

## Perspective

# A reaction engineering approach to non-aqueous battery lifetime

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## SUMMARY

**Complex side reactions drive capacity fade in modern Li-ion batteries and are a key factor in achieving extended battery lifetimes. Unfortunately, the interconnected nature of the reaction pathways means that optimizing one aspect of performance can result in a shift between benign and detrimental side reactions, and that simple Coulombic efficiency is unable to capture these differences. Because batteries are ultimately chemical reactors, reaction engineering principles can provide a suitable framework for understanding. The electrocatalytic systems of Li-O<sub>2</sub> batteries and electrochemical CO<sub>2</sub> reduction demonstrate both the importance of quantifying reaction selectivity and the key role that reactor geometry plays in this process. Recent findings from these fields suggest that battery side reactions should also be studied in reactors that have been optimized for analytics. In this reaction engineering context, we discuss the advantages and disadvantages of existing analytical tools and present pathways for designing new reactors that can directly evaluate Li-ion battery reaction selectivity. Quantification of selectivity and reaction parameters can direct materials design and improve lifetime prediction.**

## Q3 Q2 INTRODUCTION

### The challenge of side reactions and the limitations of coulombic efficiency

The ability of modern Li-ion batteries to provide large-scale energy storage is increasingly limited not by energy or power but by lifetime and cost.<sup>1</sup> Growing concern over battery disposal also motivates batteries that last longer. Research over the past 10–15 years has overwhelmingly concluded that parasitic electrolyte reduction dominates battery failure. This reduction represents a failure of the solid-electrolyte interphase (SEI) to passivate the negative electrode (anode). Considering that the SEI was first described in 1979, that batteries have been commercialized since 1991, and that the market is worth billions of dollars annually, the inability of battery scientists to “solve the SEI” is puzzling. Why is this problem so hard?

The enduring problem of SEI can be explained most simply as “to side reactions, everything matters.” The remarkable declines in cost and increases in energy since 1991 have been achieved through incremental improvements to electrodes, electrolytes, and manufacturing. Even though the SEI originates from electrolyte reduction, the electrode materials and microstructure as well as the operating conditions all affect its ability or inability to passivate the electrode. Improving a seemingly unrelated component or process can therefore de-optimize the battery longevity. As an additional layer of complexity, system-level interactions can impact SEI failure via chemical crosstalk.<sup>2</sup> Figure 1 illustrates a sampling of the complex network of side

## Context & scale

Extending the lifetime of non-aqueous batteries, particularly Li-ion, is necessary to reduce large-scale energy storage costs and to mitigate the environmental concerns of battery disposal and recycling. Better understanding of the complex side reaction networks is necessary for improved lifetime. This perspective proposes that considering battery interfaces in the context of catalytic selectivity may provide a powerful approach to this problem. Extracting meaningful measurements of reaction selectivity requires detailed attention to reactant and product transport, as illustrated by recent findings in aqueous electrocatalysis. Ultimately, new reactor designs that control interelectrode communication while maintaining a realistic battery environment must be developed to measure reaction rates directly. This knowledge in turn could enable physics-based predictive models of battery lifetime.

reactions occurring at the anode, cathode, and in the bulk electrolyte. While some side reactions are necessary and beneficial for battery lifetime, such as inorganic SEI formation reactions, others have more deleterious effects, such as metal and oxygen release from the cathode. In some cases, side reactions can initiate a self-catalyzing cycle of crosstalk reactions. For example, oligomers from solvent reduction can diffuse from the anode to the cathode, where they facilitate transition metal dissolution as chelating agents. The dissolved transition metals then diffuse to and incorporate into the SEI, where they catalyze solvent reduction and more oligomer release. The resulting “chicken and egg problem” defies a simple solution to capacity fade.

Beyond these specific degradation mechanisms, a significant consequence of reaction network complexity is the empirical testing scheme it forces. Data-driven models for lifetime prediction require copious experiments to successfully train and validate from constant-current cycling experiments to real usage profiles. Because crosstalk is specific to anode-cathode-electrolyte interactions, models must be retrained for individual chemistry combinations. In addition to sensitivity to specific chemistry, many empirical testing schemes are carried out with constant-current or constant-current-constant voltage schemes that do not accurately reflect real usage profiles. Battery lifetime and the dominant side reaction selectivity depends on the charging protocol used, and there is an interdependence between cell chemistry and usage profile in determining degradation.<sup>3</sup> In contrast to empirical data-driven models, physics-based models create mathematical representations of chemical transport and reaction. The limitation of physics-based models is the large number of rate constants, transport properties, and other physical parameters that are required as inputs. Many of these quantities are extremely challenging to measure, and published physics-based models do not yet accurately capture complex degradation chemistry.

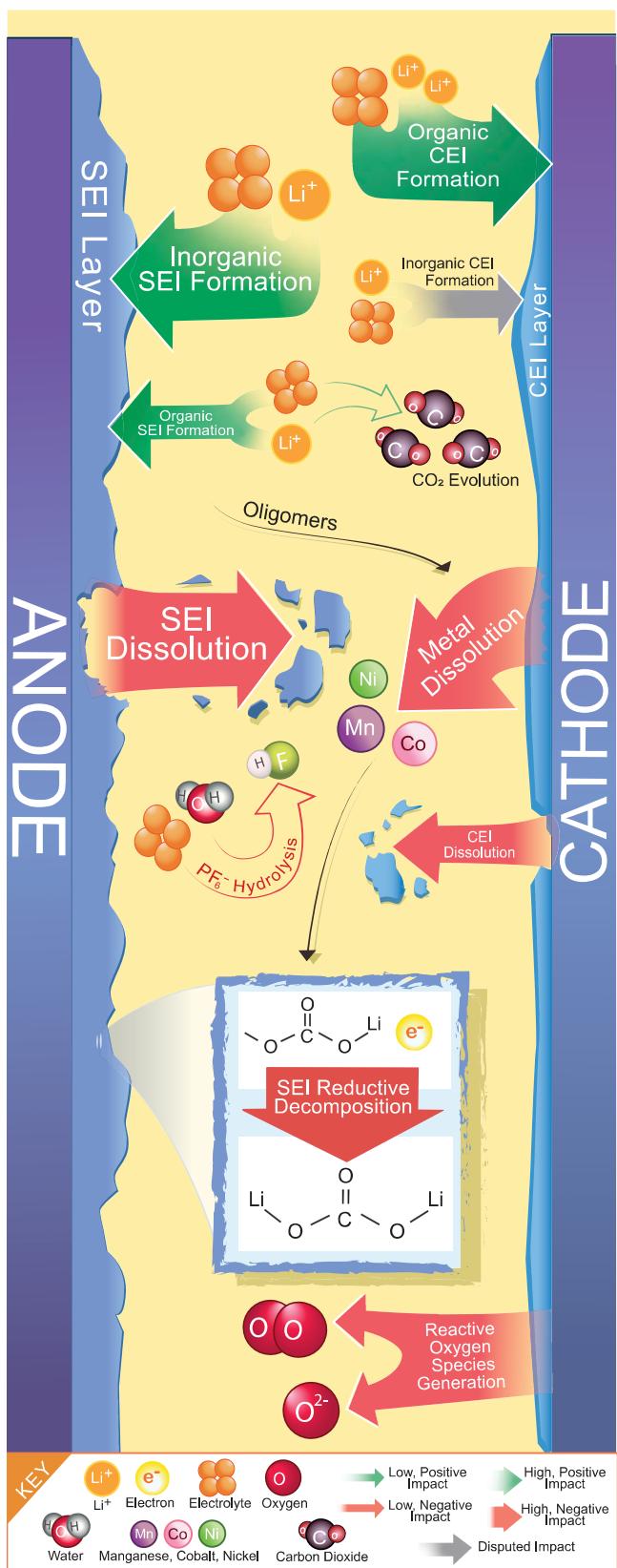
At present, the most common metric of degradation due to side reactions is Coulombic efficiency (CE), which is calculated by dividing the total coulombs passed during discharge by the coulombs passed on charge in each charging cycle. A CE of 100% can only be achieved without side reactions, and modern batteries can operate with CE as high as 99.98%.<sup>4</sup> Smith et al. showed that high-precision CE measurements can accurately quantify contributions of battery degradation processes during cycling,<sup>5,6</sup> and Burns et al. used high-precision CE to reduce screening time between cells from months to weeks.<sup>7</sup> However, below the ideal 100%, higher CE is not always better. Battaglia et al. showed that the correlation between CE and capacity fade can break down in the presence of electrolyte additives and multiple side reactions.<sup>8,9</sup> Yang et al. found that correlations between CE and capacity fade vary with cathode chemistry.<sup>10</sup> Similarly, Yi et al. compared cycling performance of LiMn<sub>1.4</sub>Cr<sub>0.2</sub>Ni<sub>0.4</sub> and LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> half-cells and found higher CE for the former but also faster capacity fade.<sup>11</sup>

Figure 2 shows a specific example of a counter-intuitive relationship between CE and capacity fade. Following Christensen and Newman,<sup>12,13</sup> we model generic independent oxidation and reduction side reactions rates, their effect on the inventory of cyclable lithium, and the subsequent capacity fade. If lithium-generating oxidation side reactions and lithium-trapping reduction side reactions are balanced, mole-for-mole, side reactions have no immediate effect on battery lifetime despite low CE.<sup>12</sup> It is, however, common for the lithium-consuming side reactions to dominate (i.e., “SEI growth”). As shown in Figure 2A, the resulting loss of cyclable lithium causes significant capacity fade, despite higher CE. Similar to Christensen and

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**Figure 1. Prominent side reactions occurring in lithium-ion batteries at anode, cathode, and in bulk electrolyte**

Green arrows represent benign side reactions and red arrows represent detrimental ones. Black arrows represent crosstalk phenomena, in which side reactions at one electrode affect processes at the other.

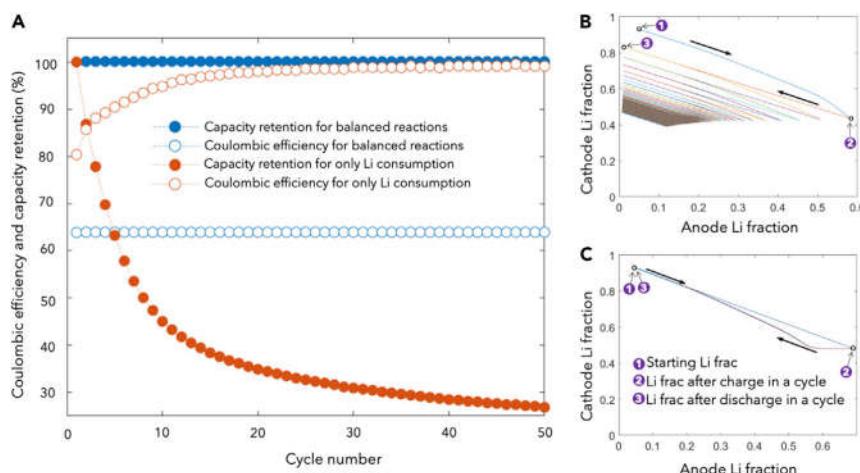
Newman,<sup>12,13</sup> plotting the lithium fraction of the anode and cathode through different cycles (Figures 2B and 2C) demonstrates the change in available lithium within the cell. The cell voltage cutoffs define the operating window for the cell. When lithium-consuming (reduction) side reactions dominate, a voltage marching occurs during cycling, forcing the battery toward one corner of the operating window, representing depletion of cyclable lithium and corresponding capacity fade (Figure 2B). When lithium-consuming and lithium-generating reactions are balanced, there is no significant net loss of cyclable lithium, and the lithium inventory does not march toward the operating window corner (Figure 2C). This model focuses on lithium inventory and does not account for solvent dry-out or impedance raise from growth of interfacial layers, which can also contribute to cell failure. However, the balanced lithium inventory highlights that the absolute magnitude of side reaction is less important than the ratio of detrimental-to-benign side reactions.

**A catalysis approach to battery lifetime: the case for measuring reaction selectivity**

The studies described, reinforced by the theoretical framework presented in Figure 2, show the limitations of CE as an unambiguous predictor of battery lifetime. A more specific metric like individual side reaction rates, reported in terms of kinetic, thermodynamic, and transport parameters, is needed for determining mechanisms of capacity fade and accurately predicting battery lifetime. In this context, the problem of battery lifetime can be identified as a problem of reaction selectivity. CE is essentially the selectivity for desirable charge-storage reactions, but lifetime is affected by selectivity of detrimental versus benign side reactions. For instance, redox reactions of existing electrolyte degradation products are likely less damaging than additional solvent decomposition. At present, methods to distinguish between these different side reactions are extremely limited. However, the field of heterogeneous catalysis has long concerned itself with directing preferred chemical transformations at interfaces and may play an instructive role in moving forward. In particular, the immature technologies of Li-O<sub>2</sub> batteries and electrochemical CO<sub>2</sub> reduction (eCO<sub>2</sub>RR) have been subject to significant focus from a catalysis framework and can provide a template for understanding how selectivity affects battery performance.

While there is substantial precedent for applying catalysis approaches to improve battery performance, most have focused primarily on activity, not selectivity. In the development of the Li-O<sub>2</sub> battery, early efforts aimed to boost performance of gas-diffusion cathodes by applying lessons from fuel cell catalysis. Exceedingly high overpotentials for charging (~1–1.5 V),<sup>14,15</sup> where oxygen is evolved from the Li<sub>2</sub>O<sub>2</sub> discharge product, motivated the exploration of nanoscale oxygen electrocatalysts to overcome kinetic barriers<sup>16</sup> and improve rechargeability of the Li-O<sub>2</sub> battery system.<sup>17</sup> Similarly, recent efforts incorporating catalysts into the sulfur cathode of Li-S batteries has been able to rapidly convert soluble polysulfides to insoluble products before they diffuse away.<sup>18,19</sup>

However, the case of Li-O<sub>2</sub> chemistry also provides more direct instruction to the problem of Li-ion battery lifetime. Researchers quickly learned that O<sub>2</sub> catalyst



**Figure 2. Side reaction model based on Christensen and Newman**<sup>12,13</sup>  
(A–C) (A) Effect of side reactions on Coulombic efficiency (blank) and discharge capacity retention (filled) during cycling for balanced lithium consumption and generation (blue) versus only lithium consumption (orange). Cathode versus anode lithium fraction during cycling for cases with (B) only lithium consumption reactions and (C) balanced side reactions.

selectivity was more important to battery lifetime and practicality than activity. Read was among the first to highlight this distinction for oxygen catalysts, specifically targeting the formation of  $\text{Li}_2\text{O}_2$  over  $\text{Li}_2\text{O}$ .<sup>16</sup> McCloskey and colleagues showed that  $\text{Li}_2\text{CO}_3$  was the primary discharge product in carbonate electrolytes, rather than the previously assumed and desired  $\text{Li}_2\text{O}_2$ , demonstrating again the importance of careful chemical analysis of the discharge product in  $\text{Li}-\text{O}_2$  systems.<sup>17</sup> By establishing  $\text{Li}_2\text{O}_2$  selectivity as a primary target for cathode development, battery researchers demonstrated the utility of applying catalysis approaches to understanding and engineering battery interfaces. More recently, Shao-Horn and colleagues drew parallels between parasitic electrolyte oxidation and hydrocarbon catalysis, including screening lithium-ion-battery-relevant oxides for dehydrogenation activity descriptors.<sup>20,21</sup> Without using the term “selectivity,” Abraham et al. proposed an “electrocatalysis paradigm” for high-voltage cathodes in which active sites oxidize either solvent or sacrificial additives, forming detrimental H radicals or passivating surface products, respectively.<sup>22</sup> Moving from a theoretical to experimental framework, leveraging these and other results into quantitative measurements of reaction rates could lead to predictive, physics-based models of battery lifetime.

### The impact of reactor design on material performance: Lessons learned from $\text{CO}_2$ reduction

Translating qualitative observations of reactivity trends and material performance into quantitative measurements of reaction activity and selectivity requires scientists to consider not only materials but also the environment in which they are tested. In particular, reactor geometry plays an often-overlooked role. Innovations in experimental design for electrochemical  $\text{CO}_2$  reduction (eCO<sub>2</sub>RR) demonstrate the significance of controlling reactor environment when screening electrode and electrolyte materials. Early studies of eCO<sub>2</sub>RR utilized aqueous batch reactors (e.g., H-cells) with low  $\text{CO}_2$  solubility.<sup>23–25</sup> As a result, device-scale limitations to  $\text{CO}_2$  transport not only allowed the competing reaction of hydrogen evolution to dominate but also limited researchers’ ability to understand fundamental material behavior.<sup>23,26,27</sup> For example, Hori et al. used an H-cell to measure faradic efficiencies for six eCO<sub>2</sub>RR

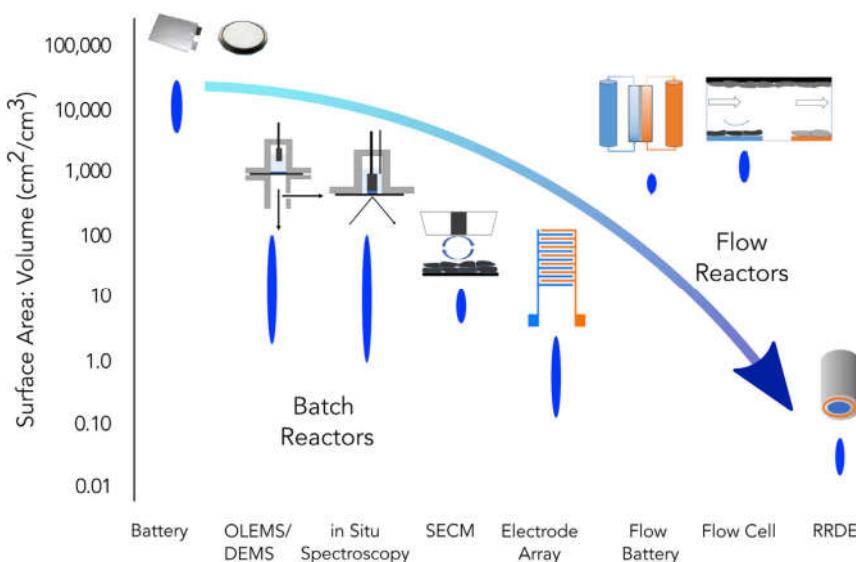
products catalyzed by copper metal.<sup>23</sup> Decades later, Kuhl et al. designed a flow reactor with a much higher ratio of electrode surface area to electrolyte volume and a feed of humidified CO<sub>2</sub>. This new reactor geometry was able to detect 16 total eCO<sub>2</sub>RR products instead of the six previously observed, thus, painting a qualitatively different and much more comprehensive reaction pathway.<sup>27</sup> More recently, gas-diffusion electrodes (GDEs) have been used to increase active surface area, allow vapor-fed reactor designs, and enable solid-state reactors with polymer electrolytes.<sup>28–30</sup> However, vapor-fed reactors that are affected by GDE hydrophobicity and porosity yield very different transport of CO<sub>2</sub>, water, and ions than aqueous phase reactors.<sup>25,28</sup> These transport differences lead to different intermediate coverages on the electrode surface. Coverage effects then in turn impact the overall selectivity of eCO<sub>2</sub>RR conversion. For example, Vennekoetter et al. compared the performance of identical materials tested in GDEs/polymer electrolytes, metal electrodes/aqueous electrolytes, and GDEs/aqueous electrolytes and found significantly different product selectivity for each.<sup>25</sup> Within these reactors, flow and geometric parameters further can affect reaction selectivity and efficiency. Billy and Co demonstrated that careful device design can differentiate between surface-versus transport-limited reactions. They demonstrated the effects of gas and solution flow rates, gas-feed placement, and diffusion-layer thickness on product selectivity and faradic efficiency.<sup>31</sup> The influence of these parameters means that differences in geometry and flow rate between experimental setups can obscure direct comparison of material performance; this underscores the importance of reactor design to reaction selectivity.

When viewed through the reaction engineer's lens of transport and kinetics, rather than the materials perspective of metals and ceramics, the underlying similarities between eCO<sub>2</sub>RR and Li-ion battery lifetime are clear. Both systems are limited by reaction selectivity, and the selectivity of nearly any system is dictated by the local concentrations of reactants, products, and intermediates at the electrode. For eCO<sub>2</sub>RR, the concentration of CO<sub>2</sub> in the electrolyte governs the CO<sub>2</sub> surface coverage, which is crucial to the subsequent reaction steps. Many Li-ion electrolyte degradation reactions, especially those involving water and protons, are similarly surface-sensitive.

### **Battery reactor design: Optimizing for performance versus analysis**

Considering the lessons learned from eCO<sub>2</sub>RR, the seemingly "mature" field of reactor design can explain why selectivity measurements in modern batteries are so challenging. Chemical engineering students are taught to distinguish stirred reactors, in which proper mixing ensures uniform (but transient) concentration, from flow reactors, in which convection ensures well-defined spatial concentrations at steady state. As poorly mixed batch reactors, batteries fit neither of these descriptions, and the applicability of traditional kinetic analysis tools is limited. Computationally, explicit recognition of the parallels between batteries and batch reactors has led to rapid and accurate "tanks-in-series" models for battery management systems.<sup>32</sup> Experimentally, explicit recognition of these parallels should lead to reactors that are designed to characterize minor products and their reactivity. Such reactors would be unlikely cost-effective power supplies but could provide targeted characterization to improve understanding of side reaction kinetics. Accomplishing this goal will require well-controlled transport, adequate sensitivity, and use of reference electrodes in addition to the battery-relevant positive and negative electrodes.

Further, determining the electrochemical reactivity of minor products requires a fourth electrode dedicated to amperometric product detection or characterization.



**Figure 3. Comparison of surface area to volume ratio for battery geometries and analytical techniques with batch and flow reactor behavior.**

The rotating ring-disk electrode (RRDE) is the best-known example of this approach, and it is widely employed in oxygen reduction catalysis and other fields to characterize the selectivity of electrocatalysts or the activity of electrochemical products. For instance, electrocatalysts for oxygen reduction in both aqueous and non-aqueous systems are routinely evaluated via RRDE analysis, where the catalyst selectivity for 4- over 2-electron reduction is the primary target.<sup>33–35</sup> Additionally, kinetic rate constants, charge-transfer coefficients, and diffusion coefficients are vital parameters for predictive physics-based models, all of which can be accessed via careful RDE and RRDE experimentation. Although ubiquitous in the electrocatalysis literature, RDE and RRDE studies have only just become more widespread in the context of Li-ion and beyond-Li batteries.<sup>36–40</sup> Thus far, applications have included investigating metal dissolution from cathode materials, evaluating solid-electrolyte interphase charge-transfer mechanisms, and the detection of soluble electrolyte decomposition products, yet, there is clearly a vast space for these tools to be further applied to the study of non-aqueous battery reactions with an eye toward reaction selectivity.

However, aspects of the RRDE are inappropriate for Li-ion batteries. The fundamental disadvantage of this technique is the unacceptably low ratio of electrode surface area to electrolyte volume. In practical batteries, such as coin cells, this ratio is on the order of  $10,000\text{ cm}^2/\text{cm}^3$ , while a typical 10 mL RRDE experiment would have a ratio of  $0.01\text{ cm}^2/\text{cm}^3$ . Surface area to volume ratios for a variety of platforms are compared in Figure 3. As discussed in Section 3, this six-orders of magnitude discrepancy has severe implications for the ability to study Li-ion battery reactions that are affected by solubility phenomena. For instance, the critical solid-electrolyte interphase (SEI) is formed when products of electrolyte reduction reactions precipitate onto the negative electrode. With an excess of electrolyte, such as in a flooded RRDE cell, those products may not reach supersaturation, and thus, the results may not accurately represent a practical Li-ion battery. Similar phenomena likely impact many conversion systems including Li-S, Li-metal, selenides, metal fluorides, and halides. Thus, while RRDE can be a powerful tool for quantitative electroanalysis,

this severe limitation of the technique points to an emerging need for new reactors designed specifically for Li-ion and beyond-Li battery diagnostics.

Considering the desirability of generator-collector measurements for studying electrocatalyst selectivity, alternatives to the RRDE deserve consideration, including techniques using microelectrodes. Microelectrodes enable fast establishment of steady-state mass transfer and high-density diffusion flux and can be leveraged to obtain accurate measurements of low concentration products in small volumes of electrolytes. Scanning electrochemical microscopy (SECM) utilizes a microelectrode probe rastered over the surface. This offers advantages over RRDE in terms of sample versatility, as it can be applied to composite electrodes and does not require a smooth, planar electrode surface. SECM has been widely used in catalysis, as it can precisely measure catalyst performance with spatial resolution.<sup>41–43</sup> SECM has seen limited applications for battery research, with a focus on electrode activity and SEI passivation.<sup>44–48</sup> Jung et al. have demonstrated the use of SECM to measure the dissociation of solvated lithium-ions in LiCoO<sub>2</sub> electrodes, and this technique can be extended to other degradation pathways.<sup>49</sup> However, SECM is limited in its ability to differentiate signals from multiple species via amperometric detection. This can be particularly challenging at the cathode where it is necessary to distinguish between electrolyte decomposition products, oxygen evolution, and transition metal dissolution. Potentiometric detection, cyclic voltammetry or ion-selective microelectrodes have been employed but increase experimental time and complexity.<sup>50</sup> Additionally, SECM requires specialized and delicate equipment including step motors or piezoelectric elements for spatial resolution. Because the SECM requires an open cell, instruments must be specifically designed for inert glove box operation, and solvent evaporation can pose additional challenges.

Interdigitated electrode arrays (IDAs) connect many alternating microbands to form fingers in two individually addressed electrodes, enabling higher signal-to-noise ratios, short diffusion lengths, and enhanced interelectrode communication. These features allow for the detection of lower analyte concentrations than those that can be achieved with a RRDE by redox-cycling intermediates between the electrodes. Unlike SECM and RRDE, there are no moving parts, and less bulky or specialized equipment is required. IDAs are capable of highly selective product detection<sup>51</sup> and have been applied to study pathway selectivity in oxygen reduction applications.<sup>52</sup> Using traditional IDAs to study selectivity in batteries is made challenging by two-way communication between electrodes; this redox cycling amplifies reversible side reactions at the expense of irreversible reactions and would obscure quantification of reaction selectivity.

While they do not enable collector-generator measurements, ion-selective membranes can be used to tailor transport of specific species and infer selectivity indirectly. Lithium-selective membranes, such as lithium-ion conducting ceramic glass, allow selective lithium transport while preventing other species from diffusing between the anode and cathode. Direct comparison of divided and undivided cells has been used to study both soluble<sup>53</sup> and gaseous<sup>54,55</sup> crosstalk products. This approach has proven useful for understanding specific reaction pathways for complementary side reaction at the anode and cathode, such as hydrogen evolution at the anode stemming from protic electrolyte oxidation products generated at the cathode.<sup>54</sup> By blocking communication in both directions one-way communication cannot be directly studied, although electrode-specific reactions can be studied by exclusively placing reactants or suspected intermediates in one compartment.<sup>55</sup> Lithium-selective membranes can be combined with differential electrochemical

mass spectrometry or on-line electrochemical mass spectroscopy (DEMS/OLEMS) to measure *in situ* production of gaseous and volatile products offering real-time insight into potential dependent reaction products and intermediates. DEMS/OEMS have been used to study the degradation of cathode materials<sup>56–58</sup> and reduction products such as hydrogen, carbon dioxide, and ethylene gas during SEI formation at the anode.<sup>59–61</sup> It is one of the best technologies at present to understand catalytic selectivity at battery interphases, providing information about mechanisms for SEI growth, electrolyte decomposition, and electrode degradation. However, there are some limitations as it does not allow one-way transport necessary to deconvolute crosstalk, it is limited by mass transport between the interphase and vacuum outlet, and it requires complementary techniques to capture non-volatile intermediates or products.<sup>62</sup> DEMS/OLEMS is also a highly specialized and expensive technique, limiting widespread use.

### Approaches for new reactor design

Considering the limitations of existing technology, new reactor designs are needed to address the need to study reaction selectivity at battery interfaces. Effective design requires several key considerations, chief among them adequate selectivity and sensitivity at the detector (e.g., ring) electrode, and quantification of reaction parameters including residence time, local transport, and surface: volume ratios. Another design consideration is the ability of one-way communication to deconvolute crosstalk mechanisms. This one-way communication can be achieved through forced convection, such as that generated by rotation in a RRDE. Accurate correlation with voltage requires minimizing the ohmic drop, which often leads to a 3- or 4-electrode cell design that incorporates reference electrodes and electrochemical detectors. Materials compatibility in non-aqueous solvents is also important for durable and accurate measurement. Leached products can obscure measurement of selectivity with electrochemical or spectroscopic techniques.<sup>63</sup>

As discussed in [Battery reactor design: Optimizing for performance versus analysis](#), microelectrodes provide one potential approach. While IDAs are subject to high feedback, highly asymmetric interdigitated electrode arrays, where the generator is significantly larger than the collector, can be used to bias feedback while maintaining collection efficiency. We have shown that by using this technique, feedback between the working electrode and probe electrode can be reduced to <10% while collection efficiencies on par with RRDE measurements

**Q5** can be achieved (Lee et al., unpublished data). Such devices can be used to study the selectivity of electrolyte decomposition reactions by measuring formation of soluble degradation products. Microfabrication techniques could also allow creation of thin film model electrode to study the interactions of specific electrode components, such as transition metals from cathodes. These electrode arrays have a surface area to volume ratio orders of magnitude lower than a battery, as seen in [Figure 3](#), but are cheaper and easier to implement than techniques like OEMS or SECM. In addition to microelectrodes, an asymmetric geometric approach can be employed with a high surface-area porous electrode as a product generator in concert with a high-precision sensor, such as a quartz crystal microbalance (QCM). Kitz et al. used such an approach to measure the formation and precipitation of degradation products on QCM.<sup>64</sup> In this study, the use of a the QCM in both electronically insulated and electronically shorted modes enabled the separate study of chemical and electrochemical processes. However, the requirement for no internal overpressure meant a considerable gap is needed between the porous working electrode and the sensor.

Alternatively, microfluidics are a proven tool for probing electrochemical reactions and electrocatalysts.<sup>29,65</sup> Compared with batch reactors, flow cell electrolyte composition can be easily be varied and analyzed. Forced flow also enables one-way communication, allowing a deconvolution of crosstalk reactions.<sup>66</sup> These devices can be used to study interelectrode communication, such as the effect of transition metal dissolution at the cathode on SEI formation at the anode, or the effect of electrolyte decomposition products on cathode degradation. In addition, flow cell fabrication allows for the implementation of commercially relevant electrodes, transcending electrode material limitations in other reactor designs, such RRDEs and IDAs. High-surface-area electrodes, combined with minimal electrolyte in microflow cells, increase the electrode surface area to electrolyte volume ratio, enabling high sensitivity for detecting dilute side products formed. Implementing strategies from recent progress in electrosynthesis microreactors and non-aqueous redox flow batteries<sup>67,68</sup> may enable reliable, modular microflow cells for studying battery crosstalk reactions.

The appropriate reactor design approach will also be guided by the desired phenomena and complementary characterization techniques. *In situ* and *operando* spectroscopic techniques offer valuable tools for identifying reaction products, and numerous reviews have been written on these techniques in recent years.<sup>69–71</sup>

To characterize solid-phase products such as insoluble SEI components, stationary (micro)electrodes would likely be preferred to avoid convection noise. For instance, FTIR has previously been combined with microelectrodes to study reaction mechanisms for methanol oxidation.<sup>72</sup> Similarly, incorporating recent advances in FTIR such as attenuated total reflectance<sup>73,74</sup> and combined micro-FTIR/Raman<sup>75</sup> could enable *operando* characterization of Li-ion side reactions coupled to meaningful kinetic analysis. NMR could also provide valuable insights into product formation, if advances in techniques and cell design can be achieved to move beyond the limitations of static measurements with *in situ* NMR.<sup>76,77</sup>

To characterize solution-phase products such as soluble electrolyte degradation products or dissolved transition metals, a microfluidic device would likely offer the advantage of on-line effluent collection and analysis. Several studies have already coupled microflow cells to on-line monitoring of aqueous and non-aqueous electrode dissolution using inductively coupled plasma mass spectrometry (ICP-MS). Ranninger et al. collected the effluent from an electroanalytical flow cell to elucidate the dissolution mechanism of platinum in methanol-based organic electrolytes,<sup>78</sup> while Geiger et al. used a similar device to relate dissolution, electrocatalytic activity, and material structure of iridium-based oxides over a range of current densities.<sup>79</sup> *In situ* ICP-MS can also be coupled to a RDE to study electrocatalyst stability in a system with well-defined transport. Lopes et al. conducted ICP-MS studies using a stationary probe which collected effluent from a nearby RDE to study the kinetics of electrode dissolution and electrolyte decomposition for transition metal cathodes.<sup>80</sup> These ICP-MS-coupled flow studies enable differentiation between the dissolved and precipitated metals and allow users to directly relate the net current to the dissolution of specific components in complicated systems.<sup>81</sup> Recent developments in hollow-core fiber-optics for *operando* Raman measurements of electrolyte degradation products<sup>82</sup> and microfluidic NMR probes<sup>83</sup> can enable the in-line characterization of organic products. While characterization techniques are valuable for identifying reaction products, extending observations from a single cycle in an *operando* measurement to the entire lifetime of a battery needs better measurement of reaction rates to inform model prediction.<sup>84</sup> Carefully designed reactors, as

described above, will be able to measure the rates of product formation as a function of reactor conditions and chemical history.

## CONCLUSIONS

Direct measurement of reaction mechanisms and reaction rates can potentially allow battery researchers to overcome the limitations of data-driven and physics-based lifetime models. These limitations include the empirical testing scheme forced by data-driven models and the high number of parameters needed to capture chemical transport and reactions in physics-based lifetime models. Introducing measured rate constants of specific side reactions into models such as the one introduced in [Introduction: the challenge of side reactions and the limitations of CE](#) can help determine the relative rates of lithium-generating versus lithium-trapping reactions, and therefore their contributions to overall capacity fade. These rate constants, combined with thermodynamic and transport parameters, can also elucidate the contributions to capacity fade of other battery phenomena, such as SEI thickening and transition-metal-driven SEI degradation. Implementing this concept will create a holistic, accurate model for battery lifetime but introduces the experimental challenge of measuring model inputs/reaction physical constants.

Ultimately, the established technology of Li-ion batteries and the emerging technologies of Li-O<sub>2</sub> batteries and eCO<sub>2</sub>RR share a common limitation of electrochemical reaction selectivity. Recent advances in eCO<sub>2</sub>RR have shown conclusively that reactor design impacts the rates and ratios of products. Therefore, capturing a mechanistic understanding of battery degradation requires experimentalists to carefully consider how the reactor environment affects reaction selectivity. The field of heterogeneous catalysis has shown that variation in species solubility, transport limitations, active surface-area-to-electrolyte volume ratio, and active site coverage can all play a role in determining reaction selectivity. New approaches to reactor design must therefore offer controlled product and reactant transport in battery-relevant environments and with adequate sensitivity for generated species. In addressing this reactor design problem, chemical and mechanical engineers have the possibility to produce the "(R)RDE of batteries." Addressing this design problem will be key to obtaining knowledge that leads to longer-lasting non-aqueous batteries.

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## AUTHOR CONTRIBUTIONS

M.T. conceived this perspective. S.E.L., O.C.H., T.S., and M.T. investigated the literature. T.S. conducted the side reaction modeling. S.E.L., O.C.H., T.S., and M.T. wrote and discussed the manuscript. S.E.L., T.S., and M.T. revised the manuscript.

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