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Sustainability and *in situ* monitoring in battery development

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The development of improved rechargeable batteries represents a major technological challenge for this new century, as batteries constitute the limiting components in the shift from petrol (gasoline) powered to electric vehicles, while also enabling the use of more renewable energy on the grid. To minimize the ecological implications associated with their wider use, we must integrate sustainability of battery materials into our research endeavours, choosing chemistries that have a minimum footprint in nature and that are more readily recycled or integrated into a full circular economy. Sustainability and cost concerns require that we greatly increase the battery lifetime and consider second lives for batteries. As part of this, we must monitor the state of health of batteries continuously during operation to minimize their degradation. It is thus important to push the frontiers of *operando* techniques to monitor increasingly complex processes. In this Review, we will describe key advances in both more sustainable chemistries and *operando* techniques, along with some of the remaining challenges and possible solutions, as we personally perceive them.

Our planet faces formidable sustainability challenges that call for game-changing research in various disciplines, including the field of electrochemical energy storage. Substantial progress in battery technology is essential if we are to succeed in an energy transition towards a more carbon-neutral society. We need new storage technologies if more renewables are to be used on the electrical grid; similarly, the electrification of transport requires much cheaper and longer-lasting batteries. The size of these batteries (in comparison to those used for portable electronics) places severe pressure on materials resources[1]. Although estimates vary widely, the predicted penetration of lithium-ion technology into these large-volume markets could result in as much as a threefold increase of production for the cathode material, reaching nearly 400,000 tonnes per year by 2020 (refs 2,3).

We need to rethink the processes, and move towards more sustainable energy harvesting and storage technologies that become part of a circular economy. Materials sustainability will become an overriding factor in the years to come, conjointly with consumer demands that are very real and ever-increasing. They include the desire to increase the driving range of more modestly priced electric cars from 150 to well over 500 km, and the need to lower the cost and provide maintenance-free technologies for grid applications. The issue is thus straightforward: can we increase battery sustainability, while lowering cost and improving battery performance?

The growing importance of sustainability has led scientists to implement life-cycle cost analysis approaches to the field of Li-ion batteries. Although the accuracy of such methods remains controversial, they do play an important role in identifying trends. Of note, they have revealed that today's battery assembly process, including materials and recycling, is not as sustainable as generally thought, 400 kWh of energy being required to make batteries that deliver 1 kWh of energy, while releasing 75 kg of CO_2 (ref. 4). The material fabrication step is by far the most problematic, accounting for 80% of the above numbers. These reports have raised scientists' awareness of the need to consider the elemental abundance of any new materials or electrolytes, motivating work on, for example, Fe-, Mn- and S-containing cathodes and electroactive organic molecules. New synthetic processes are required that are inherently eco-efficient and environmentally friendly, and anticipating feasible approaches to recycle materials.

Sustainability has driven some battery makers to redesign the assembly process to make use of renewable energy. Their coupling with solar producers, as evidenced by Tesla's 'Gigafactory' (recently unveiled by Tesla CEO Elon Musk), may drive change in the same way that Sony's production of the rocking chair battery helped to underpin the portable electronics revolution. The factory will produce, in 2020 alone, more Li-ion batteries than produced globally today, with all the energy needed to produce these batteries coming from solar energy[5]. Because of Tesla and other less vocal companies, the field of electrochemical energy storage is potentially undergoing a real revolution. A nearly threefold decrease of the stored kWh price to €200 per kWh at the pack level[6] is predicted in the next 10 years, driven at least in part by both the large volume production and the realistic prospects of a second life for electric vehicle batteries[7,8]. Under such a scenario, the production of Li-ion batteries should expand hugely over the years to come, hence reviving the issue of finite Li reserves. These reserves are indeed limited, but Li can be recycled by hydrometallurgy, although the economics of such a process has yet to be worked out[9]. This concern has driven researchers to explore new, potentially more sustainable chemistries, including Na-ion, metal–air chemistries Li(Na)–O_2, Li–S, multivalent (Mg, Ca), redox flow batteries (RFBs) and aqueous-based technologies, as discussed later.

Are there lessons to be learnt from redox processes in biological systems, where inherently sustainable but complex redox reactions proceed in a series of cascades? Such systems are optimized for various perturbations, and while incorporating many 'self-healing' mechanisms, they can be extremely fragile, with unexpected metabolism events leading to specific diseases. To understand and monitor the consequence of such events, numerous highly sophisticated analytical techniques such as magnetic resonance imaging (MRI) have been developed. As in biological systems, preventing the failure mechanisms in batteries requires that we understand the causes of degradation and how the various components of the battery interact with each other. The increasing need for batteries that last for >7 years for transport and 20–40 years on the grid, and the

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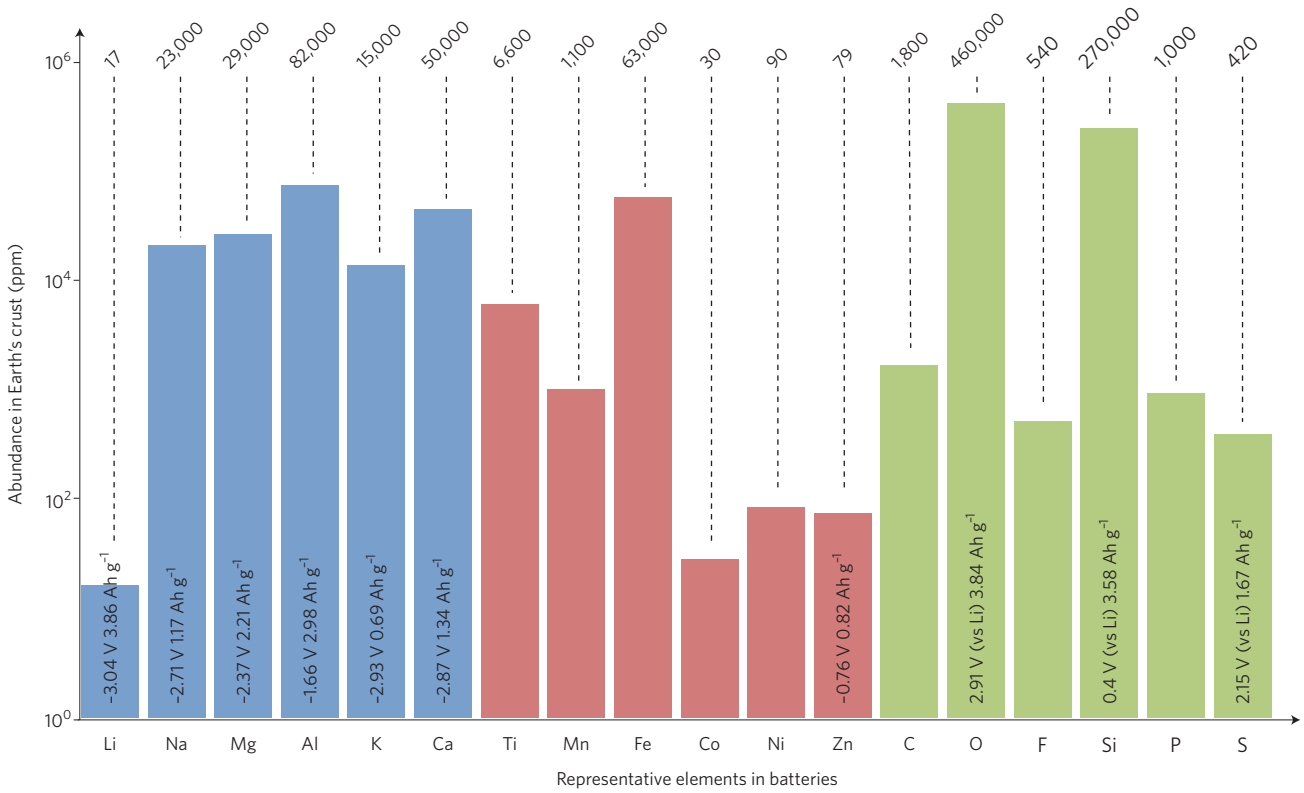

Figure 1 | Elemental resources. The abundance of the different chemical elements currently used in the systems considered in this Review, reported on a log scale as a rectangle, with the values in ppm given on top. Note the trend in abundances of Al > Ca > Mg > Na > Li, and Fe > Mn > Ni > Co. The standard redox potentials of metal anodes together with their capacities are given (in the coloured rectangles). The values for O and S correspond to their use as positive electrodes. The value for the negative electrode Si is given versus Li. Abundances for alkali and alkali earth metals are shown in blue, transition metals in red and main group elements in green.

emergence of the 'second-life' battery business, mean that predicting failure becomes even more important.

A push to develop new characterization techniques for batteries has led to spectacular advances across a range of methodologies with the development of sophisticated diagnostic tools (such as X-ray diffraction, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and transmission electron microscopy (TEM)), which can ideally operate *in situ* as the battery is cycled. More work is required, however, to push the frontiers of existing techniques and design *operando* analytical techniques (used under working conditions) not only to monitor the battery's state of health and enhance its lifetime, but also to aid in the design of new materials and to optimize existing and new electrochemistries. Note that the terms *operando* and *in situ* are used almost interchangeably in the literature, both referring to measurements that are performed on the system under real (or as close as possible to real) working conditions. An *operando* measurement usually refers to a measurement made while the battery is operating (cycling), while the more general *in situ* term (meaning on-site) may refer to the measurement of a particular variable against a parameter relevant to the system, which could be time but could also be temperature, pressure or other parameters. These analytical tools will benefit both laboratory and industrial research. As new materials and technologies move into the marketplace and are expected to function for increasingly longer lifetimes, we need methods to evaluate and optimize their functioning in real time.

This Review attempts to highlight (i) the ways in which scientists address sustainability issues when designing new materials and exploring new chemistries beyond Li, and (ii) recent advances in characterization techniques, focusing first on recent *in situ*/*operando* analytical developments in the battery field before proposing and discussing new directions and avenues for exploration. Both topics are intimately linked as batteries with longer lifetimes lead to greater sustainability; the development of more sophisticated techniques that monitor 'on the fly' key phenomena linked with both function and degradation will allow the relevant factors that increase battery life to be more rapidly identified. Although progress has been encouraging, it is certainly not sufficient to meet our planet's growing demands: we must push the frontiers faster and further in the years to come.

Advances in Li-ion battery sustainability

Past efforts devoted to developing positive electrode materials with minimum ecological footprint have been rewarded by the development and commercialization of Fe-based polyanionic compounds, most notably olivine $LiFePO_4$ (ref. 10). In many ways, $LiFePO_4$ is the ideal sustainable material as, apart from Li, it is composed of Earth-abundant chemical elements (Fig. 1) and can be prepared at moderate temperatures through a wide variety of synthetic approaches including, in addition to the more classical ceramic routes, hydro(solvo)(iono)-thermal and bio-mineralization synthesis[11], allowing particle sizes to be readily controlled. Such routes are followed by a second carbon-coating step[12] involving either chemical (pyrolysis of sugars) or physical (ball-milling) processing to alleviate the intrinsically poor electronic conductivity of $LiFePO_4$. This process results in penalties in both cost and energy density because of additional densification difficulties. For this reason, $LiFePO_4$ is, in practice, no cheaper than the less environmentally friendly Co- and Ni-containing phase of formula $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, termed NMC (ref. 13).

The $LiFePO_4$ 'success' story has triggered extensive research on Fe-based polyanionic compounds including the silicates (Li_2FeSiO_4) (ref. 14) and borates ($LiFeBO_3$) (ref. 15), but these suffer from poor

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kinetics and low redox potentials. However, the Fe-based fluorosulphate $LiFeSO_4F$ phase shows the highest reported redox potential (3.9 V vs Li^+/Li) for the Fe^{3+}/Fe^{2+} redox couple in any inorganic compound, owing to the higher electronegativity of $(SO_4)^{2-}$ as compared to the $(PO_4)^{3-}$, $(SiO_4)^{4-}$ or $(BO_3)^{3-}$ polyanions and the presence of F^- (ref. 16). This compound and its derivatives can be readily prepared by low-temperature synthesis (<300 °C) from Earth-abundant chemical elements, but a downside is their moisture sensitivity, requiring additional care in electrode manufacturing.

Considerable effort has been expended on Mn-based polyanionic compounds because of the greater natural abundance and higher M^{2+}/M^{3+} redox couple of Mn in comparison with Fe. Furthermore, it is in principle easier to activate the Mn^{2+}/Mn^{4+} couple than the Fe^{2+}/Fe^{4+}, potentially resulting in materials with higher capacity, but results so far have largely not been promising. Manganese-based polyanionic electrodes show either limited reactivity ($LiMnPO_4$) or no reactivity at all ($LiMnSO_4F$). This has been ascribed to the large structural distortions associated with the Mn^{3+} Jahn–Teller ion, and the lower electronic conductivity of the Mn compounds compared with the Fe compounds. The use of more complex anions such as pyrophosphates $(P_2O_7)^{4-}$, borosilicates, borophosphates and carbonophosphates[17] is not competitive performance-wise, owing to the weight penalty associated with the heavier polyanions. Improved polyanionic alternatives to $LiFePO_4$ have not yet been found, and chances remain slim. The most promising strategies so far involve the mixed Fe/Mn olivines, which show higher rate performances than $LiMnPO_4$ and higher energy densities than $LiFePO_4$ (ref. 18).

Turning to the use of layered oxides as positive electrodes, $LiCoO_2$ is not ideal in terms of sustainability, as Co resources are limited (Fig. 1) and Co is toxic. In principle, the resource issue can be addressed by recovering Co from electrode materials rather than extracting Co from ores[19]. Efforts to produce increased sustainability have been made by the partial replacement of Co by both Ni and Mn, leading to the development of the NCA ($LiNi_{1-y-z}Co_yAl_zO_2$) (ref. 20) and NMC[13] phases, with the Ni-rich 622 phase (that is, $Li[Ni_{0.6}Mn_{0.2}Co_{0.2}]O_2$) being the most promising for electric vehicle applications. Increasing the Ni content negatively affects the capacity retention, but this can be mitigated by, for example, developing core–shell particles[21] and gradient-concentration particles[22], where the Ni-rich core and Mn-rich coating provide the higher capacity and thermal stability, respectively.

Lithium-rich NMC phases with high Mn contents and extremely high capacities (>280 mAh g^{-1}) have been discovered[23,24], and the role of anionic network in the overall redox process[25–27] was revealed by an arsenal of complementary analytical techniques. By exploiting the anionic redox processes, advanced electrode materials such as Li-rich '$Li_4Mn_2O_5$' have been prepared[28], with one of the most abundant elements (Mn) giving an outstanding reversible capacity of 350 mAh g^{-1}. Although the cycling performance of this electrode is poor, such a finding suggests that the problem of combining high energy density and sustainability in layered oxides may not be insurmountable.

Carbonaceous materials, whose performances have improved incrementally, remain the best choice, in terms of sustainability, for negative electrodes. One of the most abundant Earth elements (Fig. 1), Si, has received considerable attention, because its capacity is 10 times that of carbon. But the Li-alloying reactions (Li_xSi, where $x \leq 3.75$) are accompanied by extremely large volume changes, owing to the large amount of inserted Li (ref. 29). Creative approaches to solving the electrode swelling issue have included the use of nanoparticles, confinement in active or inactive buffering matrixes, the use of new polymeric binders having the appropriate wetting properties as well as self-healing attributes, the tuning of the electrode porosity or formulation, and the design of a multitude of nanoarchitectures. Although progress continues to be made, limited cycle life has plagued commercialization, largely because it has not been possible to form a stable solid electrolyte interphase (SEI) on silicon, a problem made worse by the continued expansion and contraction of the Si particles on cycling[29]. The present trend involves the use of carbon electrodes with small amounts (~10%) of added Si, to achieve capacities nearly twice that of today's graphite electrodes (372 versus 700 mAh g^{-1}). Work on the Si electrodes has provided additional impetus to develop new binders such as carboxymethylcellulose (CMC)[30,31], which in addition to being prepared from natural resources are extremely important within a sustainability context, as electrode processing can now be done in aqueous solvents rather than in toxic solvents such as NMP (1-methyl-2-pyrrolidinone). This work has also inspired the development of other more sustainable polymer binders such as those derived from bio-algae[32].

Renewable organic electrodes based on redox-active molecules containing electrochemically active C=O functions, such as the oxocarbons $Li_{2+x}C_6O_6$, which can be synthesized via 'green chemistry' from natural organic sources, represent one approach to developing greener Li-ion batteries[33]. These can be combined, for instance, with carboxylate-based organic molecules (such as dilithium terephthalate, $Li_2C_8H_4O_4$) that have low redox potentials (<0.8 V) to produce a battery with an excellent ecological, carbon-neutral footprint. The recycling process of the initial raw materials is fast and uses sunlight as a free energy source. Numerous electrochemically active organic molecules/polymers have now been synthesized[34], but bottlenecks remain, such as the lack of Li-bearing positive molecules that can be oxidized at a potential of >3 V; the poor conductivity of the organics, which necessitates the addition of large amounts of conducting carbon to the electrodes; and the low volumetric energy density of the batteries, owing to the low density of organic molecules and the addition of carbon. The latter is less of a drawback for mass storage applications since volume is not such a critical issue.

The examples above illustrate the efforts made by chemists over the past decade to integrate concepts of sustainability when improving or selecting new materials for the next generation of Li-ion batteries. But these advances do not address concerns about limited Li reserves, which result from the predicted increased battery demands[2,3]. Thus, there remains a strong impetus to explore battery technologies 'beyond Li-ion'.

More sustainable technologies beyond Li-ion batteries

The continued push for cheaper, higher-energy-density and more sustainable battery technology has led to a blossoming of research activities centred on new chemistries such as Na-ion, metal–air (Li, Na, Zn), Li–S, multivalent ions and redox flow, to name but a few. Although some of these (with schematics shown in Fig. 2) are in the very early stages of commercialization, there is no clear-cut winner; several advances have, however, been made, and so optimism must prevail, motivating continued research and development of all of these technologies.

Replacing Li by more abundant metals Na, Mg and Ca. Before 1990, research was equally devoted to both Li and Na-based insertion compounds; but even though laboratory-scale Na-ion cells had already been built, Na research nearly fell into oblivion, owing to the successful commercialization of Li-ion battery technology. As Na has a much higher elemental abundance than Li, it is without a doubt the most appealing alternative to Li-based battery technology, from the viewpoint of sustainability. Research into Na-ion technology is now accelerating, progress being rapid because of the many similarities of Li-ion and Na-ion chemistry[35,36]. At present, Na-based layered materials (such as $Na_{0.7}Fe_{0.5}Mn_{0.5}0_2$) (ref. 37) and polyanionic ($Na_3V_2(PO_4)_2F_3$) (refs 38,39) compounds are mainly used as positive materials. Sodium cannot be intercalated into graphite, and hence alloying and conversion reactions have been explored, but currently

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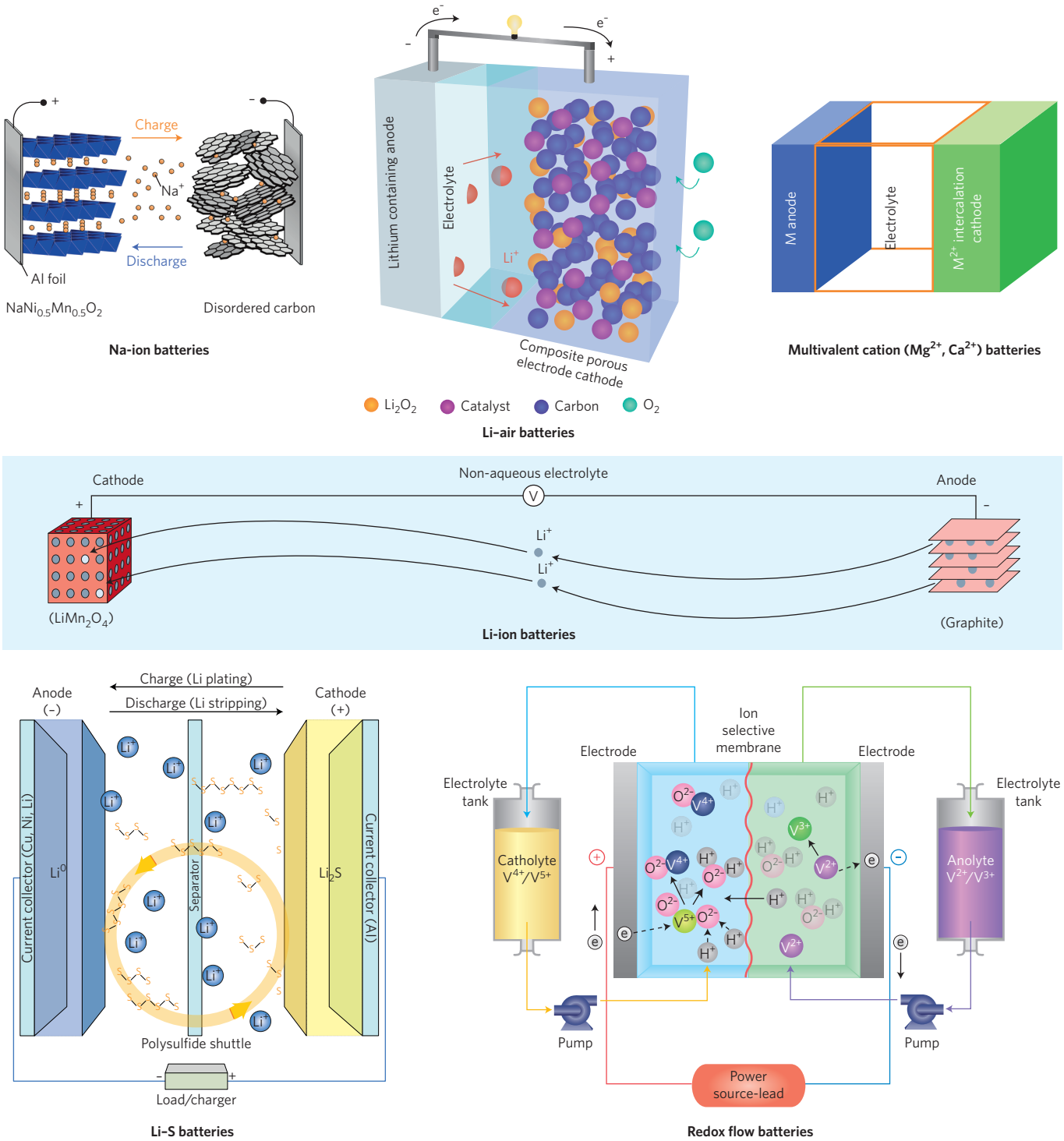

Figure 2 | Schematics of different rechargeable batteries. Cells based on monovalent (Li^+, Na^+) and divalent (Ca^{2+}, Mg^{2+}) cations generally consist of intercalation materials, separated by a membrane, which are immersed in a liquid electrolyte and serve as positive and negative electrodes. When the electrodes are externally connected, redox reactions proceed in tandem at both electrodes to deliver energy. When moving to a Li–air cell, the positive electrode is replaced by a porous carbon electrode over which the oxygen reduction/oxidation takes place. For Li–S, the positive sulfur electrode consists of a composite made of carbon, sulfur and, in some batteries, oxides. Such configurations change for the redox flow cell which comprises two electrolyte flow compartments separated by an ion-selective membrane; the electrolyte solutions are pumped continuously from external tanks that contain the soluble redox species and thus the stored energy.

hard carbon remains the most successful negative electrode in terms of capacity retention (C = ~350 mAh g^{-1}). Sodium batteries use similar non-aqueous cyclic and acyclic carbonate electrolytes and additives to Li batteries[40]. Prototype cells in the industry-standard '18650' format have been built based on $Na_3V_2(PO_4)_2F_3$/C that can deliver sustained (>4,000 cycles) energy densities of 95 Wh kg^{-1} at unexpectedly high powers[41], and the company Faradion has assembled pouch cells based on layered nickelate phases with even higher

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energy densities of >120 Wh kg^{-1} (ref. 42). It is worth remembering that while the first commercialized Li-ion cells only had an energy density of 110 Wh kg^{-1}, energy densities as high as 200 Wh kg^{-1} are now attainable. Nonetheless, because of the weight penalty of Na, and a M/M^+ vs $Na^+/Na°$ redox potential that is 330 mV higher than Li (Fig. 1), this technology will not outperform Li-ion based on specific energy density; but similar and rapid progress is expected.

Further optimization will result from better mastery of Na-ion chemistry in terms of interfaces, parasitic reactions and kinetics, together with the preparation of new and moisture-stable phases. For the $Na_xMM'O_2$ layered phases, particularly those that contain the sustainable elements Fe and Mn, it is important to push the Na contents to $x = 1$ from their current values of close to $x = 0.7$, in order to increase the overall Na content in the cell. An alternative strategy to increase capacity involves the use of materials that combine both cationic and anionic redox processes, as demonstrated for Li-ion technology. While safety concerns have yet to be fully evaluated, there is every confidence that Na-ion battery technology, which is more sustainable and potentially cheaper than its Li-ion counterparts (owing to cheaper Na-based compounds and the ability to use Al rather than Cu as the negative current collector), will reach the market place within the next 5 to 10 years, targeting mainly mass storage and high-power applications. Significant improvements in battery energy densities could be achieved if the use of Li and Na metal anodes were not plagued with the safety hazards associated with dendritic growth, but this remains a long-standing and complex problem.

Gravimetric and volumetric capacities for the more abundant elements Mg and Ca (Fig. 1) are significantly higher than that of graphite. But making batteries from these elements is far from being a practical reality[43,44]. For Mg chemistry, the difficulties are twofold — namely, the positive electrode and the electrolyte. The first challenge is to identify inorganic compounds that can reversibly take up Mg^{2+} at higher potentials than the Chevrel phases (1–1.3 V vs Mg). Mg^{2+} is inserted into cavities between the Mo_6S_8 clusters that make up these phases, the polarizability of the chalcogen (S) network assisting Mg^{2+} transport. Confirming this trend is the recent finding[45] of full Mg reversibility at 1.3 V in the thiospinel Ti_2S_4. Unfortunately, the move to materials with less-polarizable oxygen sublattices, to push up the voltage, results in a reduction in Mg^{2+} mobility. Co-intercalation of a solvent molecule or water helps to aid Mg^{2+} mobility within open structures (such as manganese birnesites[46] or layered vanadates) and possibly to reduce the energy penalty associated with the desolvation of Mg^{2+} electrolyte ions, but in many of these systems, the role of proton intercalation is unclear. Elegant approaches with mixed Li/Mg salts have been proposed (mimicking the Daniel cell), the Li-ions inserting into the cathode material and the Mg ions plating on the anode[47], but they are not without practical drawbacks. The choice of negative electrodes is wider, as Mg-alloying reactions with Bi and other metals[48] are highly reversible, as demonstrated by the assembly of $MgMo_6S_8$/Bi cells. The second major obstacle involves finding an electrolyte[49] that can reversibly strip and plate Mg, allows reversible Mg^{2+} insertion at high potentials, does not cause corrosion and is stable at high voltages. Although new Mg-based electrolytes[50] have been reported, the expectations that arose from Aurbach's proof-of-concept paper[51] in 2000 have been slow to be realized. The field requires the research expertise of physical and synthetic organic chemists that our battery community generally fails to attract.

A recent report[52] has shown that reversible Ca plating and stripping (that is, removal) in conventional alkyl carbonate electrolytes at moderate temperature is feasible, prompting moderate optimism. Yet promoting diffusion of large divalent ions in intercalation hosts involves great challenges. Overall, and despite the elegant fundamental studies, the development of a Ca-based rechargeable battery in the twenty-first century seems unlikely, unless the challenges are addressed through new imaginative approaches by battery chemists.

Replacing 3*d*-metal oxides by more abundant O_2 and S. Metal–air batteries have a theoretical energy density exceeding that of Li-ion batteries and the posibility of using unlimited fuel O_2 as the positive electrode. The first hints of reversibility within the Li–O_2 non-aqueous system[53,54] inspired considerable worldwide interest and enthusiasm for this technology. However, the unrealistic expectations of quick commercialization have diminished, as the early cells exhibited rapid capacity fade, large overpotentials, particularly on charging, and poor rate performance. Research revealed[55] that these problems originate from passivation of the cathode by Li_2O_2 films and poor electrolyte/electrode stability in the aggressive environment of the superoxide/peroxide species formed during the reduction of O_2. Furthermore, today's batteries are 'lithium–oxygen' and not 'lithium–air', and a means of filtering the air to remove CO_2, N_2 and moisture is required for a practical system.

Progress has nonetheless been made. Breakthroughs in understanding the reaction mechanisms at the oxygen electrode, and the mechanism by which the electrolyte and carbon electrode degrade, have opened new avenues for solving the challenges of Li–air. They demonstrate that Li–air does not necessarily mean a low-rate, low-capacity battery, contrary to earlier views. For example, the growth of Li_2O_2 from solution and not on the cathode surface can be promoted by high-donor-number electrolyte solutions, or by additives that solvate the LiO_2 intermediate that forms on reduction of O_2 to Li_2O_2 (refs 56–58). Redox mediators such as tetrathiafulvalene (TTF)[59], $(CH_2)_3(CMe_2)_2NO$ (TEMPO)[60] or I^-/I_3^- (ref. 61) can then shuttle electrons away from Li_2O_2 in solution to the cathode on charge, decomposing Li_2O_2. This results in significantly higher rates and capacities with much lower polarization than seen in the early cells. Lithium–oxygen cells can be cycled 1,000 times using support electrodes made of gold[62] or TiC (ref. 63), rather than carbon which reacts with Li_2O_2 during charging. Although the addition of $LiNO_3$ helps to protect the Li anode[64,65], either the generally ignored problem of the Li metal anode must be solved or it must be replaced by another (Li-containing) anode if practical batteries are to be developed.

Although research has identified strategies to solve some of the early problems, challenges such as cathode/electrolyte stability and air handling remain to be tackled. It is still unknown whether a commercial cell can be developed. Recent results have demonstrated that reversible cycling by means of discharge products other than Li_2O_2, such as LiOH (ref. 66), LiO_2 (ref. 67) and Li_2CO_3 (ref. 68) is also possible, with suitable redox mediators or catalysts. Although the reaction mechanisms at play in these chemistries need to be determined and optimized, they do provide hints that new and more flexible chemistries could be developed that are more tolerant to the various components found in air.

Sodium–oxygen batteries that operate by the intriguing reversible formation of large NaO_2 cubes during cycling[69,70] show inherently lower polarization and better kinetics compared with batteries that cycle via Li_2O_2 formation. A major drawback of this technology is that it only involves a one-electron process, since superoxides are formed, NaO_2 being more stable than LiO_2. This results in a fourfold decrease in energy density in comparison to the LiO_2 battery (3,600 Wh kg^{-1}(Li_2O_2) versus 805 Wh kg^{-1}(NaO_2)). Ongoing challenges include a fundamental understanding of the O_2/NaO_2 redox mechanisms with an emphasis on the nucleation/growth process of NaO_2. The ultimate goal is to find ways to promote the formation of Na_2O_2 (1,610 Wh kg^{-1} at 2.33 V) to increase the capacity.

The abundant element S was shown decades ago to react reversibly with Li, leading to theoretical energy densities six times that of Li-ion. But Li–S batteries were never commercialized, owing to severe hurdles, namely the solubility and redox shuttle activity of the reduced

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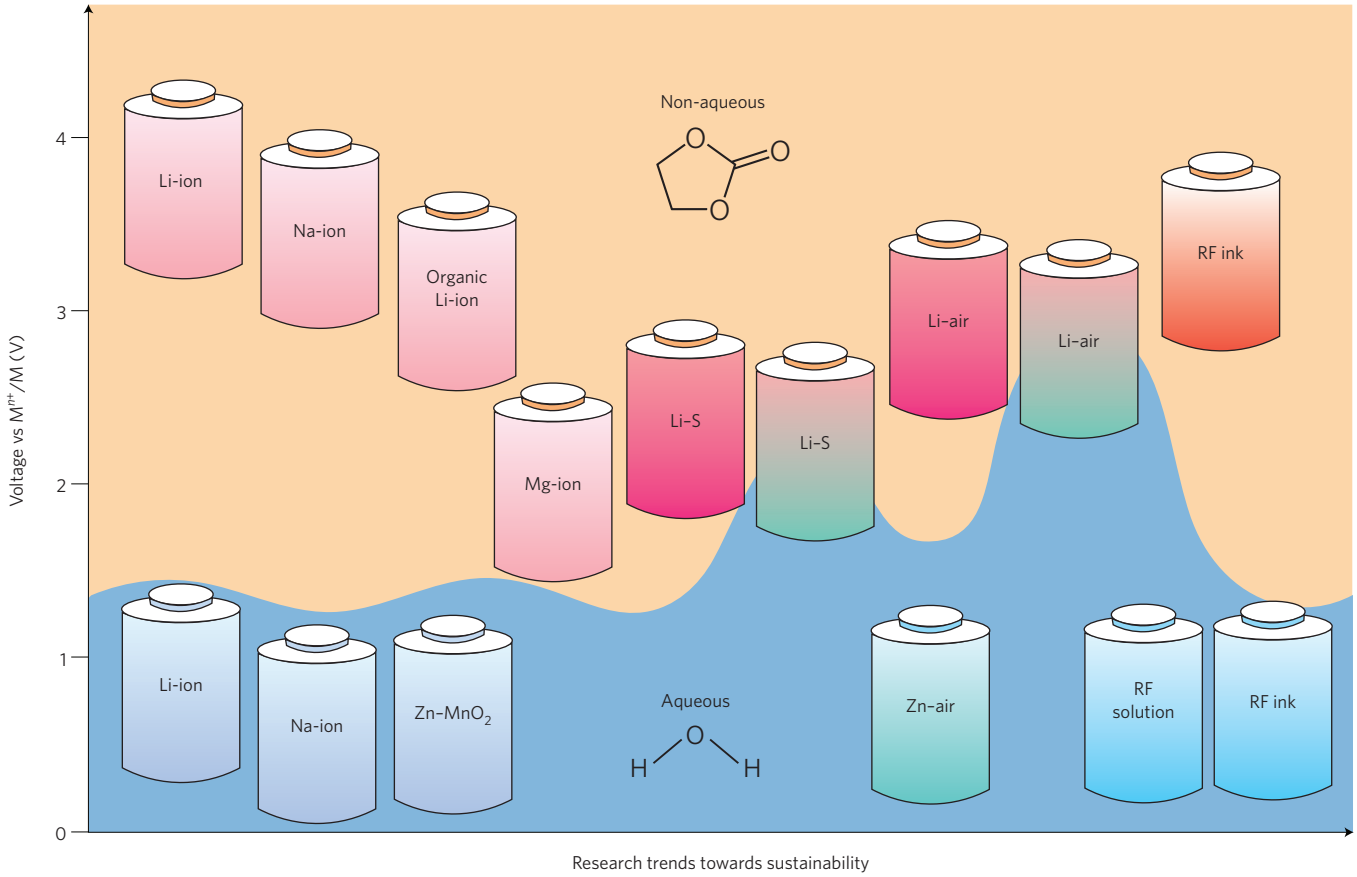

Figure 3 | Trends towards sustainability for today's batteries. Non-aqueous rechargeable systems under investigation occupy the top of this graph and correspond to the high-voltage systems, while the lower-voltage, aqueous rechargeable systems lie at the bottom of the graph. The aqueous Li–air and Li–S systems show higher potential than the other aqueous systems simply because they rely on the use of a Li negative electrode hermetically sealed between two ceramic membranes.

polysulfides. The Li–S system has been recently revisited as part of the quest for new sustainable storage technologies[71]. Elegant strategies to confine S in a variety of porous, tubular, functionalized, polymer-coated carbon nanostructures[72] or highly porous oxide structures (zeolites[73] or metal–organic frameworks (MOFs)[74]) have been attempted, to reduce polysulfide cross-over, but with limited success. In contrast, the use of electronic conducting oxides (such as Ti_4O_7 or $NiFe_2O_4$) with polar surfaces for capturing S species has allowed high sustained capacities (>2,000 mAh g^{-1}) in a 70% S-loaded positive electrode, suggesting that other electronically conducting oxides should be surveyed to further improve performance[75,X]. Such achievements were realized through the use of an excess of electrolyte, reducing the overall energy density. How easy it will be to limit the amount of the electrolyte without sacrificing performance remains an open question. Efforts to lower the carbon surface area and increase electrode wetting are encouraging, as are attempts to add fluorinated solvents with reduced polysulfide solubility to preserve viscosity. So optimism must prevail, and Li–S batteries will most likely be commercialized before any of the metal–air systems discussed above. As in the Li–O_2 system, the Li metal anode remains an issue, inevitably delaying the development of these systems further.

Green and cheaper water-based electrolytes

Aqueous electrolytes offer much lower-cost, safe and non-toxic systems, provided the overall battery performance is optimized for long-term cycling and safety, driving a resurgence of activities in this sector. The concept of adapting Li intercalation systems to aqueous electrolytes originates from the pioneering work of Dahn's group[77] in 1994, which used VO_2 and $LiMn_2O_4$ as negative and positive electrodes, respectively. This work was not pursued until the commercialization of the $Na_{0.44}MnO_2$/ $NaTi_2(PO_4)_3$, Na-ion aqueous system[78] by Aquion to provide backup power to local homes. Such 1.5 V cells show good cyclability but limited power and low energy density (30 Wh kg^{-1}).

Sustainability and cost have driven work on aqueous Li–O_2 and Li–S systems, being aided by Visco's pioneering work on the development of protected Li-anodes together with a ceramic membrane separator to obtain a two-compartment cell. This strategy, which still uses Li as the negative electrode, has enabled the development of highly reversible 3.2 V aqueous Li–O_2 cells[79] operating via the uptake and release of LiOH, and has also led to the development of 2.2 V Li–S aqueous cells[80] showing limited polarization owing to the higher solubility of Li_2S in water as compared with non-aqueous cells. Sodium analogues can readily be envisaged, motivating the development of ceramic, Na^+-conducting water-stable membranes.

The Zn–air battery represents another potentially sustainable technology, but it has been challenging to develop a rechargeable cell, owing to side reactions such as carbonization and the formation of Zn dendrites. Recent work[81] using a third sacrificial electrode indicates that rechargeable aqueous 1.2 V Zn–air cells with an energy density of 150 Wh kg^{-1} and an estimated cost of €150 per kWh could soon become a reality. Other Zn chemistries include a reversible aqueous 1.44 V Zn/α-MnO_2 cell operating by means of a conversion-type reaction that demonstrates excellent

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cyclability[82]. Although aqueous RFB chemistries (such as vanadium RFB, 1.26 V; Zn–Br, 1.85 V) have been around for a long time[83], their potential cost advantages have yet to materialize, and their market penetration is sporadic. A strategy to reduce cost is to increase the energy density (from the currently low values of 30–40 Wh kg^{-1}), by increasing either the concentration of the soluble redox species, their redox potential or both. New approaches are sorely needed. Cheaper separators must also be developed[84], and concepts such as membrane-free separators must be pursued. Redox flow cells[85] with energy densities of 80 Wh kg^{-1} were recently realized through the use of ink suspensions of intercalation materials, carbon particles (increasing the effective concentration of redox-active species) and Li-ion non-aqueous electrolytes, allowing potentials of 3–4 V to be reached. Although the use of a non-aqueous-based electrolyte pushes up the cost, this finding has opened new avenues for exploration[83], including the use of inorganic[86] or organic inks[87] in aqueous systems, with potential cost and energy-density advantages for grid-scale storage. For example, an ideal Na-ion redox flow system might use inks made up of abundant elements such as Mn, Fe and Ti, and a cheap Na-based aqueous electrolyte.

One obvious route towards increasing energy density would be to enlarge the low operating window of water (1.23 V) (Fig. 3). Kinetics are key in minimizing electrolyte breakdown in lead–acid batteries, hence enabling an operating voltage in water of up to ~2.2 V. Within this context, the recent paper by Suo *et al.*[88], opening up the operating potential window of aqueous electrolytes via a highly concentrated 'water-in-salt' electrolyte, suggests very different strategies to develop practical batteries that deliver 2 to 3 V, potentially resulting in a significant increase in energy density.

Progress in monitoring *in situ*

The move away from the traditional and well-understood battery chemistries to more complex redox processes such as alloying and conversion, and the need to optimize more established chemistries, has motivated the development of new analytical *operando* techniques that allow study of the fundamental mechanisms by which these materials operate, together with the kinetics of these processes (as illustrated in Fig. 4)[89–96]. Critically, these techniques have allowed pathways and processes that differ from those predicted based on the ground-state thermodynamics of the system to be elucidated. For example, *in situ* diffraction studies have shown that $LiFePO_4$ reacts through the formation of metastable solid-solution phases with Li concentrations outside the ground-state values of the end-member phases $Li_{1-y}FePO_4$ and Li_yFePO_4 (Fig. 4d)[90,97]. Similarly, *operando* NMR studies on Li/Si cells have revealed the existence of enlarged solid solution of the crystalline phase $Li_{15+x}Si_4$ (Fig. 4a)[93,98].

Rather than just probing a single material, *operando* techniques have provided an understanding of how the various materials function cooperatively, particularly within the working battery. This has been particularly important for the understanding of the electrode/electrolyte interface. *Operando* imaging and spectroscopic techniques such as NMR[99], MRI[95] and electron paramagnetic resonance (EPR)[94] have recently enabled the visualization and quantification of Li (and Na) microstructures (Fig. 4b,g). The electrolyte and electrode chemistry can be simultaneously monitored in the MRI experiments, allowing Li dendrite formation to be correlated with Li^+-ion depletion near the Li anode[100]; mossy Li versus dendrite formation can be distinguished, and Li microstructure formation can be quantified, allowing exploration of, for example, the effects of rate, the addition of additives and the use of different electrolytes on dendrite growth. Similarly, the complementary method, *in situ* EPR imaging[94], can be used to visualize Li morphology evolution upon cycling. Because of the greater skin depth of NMR experiments (d = 17 μm) compared with EPR experiments (d = 1 μm), NMR can detect and quantify thicker and denser microstructures, while the higher sensitivity of the EPR method enables the early stages of Li microstructure formation to be tracked.

Methods for imaging the movement of reaction fronts and reaction kinetics are becoming increasingly powerful. *In situ* high-resolution TEM[96,101] (Fig. 4e) has been at the forefront of these advances, providing in-depth insights into interfacial processes and Li-driven local structural changes (for example in SnO_2 and Si) with a much higher resolution than MRI methods. Significant advances in synchrotron methodologies have allowed spectroscopic, two-dimensional transmission X-ray microscopy, full three-dimensional tomographic reconstructions and diffraction-based methods to be performed (such as Bragg coherent diffraction imaging), often in parallel; these have been used, for example, to track particle expansion with lithiation[102], and the evolution of strains and movement of dislocations within particles[103]. EPR imaging has been used to visualize *in situ* the displacement of lithiation fronts inside paramagnetic electrodes during battery operation, providing information about the electrode kinetics[94], and complementing microfocused X-ray[91] and neutron diffraction and radiography experiments[92] on whole cells (Fig. 4). Lithium diffusion in paramagnetic materials has also been monitored by complementary spectroscopic methods, the approaches providing insights into kinetics as well as transport phenomena[104].

Considerable progress in the development of new techniques and cell designs has been made for almost all of the traditional and less-traditional laboratory analytical techniques used to study batteries, so that these methods can now be applied *in situ*; space does not allow them to be described here in detail. Many of these techniques have provided considerable insight into electrolyte and electrode degradation. For example, the gases generated during cycling can be identified and quantified by *operando* mass spectrometry, allowing the reactions taking place at the electrodes (such as SEI layer formation and oxygen evolution) to be investigated. Infrared, Raman and ultraviolet spectroscopies reveal changes in the chemical nature of species present at the interfaces, while scanning probe microscopies such as atomic force microscopy can identify structural changes at interfaces and have recently been applied to study Li^+ transport and electrochemical strain[105]. The electrochemical quartz crystal microbalance provides a highly complementary technique to the other methods described here, because it can be used to monitor small mass changes at the electrodes. Thermal analysis methods[106] that can follow heat changes in the cells associated with the reactions taking place on charge and discharge also provide insight into cell electrochemistry.

It remains a challenge to monitor the evolving SEI, primarily owing to sensitivity, cell-design issues and the general challenge of studying buried interfaces in composite structures. Could this be addressed? *In situ* NMR studies still suffer from limited resolution, but recent advances in the application of dynamic nuclear polarization methods to study catalysis[107] along with the use of, for example, ^{13}C-enriched molecules suggest that sensitivity issues could be overcome, although the low temperatures generally required for dynamic nuclear polarization are not (currently) compatible with the requirements of *in situ* experiments. Synchrotron-based experiments have an important role to play, because the new X-ray sources have beams that can be focused to nanometre length scales, allowing individual electrode particles to be imaged (Fig. 4c), and information extracted from diffraction or spectroscopic probes such as X-ray absorption spectroscopy[89,91,108]. X-ray photoelectron spectroscopy represents an extremely powerful *ex situ* technique to probe electrode surfaces to depths of 5 to 50 nm (with synchrotron sources) and provide information about the SEI composition[109]. This provides a strong motivation to push for methods to allow this technique to be performed *in situ*.

The surface-enhanced Raman (SERS) effect could be exploited, as illustrated by the detection of evolving signals from the SEI,

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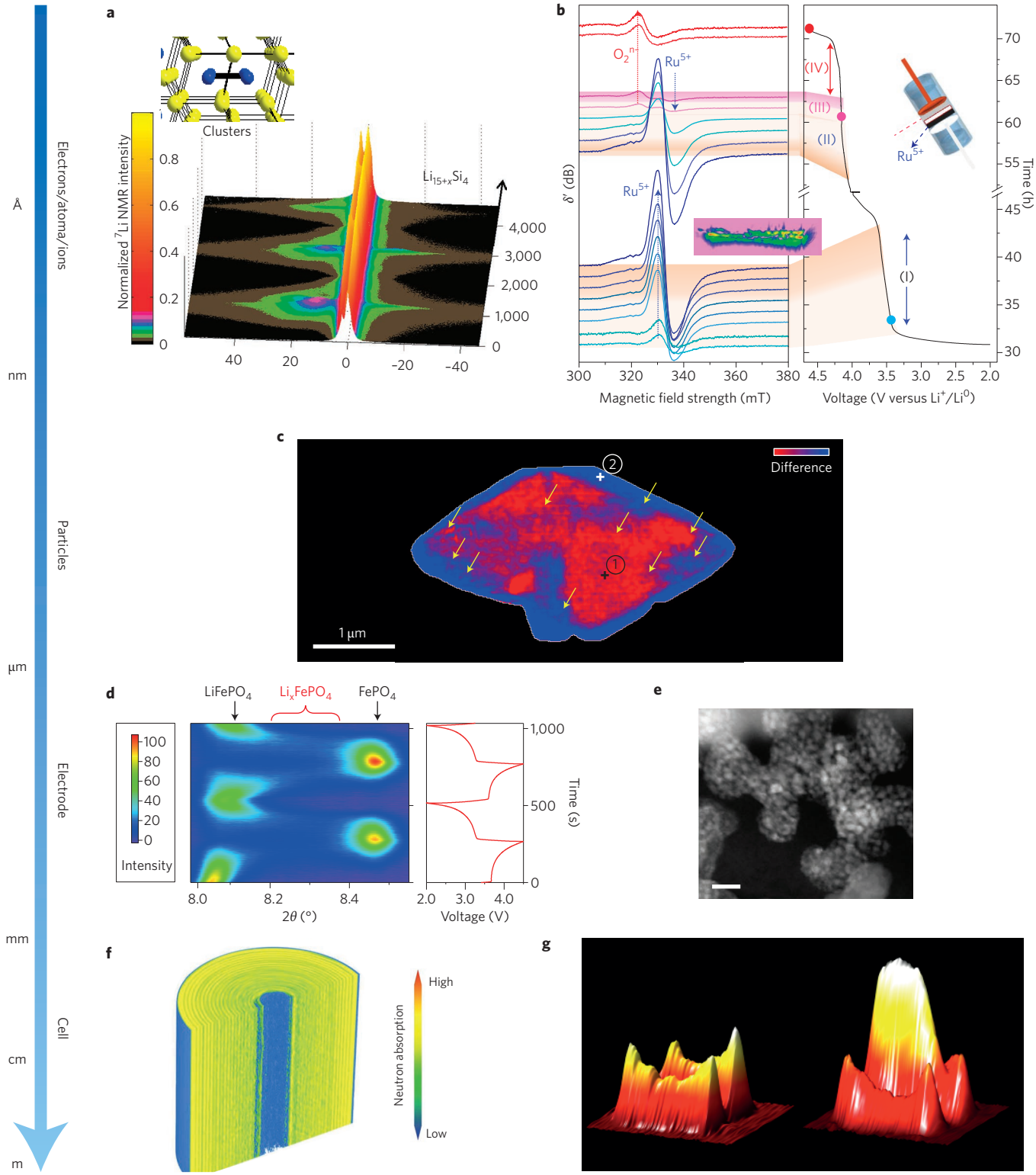

Figure 4 | Examples of *operando* techniques. **a**, ^{7}Li *in situ* NMR spectra of a battery comprising Si nanowires on a carbon support cycled versus Li, showing resonances associated with Si clusters and the $Li_{15+x}Si_4$ phase[93]. **b**, X-band EPR spectra of a $Li_2Ru_{0.75}Sn_{0.25}O_3$/Li cell during charging to 4.6 V, showing the evolving broad Ru^{5+} (blue) and peroxo-like broad (red) signals[94]. An EPR image of the cell is shown in the pink inset. **c**, Soft X-ray ptychograph of the Fe oxidation state of a $LiFePO_4$ particle. The red and blue areas indicate the highest content of $LiFePO_4$ and $FePO_4$, respectively[89]. Points 1 and 2 give rise to XAS spectra characteristic of $LiFePO_4$ and $FePO_4$, respectively. Arrows indicate defects in the crystal. **d**, X-ray diffraction shows the evolution of (200) Bragg reflections of $LiFePO_4$ and $FePO_4$ in response to the applied electrochemistry (right hand side). **e**, TEM image of FeF_2 particles after reacting with lithium, coming from the lower right, for 20.5 min (ref. 96). Scale bar, 10 nm. **f**, A model of a commercial 18650 Li-ion battery reconstructed from neutron radiography[92]. **g**, MRI (^{7}Li) images before (left) and after (right) charging showing the formation of Li moss on a plated electrode[95]. Reproduced from ref. 93, Nature Publishing Group (**a**); ref. 94, Nature Publishing Group (**b**); ref. 89, ACS (**c**); ref. 90, AAAS (**d**); ref. 96, Nature Publishing Group (**e**); ref. 92, Elsevier (**f**); ref. 95, Nature Publishing Group (**g**).

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making use of the SERS effect induced by metal particles formed during the $ZnFe_2O_4$ conversion reaction[110]. The development of *in situ* 'surface' and subsurface probes that can study the SEI could greatly help in identifying the science underpinning the complex mechanisms involved in SEI formation and other redox processes. The challenge is significant, but, given the critical role of these processes in battery cycle and calendar life, attempts to develop new tools to attack this issue must be worth the risk.

Another burning question concerns the visualization of electron transfer and redox processes at even shorter length scales. The study of nucleation/growth kinetics of phases containing peroxide-like species by EPR imaging in the layered lithium-rich oxides is a first step, even though the resolution has been limited to micrometres. Progress towards nanometric resolution, although challenging, will provide the insight required for transformational approaches to control the redox reactions (for example electron transfer) that are common to many energy-related processes, including batteries, photovoltaics and water-splitting systems.

Although spectacular, many of the above achievements do not readily translate into real-time monitoring of batteries in the field. We need methods that will allow detection, in real time, of the complex combination of intended chemical and electrochemical processes, and of the panoply of often poorly understood side reactions that significantly affect long-term performance. This will allow us to optimize cycling regimes or identify failure mechanisms more rapidly in emerging technologies. Battery history can then be determined and a health 'check-up' to be performed, allowing appropriate pricing and insurance for a battery as it enters its second-life application. Grid and transport demonstration projects and battery tests are already in progress to link traditional electrochemical responses (such as current, voltage and impedance) with test routines appropriate to the technology and produce the 'big data' needed to extract new correlations and, ultimately, predict future performance. Monitoring these parameters constitute the basics of today's battery management systems. We need to go one step further and couple these responses to relevant metrics from inside the battery 'black boxes'. Passive diagnostics (that is, methods that do not influence battery chemistry and do not draw current) are required that can couple electronic with chemical traceability and can identify key parasitic reactions that are critical to both short- and long-term cell failure.

To tackle this problem, it is important to consider which experimental observables will provide the most valuable insights into long-term battery performances and how to collect them in a non-invasive fashion. New thinking is required. Most of the aforementioned techniques such as NMR, EPR, diffraction and microscopy were developed in specifically designed homemade cells and require expensive large- to medium-scale diagnostic equipment. Cells can be charged by induction, allowing new techniques to be developed (for example magic-angle spinning *operando* studies of batteries). *Operando* neutron diffraction and tomography studies on 'real-world' (18650) batteries under realistic cycling conditions have recently allowed the visualization of Li concentration gradients across the battery, providing insight on electrode failures, degradation mechanisms and diffusion kinetics (Fig. 4)[92]. Though it is an attractive advance, this again uses large-scale instrumentation with limited access, unless neutron lines dedicated to battery research are funded. On a smaller but simpler scale, differential thermal analysis of the entire pouch cell has been used to correlate the melting point of the electrolyte to the cell's state of health[104].

Notable progress has been made over the years towards instrumental miniaturization, so that bench-top X-ray diffraction units, scanning electron microscopes and portable impedance (and even NMR) spectrometers exist, but we are still far from producing the test units needed to monitor batteries in their end application. For instance, what kind of implantable analytical devices could be integrated as part of the battery pack in the next generation of electric vehicles? As illustrated above, imaging and diagnostics methods have been successfully imported from other fields, MRI being the obvious example as it is an essential diagnostic technique in the medical field.

Can we draw inspiration from the medical field and all the tooling that is currently used during surgery or in implants, and from the increased use of sensors in advanced manufacturing? Chips are, for instance, implanted in human bodies to help to treat diabetic patients, and fibres are used to transmit and receive signals during operations. Why not include an optical fibre within an 18650 cell that can connect the inside of the battery to the outside world? Future batteries could have, in addition to the positive/negative outputs, an extra analyser output (Fig. 5). This could then be used to activate sensors located within the cell and transmit information in and out of the cells. This is not a pipe-dream; fibre Bragg gating sensors, connected to fibre optics, have been inserted in pouch cells to measure temperature and strain, and to detect states of charge[111]. Owing to the rapid development of electric vehicles, together with the new era of interconnected technology (ICT) powered by batteries, it is a certainty that intelligence will be placed in future batteries. What it will be remains an open question. Ironically, the ICT and

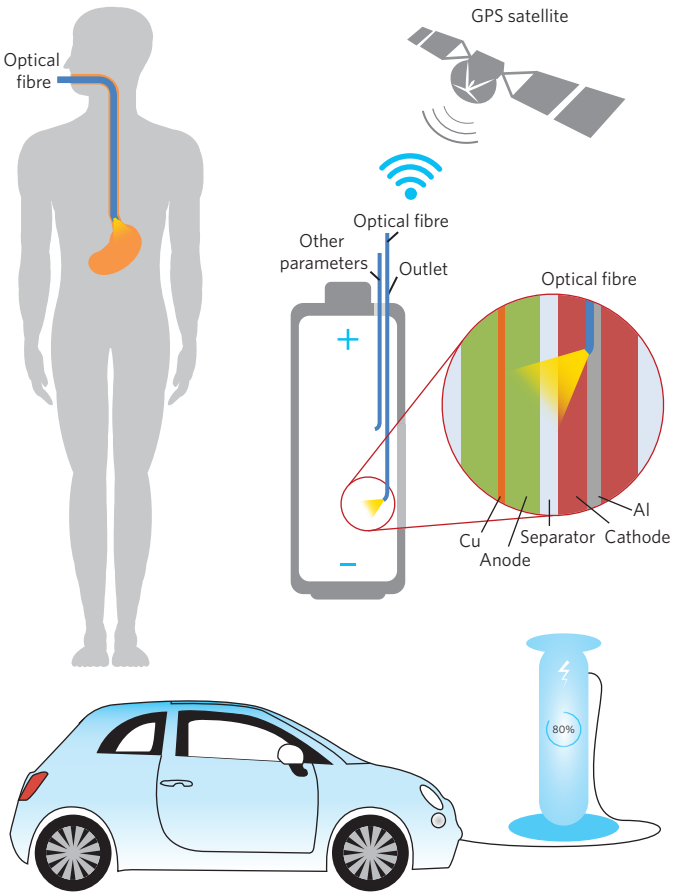

Figure 5 | Possible future integration scenario for battery management. Batteries powering electric vehicles are continuously traced by collecting basic battery management system data via satellite. Possible ways to achieve this with new diagnostic methods are inspired by current human health monitoring; similar approaches could be implemented in a battery by the insertion of optical fibres coupled with sensors, a future battery having an output analyser (perhaps comprising an optical fibre to collect parameters such as temperature, pressure, etc. along with a second fibre to activate another sensor) in addition to the classical positive and negative electrodes.

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medical diagnostics fields require advances in rechargeable batteries, but it may yet be that these fields will provide the approaches and inspiration to connect the batteries to the cloud.

Conclusions

Sustainability, which has sometimes been viewed as an extra constraint to the development of energy storage materials, has ended up being beneficial to battery research as it has triggered and inspired numerous materials and technological developments. Care has been taken to select abundant elements (such as Fe and Mn) for the design of new electrode materials; new, low-temperature, eco-efficient processes have been developed that make use of ionothermal or bio-inspired approaches. These processes have encountered difficulties at the industrial scale since most of today's electrode materials are still made by energy-hungry ceramic methods. Further synthetic efforts must be devoted to this issue. The foreseen 10% yearly increase in the number of batteries produced will inevitably rejuvenate the chemistry of recycling to recover metals whose abundance is limited: the development of clever chemistry to enable efficient recycling of materials must go hand in hand with the design of new materials. There are important lessons to be learnt from the lead-acid battery recycling industry. While this is well regulated in industrialized nations, poor regulation in low- to middle-income countries has resulted in significant health issues for populations living near recycling sites and for people working in the industry. We must minimize the widespread use of elements such as Cr, V, Ni and Co, particularly in large-scale batteries, if we do not want to repeat history.

New sustainable technologies beyond Li-ion technology have been explored. Among those that use the more abundant monovalent (Na^+) and divalent (Mg^{2+}, Ca^{2+}) ions, Na-ion technology holds great promise for future commercialization. In contrast, the future of Mg-ion technology is more uncertain, owing to materials and electrolytes issues, while Ca-ion batteries currently remain a curiosity. Metal–air technologies, based on unlimited O_2, have greatly benefited from progress in materials science and in analytical techniques. However, owing to their electrochemical chemical complexity, many challenges remain to be solved if these technologies are to make a significant impact on the future energy-storage landscape. The horizon is brighter for Li–S, but a common issue inherent to both Li–O_2 and Li–S technologies is the need to protect or ideally replace the negative Li metal electrode.

The quest for enhanced sustainability and lower cost for grid applications has also been a driver in revisiting aqueous-based electrolytes. Aside from the well-known aqueous RFBs, this has led to the development of aqueous metal–air and Li–S technologies whose functioning relies on the use of ionic conducting ceramics that prevent Li being exposed to water. Such systems have shown promising cyclability, but limited rate performance. Better ceramic membranes are essential to increase rate, and it is anticipated that this research field will gain momentum in the years to come. Equally, there is a need to design new functionalized membranes/separators for both aqueous and non-aqueous systems to specifically capture parasitic reaction products and increase cell lifetimes. Additionally, Li-free aqueous systems suffer from poor energy density, owing to their low output potential. Research aiming to widen the aqueous electrolyte stability through innovative formulations of solvent, salts and additives, and to slow down the kinetics of electrode-driven electrolyte decomposition through the design of new surface approaches, must receive greater attention as a strategy to increase energy density and lower cost.

In terms of sustainability, rechargeable aqueous Na-ion technology is attractive. But cost expectations have yet to be realized, raising the question of whether aqueous systems can ever be made cheaper than non-aqueous systems, in terms of the cost per kilowatt hour of stored energy. The somewhat controversial announcement that the price of Li-ion batteries will drop to less than US$150 per kWh at the pack level by as early as 2022 (by the company General Motors)[112] complicates the issue. The jury is still out.

Pushing the frontiers of present *in situ* analytical techniques is a must to pursue research on sustainable materials more efficiently and to develop greener Li-ion batteries. Improvements in analytical techniques that would allow the movement of electrons to be followed on the nanoscale and subnanoscale, at relevant timescales and on relevant systems and interfaces, will have great impact on the fields of electrochemistry, electrocatalysis and others. It could open up a new era for the study of transport at interfaces, which remains one of the greatest challenges of research for any electrochemist. For researchers exploring new storage concepts and engineering new interfaces, it could also provide insight into how to control the movement and redox processes of atoms.

We need new analytical methods, optimized to probe specific battery chemistries, so that new technologies can be brought to the market more rapidly to meet societal demands. New methods must be developed that will allow batteries to be controlled and traced so that they can be used for more than one application. Advances should include the development of new remote, non-invasive and passive *operando* techniques to complement present battery management systems. In short, we require methods to establish the health record of the battery, analogous to personal health records for human beings. Innovative approaches that integrate expertise of other fields are called for. One feasible strategy involves the use of optical fibres as direct readouts or for addressing, for example, magnetic, resistive, strain, temperature and optical sensors. Having identified battery faults, we need to either actively switch-on repair mechanisms, or build in self-healing processes into the original battery design. The future offers huge opportunities for our battery research field, as long as we are willing to explore new, risky but exciting paths involving increasingly ambitious interdisciplinary research that brings together research expertise from very different cultures and communities.

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Competing financial interests

The authors declare no competing financial interests.

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