TOWARDS A ZERO-CARBON WORLD: NEW BATTERIES AND CHEMISTRY CHALLENGES

CLARE GREY*

Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge, CB2 8BJ, UK

Climate change and batteries

More powerful, longer-lasting, faster-charging and cheaper batteries – made from increasingly more sustainable resources – will play a critical role in the transition to a Net Zero world. While they are currently are "fit for purpose" for many types of electric vehicles (EVs), the batteries are still too expensive for many and rely on critical or scarce metals (e.g., Co, and increasingly Ni), often with environmental and social concerns around their extraction. Developing even larger batteries that are suitable for heavier vehicles, and for storing electricity to deal with the use of intermittent renewable sources of energy on the grid, remains a massive challenge - and one where no clearcut technology winners exist. Lithium-ion batteries (LIBs) remain the most viable short-term technologies for these applications, with mass-production resulting in significant price reductions and making it difficult for other (possibly more sustainable) technologies to compete, at least in some markets. Yet, with the massive number of giga-factories being built globally, sustainability of resources will increasingly become even more of a concern. Fierce global competition must also mean that new manufacturing methods must be developed for the new players to develop a competitive advantage (and indeed even stay in the race).

Challenges

Having progressed rapidly over three decades, battery technology now faces a series of challenges in making the advances required for long-term grid storage or heavy vehicle and aviation applications. These include:
Cost: In both automotive and grid sectors, cost remains a major challenge. Much of the cost arises from the minerals themselves (mainly those used for the cathode, such as cobalt and nickel) and then the processing and synthesis of the materials.
Materials: Battery development is also challenging as there are few elements that are usable in electrodes that are cheap enough while also having (i) oxidation/redox chemistry within an appropriate voltage window, and (ii) being stable when oxidised/reduced and lithium is extracted/reinserted over multiple cycles.
Degradation: Degradation at the cathode side is generally caused by structural changes that reduce capacity and can increase impedance. These phenomena increase as more lithium is extracted and the material is pushed to higher voltage during cycling. The highly oxidised cathodes react and oxidise the electrolyte. On the anode side batteries

form a protective or passivation layer known as solid electrolyte interphase (SEI). It is fundamental to performance as it prevents degradation of the electrolyte as well as conducting ions to the anode and insulating it. However, over time, growth of the SEI consumes active lithium and the electrolyte materials, affecting both capacity and power density.

Energy density: Energy density is important in creating batteries that are compact and can power the device over long time periods. In some applications volumetric energy density is key, but in airplanes in particular, higher gravimetric energy density is important, while in grid-scale batteries both volumetric and gravimetric density are less critical but a major factor in cost. Current generations of LIBs (based on layered oxides and graphitic structures) are hitting the theoretical limits of battery chemistry, i.e., there are no more Li ions to be removed from the cathode material, and no space to insert Li ions into the anode, before Li metal plates on it. This makes enhancements to energy density more and more challenging, without consequences for battery degradation and/or safety. Use of silicon instead of graphite could theoretically increase energy density by approximately 40% at the cell level. However, when using silicon, the first cycle leads to an increased irreversible loss of capacity (over that seen for graphite) and more capacity is lost on subsequent cycles, primarily due to continued electrolyte degradation.

Battery Research – Current and Future Research Directions

Research into battery technology focuses on materials, engineering and more generally, the performance of battery systems. In terms of the materials, research has (at least) two strands. On one side, research focusses on improving LIBs as briefly outlined below. The second considers a myriad of different “beyond-Li” chemistries, which include batteries that are not based on Li, along with batteries that still contain Li but may, for example, contain a Li metal anode – to increase energy density - or a solid-state electrolyte (as in solid-state battery or “SSB”). SSBs in principle will be safer if the organic electrolyte is completely eliminated, and to have higher energy densities, if Li metal is used instead of graphite at the anode. Sodium- and magnesium-ion batteries (SIBs and MIBs, respectively) offer routes towards increased sustainability, but come with new challenges including low energy density (SIBs) and poor performance (MIBs) due to very low rates and/or low voltages and degradation (Mg). Redox flow batteries provide a route towards extremely high capacity and scalable batteries for use on the grid but cost and lifetime remain serious challenges.

Advances in the short-term involving current generation LIBs must come via increasing lifetime by reducing degradation, reducing cost, removing cobalt (e.g., by finding new cathodes), and decreasing charging times. Innovation in this field can be hampered by the need to keep costs down, essentially ruling out the use of large parts of the periodic table. Yet radically new approaches may not – at least in their first generation - be "cheap". Research is often closely aligned with mission-oriented agencies or institutions, or commercial stake-holders and there is an inherent tension between short-term wins and long-term step-change research. Close collaboration with relevant agencies/industries is extremely beneficial, by helping researchers to identify and understand the most pressing problems, for speeding up research that has clear targets and for helping to progress research results more quickly from the lab to industry. However, the community needs to ensure that fundamental science is still strongly encouraged – even in this commercially-driven field, if the really hard problems – where there is no clear route or pathway to solve them – stand any chance of being addressed. Furthermore, there are many exciting avenues in this field that require new experimental method and theory development, and use analytical techniques that are at the forefront of science. The field is massive and a short review cannot discuss then all, however, some illustrative examples are given below.

Metastability: This is a materials challenge that needs to be understood and controlled. To illustrate, a battery active material (a cathode (anode) or positive (negative) electrode material) is typically in its thermodynamic ground state when it is synthesized. Yet, when Li^+ ions are inserted or removed, the material is generally metastable towards decomposition. The kinetics and processes involving the transformation of the metastable state towards equilibrium needs to understood and then controlled – to prevent for example oxygen release from the cathode (with safety and degradation consequences, e.g., in Ni-rich cathodes this results in an increase in cell impedance) or the continued reaction of the anode with the electrolyte, consuming Li and increasing cell resistance. In a recent elegant example, a combination of theory and experiment was used to show that the degradation that is induced by cycling to high voltages is exacerbated by the structural relaxation and rearrangements that occur at lower voltages. Continued reactions with the electrolytes are more severe in higher density anode materials such as silicon and lithium, because fresh surface is continually exposed, either as the material expands and contracts on lithium insertion and removal (Si) or on Li plating.

Control of electron/ion transfer processes: Progress in, for example, Mg batteries requires an understanding of how a doubly charged cation is desolvated and inserted into a cathode material, as two electrons are – in theory- simultaneously removed from the cathode. At the anode the process involves the reduction of the cation via the transfer of two electrons from the Mg metal, a process also coupled with the desolvation reaction. While in some systems these processes are understood, they are far from being controlled and optimised – something that would lead to faster charging batteries.

The development of **Li-metal batteries** comes with its own set of questions and challenges. For example, how do the surfaces on which the Li metal plates affect the plating mechanism and Li corrosion? How can smooth Li metal deposition be ensured.

One new approach to examine Li metal – SEI interfaces is shown in Fig. 1, where microwaves, applied at the electron spin frequency (to partially saturate the Li metal electron spin resonance) result in an enhancement of the ^{7}Li metal signals via an Overhauser effect.[1] This method can in principle be used to identify species at the buried SEI-metal (Li) interface (LiF in the example given here).

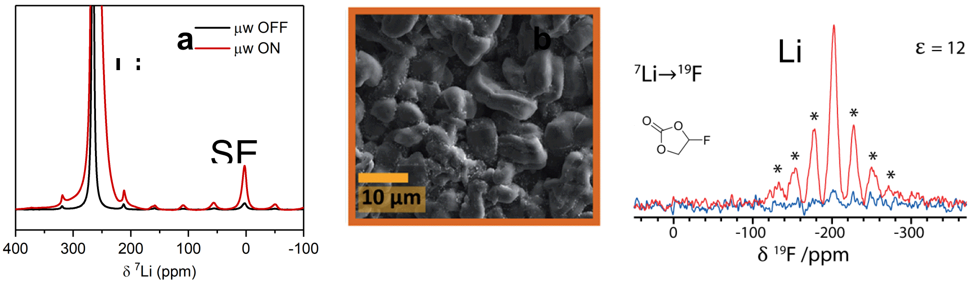

Fig. 1. Li metal dynamic nuclear polarisation (DNP) of a lithium metal electrode showing a. the enhancement of the Li metal signal and SEI on application of the microwave (mw on vs. off). b shows an SEM image of Li metal microstructure formed in an electrolyte containing a fluorinated ethylene additive. c. illustrates that the LiF at the Li-SEI interface can be detected on detection of a microwave signal (red = mw on; blue = mw off). [1]

Theoretical studies of increasingly large systems – likely aided by machine-learning approaches - will be required to help unravel the often, competing processes. However, it is not only the complexity of the systems but the various timescales over which processes occur that are huge challenges, requiring considerable method development.

The shape and structure of a material, or its morphology, can be as important as its chemical composition. New morphologies have the potential to improve batteries by for example preventing particle cracking. For example, single crystal micron sized particles may perform better (as cathode materials) than conventional polycrystalline NMC agglomerates that are subject to inter-granular cracking, resulting in extended battery lifetime.

Coatings and additives: One challenge is to design bespoke coatings that can withstand expansion/contraction. Another is to identify appropriate additives that react electrochemically or chemically to passivate the surfaces – via a less empirical approach than often used currently.

Electro-catalysis at interfaces: A better understanding of how surfaces catalyse electrolyte-electrode degradation reactions must be developed. For example, why does the electrolyte ethylene carbonate react more readily with Ni-rich electrodes than linear chain carbonates? Why are lithiated silicides more reactive than lithiated graphites? What surface and interfacial structures prevent such degradation reactions?

The development of new analytical tools that track the myriad of degradation processes on the fly is critical – including those at liquid-solid interfaces, and in the electrolyte – to provide real time information on degradation, and mechanistic insight, to understand the state of the cells, and ultimately inform how the cells are used (to minimise degradation). Synchrotron-based experiments provide exciting opportunities to interrogate batteries with ever-faster and higher resolution techniques, but simpler metrology that could be used more widely is also vital. To illustrate, Fig. 2 shows a recent technology advance for batteries, interferometric scattering microscopy (iSCAT), which has allowed for example different phase transition mechanisms to be determined, lithium-ion diffusion coefficients to be extracted (with continuum modeling) and particle cracking to be visualized in real time.[2]

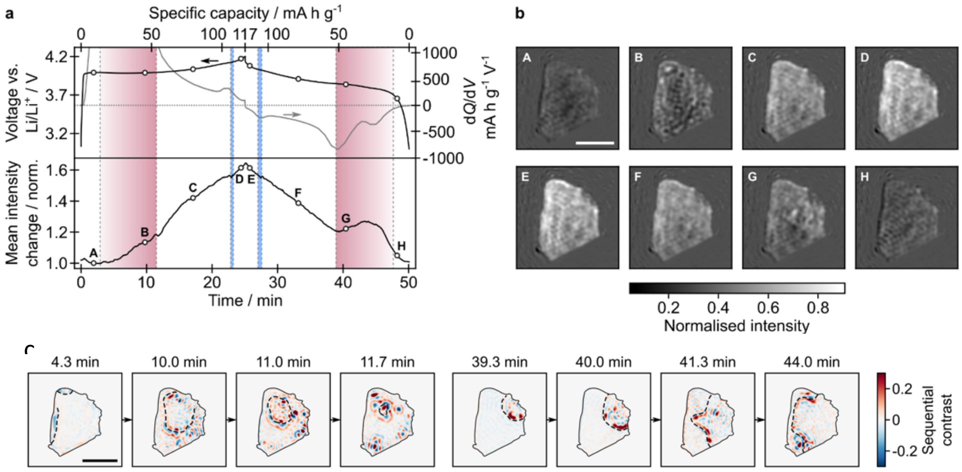

Fig. 2. Optical imaging of $LiCoO_2$ particles showing a. the voltage profile (top) and the optical intensity below, extracted from the single particle seen in b. The images in b are extracted at points A – H on the cycling curve. c. Shows the images taken in the pink shaded region in a, illustrating the progression of the insulator to metal phase transition that occurs on removing Li from the structure. Adapted from reference [2].

Recycling: New and cheaper routes for recycling used materials are needed together with the development of battery materials that are inherently easier to recycle.

Sustainability: We must pursue develop chemistries with materials that are abundant and sustainable, to include a greater emphasis on sodium ion batteries with earth-abundant electrode materials, and new, more sustainable LIB cathodes. While lithium-ion phosphate will play an important role in some batteries, higher energy density materials are still needed.

In conclusion, research challenges span synthesis of new materials, new characterisation approaches and new processing approaches – and demand interdisciplinary teams and longer term strategies and research programmes.

Acknowledgments

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References

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