et al prepared graphite//NMC111 (Li[Ni1/3Mn1/3Co1/3]O2) cells with a Li reference electrode and N:P ratios of 1:3 and compared the effect of an electrolyte with and without vinylene carbonate (VC) additive [19]. Although the cell with VC had a higher CE, it had slightly more rapid capacity fade. Both systems exhibited cell marching on charge and discharge, indicating both oxidative and reductive side reactions. The imbalanced rate of oxidation and reduction side reactions led to LCL, which was determined to be responsible for 93% of the observed capacity fade. However, the side reaction itself seemed to have minimal effect on cell lifetime. Integrating the total coulombs passed to side reactions over 600 cycles yielded an equivalent of 38% of the initial LiPF6 salt present. Considering the lack of detrimental effects on rate performance and the minimal capacity fade, this finding suggested that some of the side reactions were reversible. While the authors did not calculate irreversible solvent consumption, using an approach derived
from Xu et al gives a consumption of 3% of the initial solvent ethylene carbonate–diethylene carbonate (EC–DEC).

Xu et al completed a follow-up study to compare N:P ratios of 1:2 and 4:5 [44]. The cell with N:P of 4:5 also exhibited lower CE and slower capacity fade. Additionally, although the cathode was identical, it exhibited higher rates of side reactions, indicating that the higher surface area of the graphite was causing more cross-talk and lower CE. This behavior is explained by a higher proportion of soluble reduction products, which are able to diffuse through the cell and oxidize at the cathode, and therefore do not contribute to overall capacity fade. These findings emphasize that CE is not always an accurate predictor of cycle life or stability, and that cross-talk can obscure traditional measures of battery performance.

2.2. Chemical analysis

2.2.1. GC-MS of pouch cell headspace

Because H₂ and O₂ are known cross-talk agents in aqueous chemistries, gases are likely candidates for cross-talk phenomena in Li-ion batteries as well. During the formation of Li-ion batteries, gases are evolved as the electrodes react with the electrolyte and additives to form passivating layers on their surfaces. Many manufacturers remove these gases to prevent deformation of the cell, especially in pouch cells where the casing is flexible, and a uniform pressure is required during use. Dahn’s group developed a device based on Archimedes’ method to quantify gas production during battery operation and storage [17, 45]. Figure 2 shows an example of this measurement in Aiken’s survey of high-voltage formation. Gas is generated during cell charging and consumed during storage [17].

While it is difficult to determine the source of gas evolution in standard pouch cells, studies have been able to measure the high-potential evolution of H₂, CO₂, CO, and C₂H₄ via gas chromatography–mass spectroscopy (GC-MS) at each charged-state electrode by combining chemical analysis of both full pouch cells and charged individual electrodes, called ‘pouch bags’ [16, 46]. To assemble pouch bags, pouch cells were formed, degassed, charged, and cut open before their electrodes were separated and placed into individual sealed bags with either electrolyte or LiPF₆-free solvent. Non-degassed and degassed pouch cells were also studied as controls. To measure gas evolution during long storage periods, volume was measured via Archimedes’ method and composition was measured by extracting the gas with a syringe and performing GC-MS [16], or through a gas extraction device which was inserted directly into a GC [46] that could detect H₂, CO₂, CO, and light hydrocarbons. To measure consumption of gaseous products, a known volume of gas was inserted into pouch bags containing a single charged electrode, and volume change during storage was measured using Archimedes’ method [46]. In non-degassed full cells, the gases were consumed over time [46].

2.2.2. OEMS/DEMS in one- and two-compartment cells

On-line electrochemical mass spectrometry (OEMS) or related differential electrochemical mass spectrometry (DEMS) can also be used to determine the impact and extent of cross-talk. For example, experiments show more electrolyte oxidation products are produced at the cathode when the anode is
Figure 2. Voltage- and capacity-normalized volume change for graphite/NMC pouch cells that were charged at \(\sim \text{C}/10\) at 40 \(^\circ\)C and left at open circuit. The cells illustrate general differences between the gas evolution in regular cells and high-voltage cells. Reference curves for Li\([\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}]/\text{O}_2\) (NMC442) and graphite are included to show the approximate behavior of each electrode in the NMC442 cell during the charge. Data during the 24 h hold at 1.5 V has been omitted to provide a closer view of data during the charge. From reference [17], © The Author(s) 2015 used under CC BY-NC-ND 4.0.

Figure 3. Schematic illustration of gassing-related processes for (a) SLP30//NMC full cell in a one-compartment configuration and (b) an NMC//Li half-cell in an Al-sealed two-compartment cell. In both cases, electrolyte oxidation generates CO\(_2\)/CO and protic decomposition products, abbreviated as R-H\(^+\); however, only in a one-compartment cell can these protic species diffuse to the anode and be reduced under release of H\(_2\). From reference [48], © The Author(s) 2016 used under CC BY-NC-ND 4.0.

LiFePO\(_4\) (LFP) instead of Li metal or graphite, because the low potential scavenges oxidation products [47]. Metzger et al proposed a two-compartment OEMS cell to rigorously separate the effects of cross-talk and to measure real-time gas composition at each electrode \textit{in operando} [48]. In the design (figure 3), a Li-ion conductive glass ceramic (LiCGC) separates cells into two compartments, so gases and liquid-phase products evolved at one electrode may not interact with the other electrode [48, 49]. OEMS/DEMS also allows isotopic labeling experiments to determine the source of carbon, oxygen, and other elements in various decomposition products.
2.3. Four-electrode measurements

While four-electrode techniques are much less common in battery systems than in aqueous electrochemistry, evidence has shown that electrolyte degradation products can be detected electrochemically. Read et al. developed a chemistry based on intercalation of Li$^+$ and PF$_6^-$ into graphite at low and high potential, respectively, and hypothesized that low CE in full but not half-cells was due to electrode cross-talk [50]. Adding a second Li and a Pt ‘sensing’ electrode to the edge of a graphite//Li coin cell showed the appearance of new voltammetry features during cycling of the Li//graphite, as seen in figure 4 [50].

Scanning electrochemical microscopy is an example of a generator–collector technique, in which a collector electrode amperometrically detects redox products from a generator electrode. It has been used to probe characteristics of battery interfaces [51] and to observe Co$^{2+}$ dissolution from LiCoO$_2$ (LCO) in an ionic liquid electrolyte [52]. The most common generator–collector device is the rotating ring-disk electrode (RRDE). An example of generator–collector operation of an RRDE is shown in figure 5(a), where products from LNMO particle oxidation at the disk electrode (generator) travel to the ring electrode (collector) and may participate in SEI formation reactions. RRDE generator–collector experiments have also been used to quantify radical superoxide stability in Li–air electrolytes [53], identify reaction intermediates in Li–S systems [54], and even quantify Mn dissolution from spinel Li$_x$Mn$_2$O$_4$ (LMO) [55]. Our group recently applied RRDE generator–collector methods to study electrode cross-talk, specifically by tracking the effect of metal dissolution induced by high-voltage oxidation of LNMO particles (disk) on SEI formation (ring), shown in figure 5(b). Other electrochemical detection apparatuses that utilize the generator–collector approach include interdigitated electrode arrays and laminar electrochemical flow cells. Both of these may become powerful tools for in situ observation of electrode cross-talk.

3. Phenomena originating at the cathode

3.1. Transition metal dissolution

Metal dissolution from cathode materials is a major source of capacity fade in high-energy Li-ion batteries and a well-known example of detrimental electrode cross-talk. Evidence of metal accumulation at the anode was first reported in 1994 by Tarascon using Rutherford backscattering to detect Mn on the surface of a Li anode that was cycled against LMO [57]. Abraham later used secondary ion mass spectrometry to detect Ni and Co, in addition to Mn, on a graphite electrode cycled against Li$_{1.05}$(Ni$_{0.33}$Co$_{0.33}$Mn$_{0.33}$)$_{0.95}$O$_2$, as shown in figure 6 [58]. Many other researchers have detected metals at the SEI for a variety of cathode materials, anode materials, electrolyte compositions, and cycling conditions [11, 57–68]. While dissolved metals are known to travel to the anode and impact the formation and growth of the SEI, there is not yet consensus on how these reactions occur or why they are so detrimental to battery lifetime.

3.1.1. Mechanisms of metal dissolution

Several transition metal oxide chemistries, including LMO, LNMO and various NMC forms (Li$_x$Ni$_{0.5}$Mn$_{0.5}$CoO$_2$, Li- and Mn-rich xLi$_2$MnO$_3$ · (1-x)LiMO$_2$ [M = Mn, Ni, or Co]), are known to suffer from metal dissolution. Operation at elevated temperature often exacerbates this phenomenon, while increasing the upper cut-off voltage during cycling has been shown to accelerate metal dissolution.
Figure 5. RRDE performing a generator–collector experiment to detect cross-talk between an LNMO-coated disk and glassy-carbon ring. From reference [56]. Reprinted with permission J. Phys. Chem. C, 122, 20632–41 (2018). Copyright 2018 American Chemical Society.

Figure 6. Elemental content data as a function of sputter depth in fresh, formed and aged graphite anodes. The X-axis shows sputtering time in seconds, and the Y-axis shows counts per second. From reference [58]. Reprinted with permission from Electrochem. Solid-State Lett. 2008 11 (12) A226. Copyright 2008 The Electrochemical Society.

[58, 69–76]. Additionally, electrolyte identity can strongly influence metal dissolution, with fluorinated salts, particularly LiPF₆, promoting dissolution due to HF impurities [77]. While the trends of dissolution with voltage, temperature, and salt are clear, the mechanism by which metals dissolve out of these active materials remains an area of active research.

The earliest works aiming to understand metal dissolution from transition metal oxide active materials were investigating LMO-type electrodes. Thackeray and colleagues attributed Mn dissolution from LMO [78] to the Hunter disproportionation reaction [79], whereby surface and bulk Mn³⁺ react to form bulk Mn⁴⁺ and a surface Mn²⁺ which dissolves into solution. Aurbach proposed another mechanism of high-potential dissolution caused by HF corrosion [80], where electrolyte oxidation induced high Lewis acid concentrations that catalyzed dissolution and passivated the surface with LiF and MnF₂. Amatucci and colleagues found that the concentrations of dissolved Mn and HF increased proportionally when LMO electrodes were left submerged in electrolyte for several weeks [81]. Blyr similarly showed that intentional electrolyte contamination by water increased the extent of Mn dissolution from LMO [77], and both Blyr and Amatucci clearly demonstrated that storage at elevated temperatures exacerbated this dissolution [77, 81]. Blyr also showed that Mn loss was greatest when LMO was stored in LiPF₆-containing electrolyte.
compared to other fluorinated salts such as LiBF₄ and LiAsF₆, indicating that the instability of the PF₆⁻ anion plays an important role in Mn dissolution.

Terada used total reflection x-ray fluorescence to track electrolyte Mn concentrations [82], and found the oxidation state of dissolved Mn to be Mn²⁺. Recently, Banerjee used electronic paramagnetic resonance (EPR) paired with inductively coupled plasma spectroscopy and x-ray absorption near-edge spectroscopy (XANES) to determine the oxidation state of dissolved Mn in an LMO–graphite battery [83]. They found that dissolved Mn existed mostly in the Mn³⁺ state, with an average oxidation state of 2.6 ± 0.2, disputing early assumptions of dissolved Mn²⁺, and providing evidence for an alternative mechanism of Mn dissolution. Phase transformation at high voltages involving the formation of a soluble Mn₃O₄ phase could account for Banerjee's findings, since this mechanism involves direct dissolution of Mn(III) and Mn(II).

Tang used scanning transmission electron microscopy to confirm the presence of Mn in the LMO, and found the phase disappeared or dissolved during discharge [84]. An important distinction between the phase transformation and disproportionation mechanisms is not only the valence state of dissolved Mn, but also the concomitant oxygen release under phase transformation. While the disproportionation mechanism was extensively considered in early works, it does not fully encompass all modes of metal dissolution such as at high voltages or for Ni and Co dissolution from LNMO and NMC chemistries. Thus, disproportionation of Mn³⁺ may contribute to metal dissolution from high-energy cathodes, but it is neither the sole mechanism nor the most deleterious.

Similar mechanisms have been considered to better understand metal dissolution in other high-energy cathode materials. For instance, the disproportionation mechanism was later applied by Gallus to explain metal dissolution from NMC111 at low states of charge, while also considering HF corrosion as the cause of degradation at high states of charge [73]. Other proposed mechanisms involve dissolved organic species facilitating metal dissolution by forming soluble chelation complexes with those metals, such as fluorescent acetylacetonate complexes formed at LNMO [63, 85]. Lastly, researchers have shown that some cathode degradation pathways in layered NMC electrodes, such as oxygen release [84, 86–89], do not directly involve metal dissolution but rather create conditions favorable to dissolution on subsequent cycles. For instance, oxygen loss is thought to be accompanied by surface reconstruction and vacancy evolution, encouraging transition metal motion from bulk sites to surface sites, causing surface instabilities, and ultimately leading to the dissolution of the unstable, reduced transition metal surface layers [67, 88, 90, 91]. Efforts to impede metal dissolution primarily focus on coatings, which may increase impedance, or additives, which must not introduce new detrimental effects at the anode.

3.1.2. Metal transport across the separator and deposition at the anode

While the prevailing consensus is that dissolved Mn is present as Mn³⁺ or Mn²⁺, there are few reports on the oxidation states of dissolved Ni and Co and the assumption of Ni²⁺ and Co²⁺ has been largely unchallenged [64, 92]. Additionally, mitigation efforts to scavenge or trap metals before reaching the SEI are hampered by uncertainty over the transport mechanism of dissolved metals. The simplest explanation for metal transport is a migration mechanism in which charged Mn, Ni, and Co ions travel along electric field paths to the anode (figure 7(a)). However, this interpretation breaks down when considering the relative concentrations of dissolved metals. Terada measured Mn concentrations of ~10 ppm for LMO cycled at room temperature and ~400 ppm at 50 °C [82], while Amine more recently measured ~20 ppm each for Mn, Ni, and Co dissolved from a Li₁₋ₓ(Niₓ₋₃MnₓCoₓ)₁₋₃O₂ electrode left soaking at 55 °C for one month [93]. Lee summarized the work of many groups and found that 50–200 ppm was a reasonable concentration range of dissolved metals for model and theoretical studies [94]. Clearly, these metals are extremely diluted when compared to conductive salts at concentrations of 1 M or greater. Thus, dissolved transition metal ions are effectively in the supporting electrolyte, and their transport is governed by diffusion alone.

Shkrob originally suggested that electrolyte degradation products, such as oxalate, carbonate, or ethylene dicarbonate, form stable complexes with Mn²⁺, thus facilitating metal dissolution from the cathode [95]. They demonstrated the preferential deposition of Mn on mineralized SEI components and found through electron spin echo envelope modulation that Mn²⁺ was always coordinated to an organic ligand. These findings further discredit a transport mechanism based on migration of charged metal species. Shkrob then considered an alternate transport mechanism, shown in figure 7(b), in which metal ions are coordinated by electrolyte decomposition products such as Li ethylene dicarbonate (LiEDC). They reasoned that these decomposition products must be stronger chelating agents than outer SEI organic species, since only the strongly chelating carbonates present in the inner SEI layers can supplant the proposed chelating agents that facilitate metal dissolution at the cathode. Jarry and colleagues later used findings from an x-ray fluorescence study to propose that electrolyte oxidation at LNMO generates β-diketonate ligands which chelate surface metals and together dissolve as a neutral complex, and travel to the anode in this form before deposition (figure 8) [63].
Figure 7. Two models of transport and deposition of Mn\(^{2+}\) ions in Li ion batteries. (a) Mn\(^{2+}\) ions are solvated by carbonate molecules in the same fashion as Li\(^{+}\) ions, and drift along the field lines penetrating through the outer (organic) SEI (ii) and become deposited into the inner (mineral) SEI layer at the graphite particle surface (i). (b) Electrolyte decomposition products with chelating groups reach the cathode and form neutral complexes of Mn(II) that diffusively migrate to the graphite surface, bypassing the outer SEI, and these complexes become chemisorbed on the surface of lithium carbonate crystallites in the inner SEI layer that serves as an ion exchanger. From reference [95]. Reprinted with permission from J. Phys. Chem. C 2014 118 (42) 24 335–48. Copyright 2014 American Chemical Society.

Figure 8. Optical and x-ray fluorescence images of the graphite anode from a tested Li-ion cell. (a) Optical fluorescence image. (b, c) Fluorescence maps of the (b) Mn and (c) Ni elemental distribution. From reference [63]. Reprinted with permission from J. Am. Chem. Soc. 2015 137 (10) 3533–9. Copyright 2015 American Chemical Society.

Tornheim and colleagues recently provided more evidence for this complexing mechanism by performing carefully designed pre-formation experiments [96]. Their work suggests that reduction products generated at the anode not only play a role in metal dissolution at the cathode, but also that metal penetration into the SEI is dependent on the chemical nature of the electrolyte used to pre-form the SEI. In fact, anode-dependent impedance rise at the cathode may be understood to involve this exact cross-talk mechanism. Rodrigues demonstrated that metal deposition rates on graphite were almost double those for the ‘SEI-free’ LTO [66], which may be indirect evidence that metal dissolution is inhibited by pairing cathodes with higher-potential anodes that do not generate the same chelation agent byproducts as graphite.

In a more recent communication, Tornheim showed that the coordinating ion of dissolved Mn strongly impacts cell cycling behavior: PF\(_6^–\) -coordinated Mn showed persistent side reactions and constantly decreasing CE, while TFSI\(^–\)-coordinated Mn had a large initial capacity loss, but stable CE during cycling.
Figure 9. (a) Capacity vs. cycle number for graphite//LFP cells containing baseline electrolyte, 1.2 M LiPF$_6$ in EC/EMC, ("Gen2"), and electrolyte doped with Mn(PF$_6$)$_2$, and Mn(TFSI)$_2$. (b) Corresponding CEs. Averages of three cells with standard deviations are plotted at each point. From reference [98]. Reprinted with permission from J. Electrochem. Soc. 2019 166 (10) A2264–6. Copyright 2019 The Electrochemical Society.

Wang’s recent communication complements Tornheim’s studies, using theoretical interaction energy calculations and storage tests to determine that dissolved Mn$^{2+}$ is preferentially solvated by TFSI$^-$ over PF$_6^-$, yet the coexistence of PF$_6^-$ and Mn$^{2+}$ in electrolyte results in the greatest destabilization and degradation of the electrolyte [97]. This may explain why Tornheim observed that Mn(TFSI)$_2$-doped PF$_6^-$-containing electrolyte does not show the same performance as Mn(PF$_6$)$_2$-doped electrolyte: Mn$^{2+}$ mostly remains solvated by TFSI$^-$ anions, whereas the PF$_6^-$ originating from the LiPF$_6$ salt induces similar side reactions to if no Mn salt were present (i.e. CE match between Gen2 and Mn(TFSI)$_2$ in figure 9(b)). Perhaps more importantly, Wang demonstrated that Mn$^{2+}$ is preferentially solvated over Li$^+$ by EC, TFSI$,\text{PF}_6^-$, etc, and concluded that even before reaching the SEI, dissolved Mn parasitically destabilizes solvation sheath members for chemical decomposition and activates electrolyte components for electrochemical reduction at the anode. This indicates that mitigation strategies based on SEI engineering may not completely prevent metal-induced parasitic reactions and overlook a mode of dissolved metal-induced capacity fade. These findings further corroborate Shkrob’s proposed mechanism of metal transport between electrodes and underscore the importance of understanding the chemical nature of dissolved metals, since the identity of metal-coordinating species corresponds to different degradation pathways and battery lifetime outcomes.

Tornheim’s and Wang’s results taken together demonstrate that the solvation environment of metals within the electrolyte governs their deposition at the anode [96, 97, 98]. It is clear that neither electrochemical reduction to a metallic state nor ion exchange with –CO$_2$Li$^+$ members of the organic SEI layer are occurring, due to the predominant location of Mn$^{2+}$ on inorganic Li$_2$CO$_3$ crystallites [95]. Rather, metals are incorporated in the SEI layers by a mechanism involving their chelating agents, and their destination within the SEI is governed by the chemical character of the SEI. For instance, Mn is commonly observed near the surface of an SEI formed in highly fluorinated electrolyte, whereas higher bulk Mn concentrations are observed for SEI formed in conventional electrolyte [96]. Once trapped in the SEI, these metals destabilize the protective layer leading to unabated capacity fade.

3.1.3. Consequences of metal incorporation into SEI

The main source of capacity fade in high-energy Li-ion batteries originates from metal contamination of the SEI, yet there is no generally agreed-upon mechanism of SEI failure. Delacourt suggested that the SEI’s insulating properties are circumvented by metallic Mn deposits forming an electronically conductive pathway (figure 10(b)) [60], which Gowda later supported based on their finding of Mn(0) in the SEI of charged graphite with XANES [59]. Delacourt suggested another possibility for Mn-induced capacity fade involving the formation of a highly porous SEI that allowed facile electrolyte transport to the anode for reduction (figure 10(c)) [60]. Ochida similarly reported that Mn particles decompose surface films (i.e. SEI), and Joshi specifically ascribed metal-induced capacity fade to the decomposition of LiEDC, revealing fresh graphite surfaces for electrolyte reduction [8, 68]. Joshi also noted that Mn promotes the formation of inorganic LiF and Li$_2$CO$_3$ species within the SEI, as products of LiEDC decomposition [8]. Shkrob used extended x-ray absorption fine structure and EPR to show that the SEI contains a reduced form of Mn below the $+2$ valence state, but not metallic $\alpha$-Mn(0) [95].
Figure 10. Schematic of the mechanism proposed for SEI growth on copper electrode (a) during formation in a Mn-free electrolyte, (b) during formation in a Mn-contaminated electrolyte, and (c) during cycling of a Mn-contaminated SEI in a Mn-free electrolyte. ‘S’ stands for a solvent. From reference [60]. Reprinted with permission of the Electrochemical Society from J. Electrochem. Soc. 2013 160 (8) A1099–107. Copyright 2013.

Figure 11. Schematic representation for Leung’s electrocatalytic mechanism for Mn\textsuperscript{II} ions in SEI. Complexation of radical anions by Mn\textsuperscript{II} in the SEI matrix yields an active center (complex i) that after accepting electrons (complex ii) can reduce these anions straight to alkoxide anions (RO\textsuperscript{-}) and yield carbon dionide radical anions CO\textsubscript{2}\textsuperscript{-}· that diffuse through the outer SEI matrix toward the solvent and reduce it therein, converting to CO\textsubscript{2} and trapping lithium. In this way the reductive equivalents become ‘transferred’ from the inner SEI outwards. As the carbonates replace oxides in the inner sphere of complex ii, there is a turnover of the electrocatalytic center i. From reference [75] under CC BY 4.0.

Shkrob interpreted this finding as evidence for Mn acting as a catalytic center for SEI decomposition. Vissers found that inorganic SEI species are able to sequester Mn ions [99], and supported Shkrob’s proposed mechanism by asserting that Mn is reduced to the +1 oxidation state during graphite lithiation and subsequently oxidizes to +2 by catalytically reducing adjacent electrolyte molecules. Wang found evidence supporting an electrocatalytic reduction cycle involving Mn\textsuperscript{2+}, and showed that Mn\textsuperscript{2+} is more effective than Mn\textsuperscript{0} at inducing electron transfer from the anode to facilitate EC reduction [97]. Based on calculated electron affinities of electrolyte reduction reactions, Wang asserted that single electron reduction of a solvated Mn\textsuperscript{2+} is far more likely than two-electron reduction [97].

Gilbert combined insights from Leung [100] and agreed that metal-facilitated capacity fade occurs via an electrocatalytic process of metal reduction and decomposition of organic SEI components (figure 11) [75]. More recent work from the Gasteiger group has provided support for this electrocatalytic metal redox mechanism of SEI decomposition, while also linking metal contamination to gassing events in Li-ion batteries [61, 101]. Our own recent efforts have found that predicted voltammetric curves of the electrocatalytic mechanism are quantitatively consistent with experimental measurements. However, the trends predicted by the thermodynamic redox potentials of Mn, Ni, and Co were obscured by kinetic differences between the metals. These findings further emphasize the importance of local coordination environment for metals within the SEI [56, 102, 103]. Understanding how ligands and anions affect the location and reactivity of metals within the SEI will be necessary to design mitigation approaches.

Perhaps the most effective single approach to mitigating the effects of metal dissolution is engineering a more robust SEI. However, preventing metal incorporation into the SEI with SEI additives or active-trap separators does not prevent dissolved metals from destabilizing electrolyte components and consuming cyclable Li. The literature thus suggests that only a strategy based on eliminating dissolution can achieve high
CE and cell lifetimes while maintaining the improved energy and power densities that motivate the use of these cathodes. As such, SEI engineering can help limit metal dissolution by preventing generation of soluble higher-molecular-weight electrolyte degradation products. These products can be particularly detrimental if they promote transition metal dissolution by acting as chelating agents or generating protons during cross-talk oxidation. Therefore, careful design of the SEI to avoid soluble products can impede cathode degradation and diminish the extent of metal dissolution, but it cannot fully eliminate this phenomenon. To move forward, researchers must focus on low-impedance coatings that stabilize the cathode surface or CEI-formation additives that neutralize the various mechanisms of metal dissolution. Additives that promote Li$_2$O, LiF, and Li$_2$CO$_3$ may be of particular interest, as these species are understood to provide important passivation at the anode. However, care must be taken to ensure that additive decomposition does not initiate new, harmful cross-talk mechanisms. Ultimately, continued investigation into how the CEI regulates metal dissolution will better inform advanced cathode designs for next-generation Li-ion batteries.

3.2. CO$_2$/CO generation and consumption

3.2.1. Sources of CO$_2$ and CO

At thermodynamic equilibrium, the carbon and oxygen atoms of organic electrolytes will be converted into CO$_2$. However, a 5 V battery operates very far from equilibrium. It is thus not surprising that CO$_2$ is both generated and consumed by a number of heterogeneous and homogeneous processes throughout a battery. The most obvious source of CO$_2$ in a Li-ion battery is electrochemical oxidation of the organic electrolyte. Early voltammetry studies of a variety of carbonate electrolytes reported anodic stability limits between 3.3 and 4.3 V on planar gold, aluminum, and platinum electrodes [104, 105]. It was assumed that the current was due to solvent and salt oxidation with products of CO$_2$, CO, and aldehydes. However, this interpretation is inconsistent with the performance of commercial batteries, as noted by Jung et al [106]. At a typical commercial electrode loading of 10 mg cm$^{-2}$ oxide and 0.2 mg cm$^{-2}$ conductive carbon with specific surface areas 0.25 and 65 m$^2$ g$^{-1}$, respectively, Moshkovich’s measurements at 4.5 V predict a parasitic current due to solvent oxidation that is at least 100 times the C-rate. Because of this complexity, direct detection of gaseous products using OEMS and DEMS is generally accepted as necessary to deconvolute solvent decomposition from other oxidation processes. Even then, there are a variety of reports in the literature regarding the potential at which electrolyte degradation occurs and its surface sensitivity, as discussed below. CO$_2$ and, to a lesser degree, CO are evolved at potentials as low as 4.2 V vs. Li, depending on the exact system. For many systems, almost all the gas in the first charging cycle can be attributed to the oxidation of residual carbonate impurities on particle surfaces [107]. Direct electrolyte oxidation is then not observed until almost 4.8 V. Many electrolyte additives are also preferentially oxidized at relatively low potentials [108], and CO$_2$ generation from this process has been directly observed.

The surface sensitivity of electrochemical solvent oxidation reactions is important for interface design but remains a subject of open debate in the literature. Certain cathode materials are clearly more active for CO$_2$ and O$_2$ evolution than others. Chemical intuition additionally suggests that electrocatalysis plays a role because solvent oxidation requires multiple electron and/or proton transfers. Multi-electron reactions are most commonly inner-sphere reactions that proceed through several adsorbed intermediates. Because the free energy of adsorption is surface-specific, this would indicate a surface-sensitive or electrocatalytic reaction. Density functional theory calculations predict that carbonate adsorption and dissociation is preferred on oxides with lower p-band centers [109], and other evidence suggests that electrolyte preferentially oxidizes at oxide vacancies or defects [63, 110]. Computational evidence against electrocatalytic solvent oxidation proposes that organic carbonate oxidation is initiated by removal of one electron to form a cation radical [111, 112]. This outer-sphere reaction would likely be much less sensitive to electrode surface structure. Experimentally, Jung et al showed that, after normalizing for surface area, C65 carbon and LNMO had the same profiles for current and CO$_2$ evolution with potential (figure 12). While layered NMC622 (Li[Ni$_{0.2}$Mn$_{0.4}$Co$_{0.4}$]O$_2$), NMC111, and NMC811 (Li[Ni$_{0.8}$Mn$_{0.1}$Co$_{0.1}$]O$_2$) had lower onset potentials for current and CO$_2$ and CO evolution, the gases were shown to originate from homogeneous reaction of solvents and electrochemical generation [106]. Metzger et al determined via isotopic labeling that a majority of CO$_2$/CO evolution occurs from electrolyte oxidation, while the remainder comes from electrode oxidation [113]. Furthermore, the electrolyte is more sensitive to oxidation at elevated temperatures than the electrode.

Homogeneous electrolyte decomposition initiated by electrochemically generated species explains much of the variation between electrode materials. Oxygen can be released from metal oxides at very low levels of lithiation or high state of charge. While the state of charge corresponds with potential, oxygen release is often driven by structural instability, rather than electronic driving force. Wandt et al and Mahne et al showed that singlet O$_2$ was released from both active materials and Li$_2$CO$_3$ [114, 115]. Castel et al suggested that trace water could result in a variety of reactive oxygen species [116]. The subsequent reactions between reactive oxygen and organic electrolytes generate CO$_2$ and other products, which can then diffuse to the anode. The
possibility that reactive oxygen remains stable long enough to react heterogeneously at the anode is discussed in section 3.3.

CO$_2$ can also be generated thermally at elevated temperatures. Sloop et al showed using thermogravimetric and chemical analysis that LiPF$_6$ decomposes into LiF and PF$_5$ at temperatures as low as 50 °C [14]. As a strong Lewis acid, PF$_5$ reacts with EC to form oligomers and CO$_2$. Xiong et al observed more CO$_2$ evolution in a pouch bag with a delithiated cathode than in a full pouch cell and no CO$_2$ evolution in a bag with a charged anode [16]. There was also less CO$_2$ evolution with no LiPF$_6$ in the solvent [16]. A number of other studies have reviewed the thermal decomposition reactions of salts and solvents [108, 117, 118].

3.2.2. Consumption of CO$_2$ and CO
The presence of CO$_2$ in Li-ion cells seems, from most reports, to be strongly beneficial to cell lifetime. CO$_2$ was an early electrolyte additive; Plichta et al attributed improved cycle life of LiCoO$_2$–Li to reaction between CO$_2$ and trace LiOH and Li$_2$O cells to form Li$_2$CO$_3$ [119]. Aurbach found similar results, and speculated that trace CO$_2$, introduced from decomposition during solvent purification, could be a source of irreproducibility between research groups [120]. More recently, Krause found greatly improved lifetime on a Si anode when a small amount of dry ice was incorporated into the cell [121].

Because LCL at the anode dominates most capacity fade, the mechanism of successful electrolyte additives is most likely improving the passivity of the SEI. Lucht et al showed that in the absence of CO$_2$, SEI chemistry contained very little Li$_2$CO$_3$ [122, 123]. Electrochemical reduction of CO$_2$ in aprotic media was studied extensively by Saveant’s research group and concluded that on inert electrodes such as mercury and lead, reaction proceeded through the CO$_2$ radical anion [124–126]. Conductive carbon such as graphite is also generally considered catalytically inert and would likely follow a similar reaction scheme. Schwenke et al
completed a rigorous OEMS study of CO$_2$ at low potentials [127]. Flowing isotopically labeled [13] CO$_2$ into the OEMS cell showed that CO$_2$ is not reduced to CO. Instead, it is consumed primarily by three processes, depicted in figure 13. At 1.5 V, electrochemical reduction of trace water increases the pH and converts CO$_2$ to CO$_3^{2-}$, which then precipitates as Li$_2$CO$_3$. At 0.7 V, CO$_2$ is reduced directly to CO$_2$•. Following the findings of Saveant [124–126], the radical can combine with trace protons to formate or can dimerize to oxalate. Finally, at 0.01 V, CO$_2$ can be reduced to solid amorphous carbon and carbonate. Carbonate and oxalate have very low solubility in the electrolyte, and thus form more passivating layers than organic SEI products, thereby explaining the beneficial effects of CO$_2$ on cycle life.

While CO$_2$ has generally been shown to benefit cell lifetime, CO$_2$• may also be detrimental, as it is highly unstable and can react homogeneously with solvent as well [100]. Tang et al and Ma et al used an interesting cell design to flow gases while cycling a cell and found that the capacity fade in several cell chemistries was twice as rapid when cycled in 1% CO$_2$ in Ar vs. pure Ar [130, 131]. The net benefit of CO$_2$ in a battery will certainly depend on the relative rates of dimerization, precipitation, and further reaction with solvent, all of which are likely sensitive to local transport and electrode geometry as well as surface chemistry.

Along with CO$_2$, CO is also typically generated in electrolyte degradation processes, but at lower concentrations. There is very little research on the direct effects of CO. Aqueous electrochemical research on CO$_2$ reduction shows that CO$_2$ and CO reduction often yield similar end products. If this trend applies in nonaqueous batteries as well, CO reduction is likely also beneficial to anode passivation. However, unlike aqueous electrochemistry, CO$_2$ reduction in battery solvents does not yield CO as a product [127], showing that more work is necessary to understand this family of reactions.

### 3.3. Reactive oxygen species

Oxygen from oxide active materials and carbonate surface impurities is electrochemically released at high potential in the form of singlet oxygen, superoxide anions, and other reactive oxygen species. Guéguen et al showed that reactive oxygen caused hydrolysis of PF$_6^-$, which ultimately was detectable as POF$_3$ gas in OEMS experiments [128]. Leanza et al suggested follow-up reactions to a variety of species including acyl fluorides, carboxylates, and alkyl carbonates [67]. The reactivities of excited oxygen and organic electrolytes have implications for metal–O$_2$ batteries, and the literature in this field has explored reaction networks in more detail [132].

Several studies have shown that byproducts of reactive oxygen are involved in cross-talk at the anode. It is unlikely that reactive oxygen itself can survive long enough to react directly at the anode. For example, the lifetime of singlet oxygen in the most stable solvents is reported as 500–700 µs [133, 134]. For a typical
Figure 14. Plots of the CO$_2$ and O$_2$ evolution rate and approximate evolution rate for H$_2$ (m/$_z$ = 2) and POF$_3$ (m/$_z$ = 85, 104) for the two first galvanostatic cycles. (a) High-energy nickel–cobalt–manganese-oxide cathode (HE-NCM) vs. Li with glass fiber separator and 1 M LiPF$_6$ in EC:DEC (3:7), (c) HE-NCM electrode vs delithiated LiFePO$_4$ with glass fiber separator and 1 M LiPF$_6$ in EC:DEC (3:7). Adapted from reference [128], used under CC BY 4.0.

liquid-phase diffusivity of 10$^{-6}$ cm$^2$ s$^{-1}$, a thin 10 µm separator yields a diffusion time constant of 10 ms. Thus, it is much more likely that the products of subsequent reactions with the electrolyte, rather than the reactive oxygen itself, are capable of cross-talk. Accordingly, Guéguen showed that POF$_3$ was consumed on graphite and Li electrodes, but not on delithiated LFP, as shown in figure 14 [128]. Leanza detected a thin (<2 nm) layer of organic species on the LTO counter electrode due to cross-talk [67]. Freunberger found thick, gel-like deposits on an Li counter electrode in a Li–O$_2$ cell and attributed them to OC$_3$H$_6$O generated by reactive oxygen in the carbonate electrolyte [132].

The impacts of reactive oxygen cross-talk on anode performance are not clear. Higher-molecular-weight (MW) products are most likely detrimental to cell performance. While LTO is considered an SEI-free anode, organic cationic species, formed by electrolyte oxidation at high-voltage LNMO cathodes, were shown to form a film at the LTO interface, increasing the impedance [137]. Oxidation products from NMC have also been shown to contribute to the formation of a thick film at the graphite interface which causes kinetic limitations and can eventually become fully ion blocking [136, 137]. On the other hand, it is possible that the beneficial effects of CO$_2$ (section 3.2.2) on SEI passivity outweigh these effects, at least for graphite anodes.

Cross-talk of oxidation products, meanwhile, appears to have significant positive effects on the cathode. Removing oxidation products by electrochemical reduction or chemical reaction at the anode results in less precipitation of byproducts at the cathode. Xiong showed that the impedance of a single NMC electrode increased greatly when stored in electrolyte for 500 h at either 40 or 60 °C [16]. When the electrode was stored with a graphite counter electrode, less CO$_2$ was generated, and the impedance rise of the NMC was smaller. Any detrimental effects of the scavenging process on graphite were not reported. Similarly, Leanza did not report any impedance rise on the LTO counter electrode with cross-talk precipitates [67]. The higher sensitivity of cathode than anode materials to reaction products may be explained by local conductivity effects. Cathode materials are typically poorly conducting oxides, and the presence of insulating surface films can greatly weaken the short-range electronic contacts that limit electrode performance [138, 139]. Alternatively, reduction of reactive oxygen byproducts at low potential may form less insulating products. More work is necessary to explain why cross-talk products have such detrimental impacts at the cathode, but not the anode.

Potentially beneficial impacts of cross-talk may provide a potential mechanism to protect from detrimental effects of O$_2$ release. Recent work has focused on the impact of singlet oxygen on electrolyte decomposition, in particular EC. Freiberg et al reported a tradeoff between chemical stability to singlet O$_2$ and electrochemical stability at elevated potential [140]. Petit developed a singlet oxygen quencher that was stable at high voltage [141]. Because developing stable and active quenchers for the variety of reactive species that can be formed under oxidizing conditions is challenging, an alternative possibility could be to provide a scavenger that is intentionally unstable, but decomposes into CO$_2$ instead of other, more detrimental products.
Figure 15. Proposed chemical structures for molecules corresponding to detected \( m/z \) peaks for species only present in electrolyte where cross-talk reactions occurred. From reference [129]. Reprinted with permission from Chem. Mater. 2019 31 (8) 2884–91. Copyright 2019 American Chemical Society.

4. Phenomena originating at the anode

4.1. \( \text{H}_2 \) and other gases

4.1.1. Gas generation

The SEI formation process is known to result in gases including \( \text{H}_2 \), \( \text{CO}_2 \), \( \text{CO} \), \( \text{CH}_4 \), \( \text{C}_2\text{H}_4 \), and \( \text{C}_2\text{H}_6 \). Gas generation is known to increase with higher water content, which can happen due to contamination during cell assembly or when electrodes are poorly dried. Bernhard \textit{et al} used OEMS with one- and two-compartment cells to investigate one-electron reduction of water at the anode forming \( \text{H}_2 \) and \( \text{OH}^- \) [49]. They proposed that the \( \text{OH}^- \) triggers a ring-opening reaction of cyclic carbonates, causing solvent decomposition into \( \text{CO}_2 \). Metzger and colleagues used the same OEMS setup to observe that without \( \text{H}_2\text{O} \) contamination, the source of \( \text{H}_2 \) evolution is due to protic electrolyte oxidation species (R-H\(^+\)) that diffuse from the cathode and subsequently are reduced at the anode [48].

4.1.2. Gas consumption

Unlike \( \text{O}_2 \) and \( \text{CO}_2 \), which are generated and consumed at different electrodes, reduction gases seem to be both generated and consumed primarily at the anode. Ellis \textit{et al} injected pure \( \text{H}_2 \), \( \text{CO}_2 \), \( \text{CO} \), \( \text{C}_2\text{H}_4 \), \( \text{CH}_4 \), or \( \text{C}_2\text{H}_6 \) into pouch bags with only one electrode in order to determine the reactivity of gases at each electrode [46]. Large volumes of \( \text{CO}_2 \), \( \text{CO} \), \( \text{H}_2 \), and \( \text{C}_2\text{H}_4 \) were consumed at the anode, presumably by the mechanisms discussed in section 3.2. At the cathode, \( \text{H}_2 \) was partially consumed, and although no volume change was observed with \( \text{C}_2\text{H}_4 \), a large charge transfer resistance increase was attributed to \( \text{C}_2\text{H}_4 \) oxidation. No saturated hydrocarbons were consumed in either case. In full cells, where the anode was able to consume evolved gases, no adverse effects on cell performance were observed [46]. There has been very little investigation on direct effects of gases other than \( \text{CO}_2 \), but one study found that \( \text{CH}_4 \) on its own can increase capacity fade, but is counteracted by \( \text{CO}_2 \), so that when both are present in the cell no capacity fade is observed [130]. A specific mechanism is uncertain; however, alkanes formed at the anode during SEI formation can be oxidized at the cathode, generating protic species (as discussed in 4.1.1) while \( \text{CO}_2 \) has been shown to act as a proton scavenger (as discussed in 3.2.2) reacting with protic species to generate formate and passivate additional reactivity [127, 142].

For gases produced at the anode, cross-talk to the cathode seems to be generally detrimental. Rodrigues found that if gases were not consumed by the graphite anode, their diffusion to the cathode caused an
impedance increase [66]. However, it is not clear that gases, rather than higher-MW products (section 4.2), were responsible for the impedance rise. Venting the cell after formation cycles can significantly reduce capacity fade, pointing to the detrimental long-term role of gas chemistry. H$_2$ gas formed at the anode has also been reported to accelerate capacity fade and increase impedance at the cathode in graphite/LCO cells [130]. Metzger argued that electrochemical H$_2$ oxidation at the cathode forms protons that react with PF$_6^-$ anions to form HF. HF can react with Li salts to precipitate as insulating LiF. HF also accelerates metal dissolution and associated problems (section 3.1.2). In the same work, electrode cross-talk was shown to accelerate H$_2$ production [48]. NMC/graphite full cells showed higher H$_2$ product relative to graphite half-cells due to diffusion of protonated electrolyte oxidation products from the cathode to the anode [48]. H$_2$ has also been shown to increase cracking in the cathode [66, 130]. H$_2$ is known to embrittle steel and other materials, and Rodrigues et al proposed a similar mechanism via crack propagation induced by local changes to the plasticity and critical stress. Ma proposed a proton-induced decrease in the cohesive strength of O$_2^-$ sites within the oxide leading to crack formation and mechanical failure.

4.2. Higher-molecular-weight products
Degradation products from electrolyte reduction at the anode can cross over to the cathode, affecting CE, cell cycle life, electrode impedance and character of the film formation at the cathode–electrolyte interface (CEI). These products are most frequently thought to be alkyl carbonates, alkyl oxides (ROLi, R = Me or Et) or reactive radicals. Sahore et al used LiCGC to create two-compartment cells for cross-talk-free battery cycling, and identified anode- and cathode-specific degradation products, in addition to more than 12 unique products that are formed via cross-talk between the two electrodes, as shown in figure 15 [129]. They proposed a cross-talk mechanism in which organophosphate species, generated at the anode, are oxidized at the cathode to form complex structures.

The interactions of these degradation products can impact CEI formation, which in turn affects capacity fade and cell impedance. Jung et al showed that stabilizing the surface of a graphite anode with atomic layer deposition of Al$_2$O$_3$ improved battery lifetime by reducing cross-talk-induced CEI growth on LCO [143]. The CEI grown in the presence of cross-talk from a bare graphite electrode had different organic products, much higher LiF content, and higher electrode impedance. Fang et al showed that contributions of reduction products to CEI formation in NMC cells can also be mitigated by increasing the pathway between the two electrodes through the use of additional separators or replacing graphite with an SEI-free anode such as ITO [144]. The authors also showed that cross-talk could be mitigated through a thin layer of Al$_2$O$_3$ on the cathode, which may subsequently dissolve and form a protective layer on the anode. The cross-talk is not the sole contributor to CEI growth, but a reduction in products by ~30% for C-based components and ~60% for fluorine-containing products was observed through both approaches.

In addition to the growth and composition of the CEI, cross-talk affects performance by increasing impedance at the cathode. Impedance rises have been shown to decrease when the crossover of soluble products is hindered chemically, by using FEC [96], or physically, using LiCGC [145]. Similarly, Bolli et al used OEMS with TMPsA, a F$^-$ scavenger, to detect HF generation in situ [47]. As shown in figure 16, graphite/NMC cells showed the most HF generation, followed by Li//NMC, and then LFP/NMC. This trend was explained by a combination of potential and surface area. The graphite and Li both produced alkoxides, semicarbonates, and other species that were oxidized to H$_2$O. HF production from species oxidation can also be particularly detrimental because it promotes transition metal dissolution, as discussed in section 3.1.2.

While the cross-talk mechanisms that affect capacity fade and cathode impedance are detrimental, not all cross-talk is bad for the battery lifetime. Cross-talk of oxidation products from the cathode can also have a stabilizing effect on the cell. While cathode degradation products cause capacity loss and impedance increase in isolation, cross-talk between the anode and cathode can result in consumption of detrimental species, and formation of new species, such as dimethyl-2,5-dioxahexane carboxylate, which in turn stabilize the interface, improving capacity retention and decreasing impedance [146].

In some cases, cross-talk reactions can represent a loss of CE without a decrease in capacity or measurable effect on battery lifetime. It is possible that after diffusing across the cell, electrolyte reduction products can participate in a redox cycle and be oxidized. As discussed in section 2.1, this cycle results in additional charge capacity without affecting the stock of available cations for cycling. While the balance of cyclable Li in the cell is maintained, these additional side reactions represent a penalty in CE as additional electrons are involved. It is proposed that this shuttle follows a scheme of

$$\text{SLi}_2 \rightarrow S' + 2(Li^+ + e^-)$$
where S and S’ may or may not be the same species [19, 44]. The identity of a reversible shuttle molecule is not readily apparent. Several groups have suggested an oxalate–CO$_2$ shuttle, where CO$_2$ reduces to form oxalate at the anode and then the oxalate diffuses to the cathode and is oxidized to reform CO$_2$ [15, 44]. Oxalate has a limited solubility in solution, and, as discussed in section 3.2, part of the improvement in performance from CO$_2$ is attributed to the formation of highly passivating SEI products including lithium oxalate [147]. As a result, this shuttle would be limited by the available oxalate in solution. Carbon–oxygen groups, such as ketones, have shown potential as a successful redox couple, undergoing reversible reduction to R–C–O–Na in functionalized carbon electrodes [148]. While alkoxides are known byproducts of electrolyte degradation in Li- and Na-ion batteries, this mechanism is less likely to apply to small linear molecules where the charge cannot be delocalized in the same manner. Although the specific shuttle is unknown, improving interfacial stability can improve battery efficiency by preventing such reactions from occurring. While a lower CE will increase the battery operating costs, these cross-talk mechanisms result in a recovery of available capacity and therefore do not immediately affect battery lifetime. In the case of an irreversible shuttle involving single-electron solvent reduction, Xu et al calculated the consumption of 7.7% of the original solvent after 1500 h in the highest-reaction case [44]. As the shuttle most likely involves a series of reduction and oxidation products traveling between the two electrodes, the actual solvent consumption would be lower and it would take a significant amount of time until battery operation would be affected by drying out of the cell. Thus, the reversible shuttle proposed by Deshpande et al [19] may not be truly reversible, but rather irreversible solvent decomposition that is slowed by participating in multiple cross-talk reactions.

4.3. Higher-molecular-weight products in other cation chemistries
Additional insight into the identity and characterization of high-MW degradation products can be found in the Na-ion literature. Similar to Li, soluble degradation products formed at the anode in Na-ion batteries can diffuse to the cathode and react to provide additional apparent capacity. In Na-ion batteries, the phenomenon is even more pronounced owing to the increased solubility and reactivity of products [149]. Increased irreversible charge capacity from the oxidation of soluble products was shown at Na$_3$V$_2$(PO$_4$)$_2$F$_3$ cathodes [150], leading to lower CEs. Our group has also recently shown that soluble products formed at the surface of the Na metal can be oxidized at particularly low voltages following diffusion to the working electrode. This cross-talk can impact the study of electrode storage mechanisms and accurate CE calculations [151]. Transport of soluble degradation products from the Na metal anode to cathodes including Na$_3$V$_2$(PO$_4$)$_2$ [152] and Na$_3$Fe$_2$(PO$_4$)$_2$(P$_2$O$_7$) [153, 154] have also been shown to accelerate capacity decay. One pathway for cross-talk is the formation of sodium alkyl carbonate or alkyl oxide species from linear carbonates which undergo oxidative decomposition at the cathode [154, 155]. Additionally, radical species (CH$_3$*, CH$_2$CH$_2$*) can form during carbonate reduction and either cause additional sodium alkyl carbonate formation via ring opening of cyclic carbonates or by directly crossing over to the cathode and accelerating anion decomposition [153, 154]. Overall, Na has been the subject of fewer studies, so cross-talk has not been studied as rigorously as it has in Li-ion systems. However, it is likely that many of the phenomena that are detrimental or beneficial in Li-ion batteries have similar effects in Na-ion batteries as well.

5. Conclusions

The Good: There are at least three examples of ways in which cross-talk is beneficial to battery lifetime. First, CO$_2$ is generated from the oxidative decomposition of solvent and carbonate surface impurities at the
cathode, among other mechanisms. Its incorporation into the SEI forms Li₂CO₃ and generally improves passivity and battery lifetime. This mechanism of SEI improvement may suggest a route towards electrolyte additive design, in which additives are targeted to decompose completely to CO₂, rather than incompletely to higher-MW products. Such a strategy could be particularly impactful when scavenging reactive oxygen species that are released from the cathode at high voltage. Second, in another case of beneficial cross-talk, reactive oxygen and other oxidation species are electrochemically scavenged at low-potential anodes, thereby avoiding impedance rise at the cathode. Finally, evidence suggests that reversible cross-talk may mitigate LCL at the cost of lower CE. A shuttle reaction between CO₂ and carboxylates has been proposed, but seems unlikely based on the low solubility of oxalate and proton activity in formate. A related possibility is that cross-talk provides several intermediate reactions before the solvent eventually degrades to CO₂. Identifying these shuttles, if they exist, would lead to the design of appropriate electrode–electrolyte interactions that direct decomposition reactions to benign products or slow the rate of solvent consumption.

The Bad: First and most simply, cross-talk increases the operational cost of batteries by decreasing the CE. Second, many cross-talk reactions originate from irreversible consumption of the electrolyte, leading to LCL and capacity fade. In particular, metal dissolution from cathodes is almost certainly the most harmful cross-talk mechanism in advanced Li-ion batteries, and preventing it remains one of the most important research goals in the field. SEI engineering can help limit metal dissolution either by trapping metals and limiting their activity, or by preventing generation of higher-MW products. These products are particularly detrimental if they promote transition metal dissolution by acting as chelating agents or generating protons during cross-talk oxidation. Electrolyte degradation species can migrate from the anode to the cathode (or vice versa) and directly contribute to interfacial film growth. In particular, some products are passivating at the anode, but increase impedance or contribute to additional reactions at the cathode. Understanding why some species are more resistive or reactive in some local environments than others is a remaining scientific challenge.

The Ugly: Perhaps the most overlooked consequence of cross-talk in Li-ion batteries is the weakened correlation between CE and overall lifetime, which complicates efforts to predict battery lifetime and state of health. Additionally, chemical exchange across the separator is inherently tied to the anode and cathode chemistry. Therefore, mechanisms and consequences of cross-talk in one battery system do not necessarily apply to another anode/cathode pairing. This lack of transferability limits the ability of statistical, data-driven models to describe different materials. Instead, predictive physics-based models are needed to bridge this gap. Developing such predictive models requires a wealth of experimental data, such as the concentrations of cross-talk species, their kinetic rate constants, and transport properties. These key parameters are not easily determined through full-cell cycling data. Novel three- and four-electrode reactor designs that can adequately isolate reactions and control transport are needed to quickly and inexpensively measure thermodynamic, kinetic, and transport parameters of cross-talk reactions. Ultimately, deepening the fundamental understanding of cross-talk mechanisms will accelerate the development of physics-based models that accurately predict battery lifetime.

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References

[1] Bloom I et al 2014 J. Power Sources 249 509–14
[2] Trask S E, Li Y, Kubal J J, Bettge M, Polzin B J, Zhu Y, Jansen A N and Abraham D P 2014 J. Power Sources 259 233–44
[3] Xia J, Nelson K J, Lu Z and Dahn J R 2016 J. Power Sources 329 387–97
[4] Abraham D P, Knuth J L, Dees D W, Bloom I and Christophersen J P 2007 J. Power Sources 170 465–75
[5] Smith A J, Burns J C, Xiong D and Dahn J R 2011 J. Electrochem. Soc. 158 A1136
[6] Burns J C, Jain G, Smith A J, Eberman K W, Scott E, Gardner J P, Dahn J R and Bhj C 2011 J. Electrochem. Soc. 158 A255
[7] Sinha N N, Burns J C and Dahn J R 2013 J. Electrochem. Soc. 160 A209–14
[8] Joshi T, Eom K, Yushin G and Fuller T F 2014 J. Electrochem. Soc. 161 A1915–21
[9] Li Y, Bettge M, Polzin B, Zhu Y, Balasubramanian M and Abraham D P 2013 J. Electrochem. Soc. 160 A3006–19
[10] Ziv B, Borgel V, Aurbach D, Kim J-H J, Xiao X and Powell B R 2014 J. Electrochem. Soc. 161 A1672–80
[149] Iermakova D I, Dugas R, Palacin M R and Ponrouch A 2015 J. Electrochem. Soc. 162 A7060–6
[150] Dugas R, Zhang B, Rozier P and Tarascon J M 2016 J. Electrochem. Soc. 163 A867–74
[151] Lee S E and Tang M H 2019 Electrochem. Commun. 100 70–3
[152] Schafzahl L, Hanzu I, Wilkening M and Freunberger S A 2017 ChemSusChem 10 401–8
[153] Jang J Y, Kim H, Lee Y, Lee K T, Kang K and Choi N S 2014 Electrochem. Commun. 44 74–7
[154] Lee Y, Lee J, Kim H, Kang K and Choi N S 2016 J. Power Sources 320 49–58
[155] Yan G, Alves-Dalla-Corte D, Yin W, Madern N, Gachot G and Tarascon J-M 2018 J. Electrochem. Soc. 165 1222–30