



### **A Paradigm of Storage Batteries**

Journal:	<i>Energy &amp; Environmental Science</i>
Manuscript ID	EE-REV-07-2019-002356.R1
Article Type:	Review Article
Date Submitted by the Author:	04-Sep-2019
Complete List of Authors:	Ji, Xiulei; Oregon State University, Department of Chemistry

## ARTICLE

## A Paradigm of Storage Batteries

Xiulei Ji

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Research on batteries is at the crossroads. The research goal of Li-ion batteries is laser-focused, which is to push the performance limits of electrodes and electrolytes for an ever-higher energy density. However, the primary evaluation metric of storage batteries is the levelized energy cost, and there may exist pluralistic routes to reach a cost target. Therefore, it becomes urgent for researchers to have a roadmap for this new paradigm of storage batteries. In this article, I describe five dimensions of storage battery research from a chemical reaction's point of view, where electrode materials and ion charge carriers represent the reactants, electrolytes provide the medium for the reaction, battery operation principles describe the configurations of the reactors, and electrode-ion chemical bonding reveals the nature of the reaction. The permutations of these five dimensions create 10 unique research planes, and the research activities on Li-ion batteries have been in one such plane: electrode materials  $\times$  electrolytes. For LIBs, the electrode-ion interactions are largely taken as purely ionic; in contrast, the electrode-ion interplays may be of a good extent of donor-acceptor covalency when charge carriers are no longer small metal cations. Covalent-ionic bonding in batteries may represent the nexus to engender a constellation of new solutions in energy storage. Design of storage batteries entails a panoramic view with these five dimensions holistically considered. A deeper understanding of the chemical-reaction nature of batteries will be a vantage that unifies rather than compartmentalizes a paradigm of storage battery research.

### Introduction

Renewable energies such as solar and wind cannot be transported or stored directly; thus, such powers need to be converted to electricity first, a universal 'currency' of energy. However, to date, electricity, as a primary industry commodity, has no shelf life, which is not widely stored for futuristic usage. In the existing grid infrastructure, the generation and consumption of electricity must be simultaneous,<sup>1</sup> where the grid is incongruous with the intermittency and, sometimes, the unpredictability of the power generated from renewable sources.<sup>2</sup> This incompatibility creates an enormous problem when a large percentage of electricity coming from renewable sources finds no users behind the meters, which could cause catastrophic failure of the aging grid.<sup>3</sup> The grid interruptions cost the economy of the United States \$150 billion annually, which is still rising.<sup>4</sup> The solution to this challenge is to secure the grid with storage capacity, which puts away the electricity surplus by peak shaving and later fills the valley when the demand outpaces the concurrent power generation. Nowadays, electricity-saving at the societal level has become an absolute necessity, and the storage facilities will serve as the 'banks' of electricity.

Energy storage for electricity is usually done indirectly, where electricity is converted to other forms of energy reversibly, including potential energy by pumped hydropower

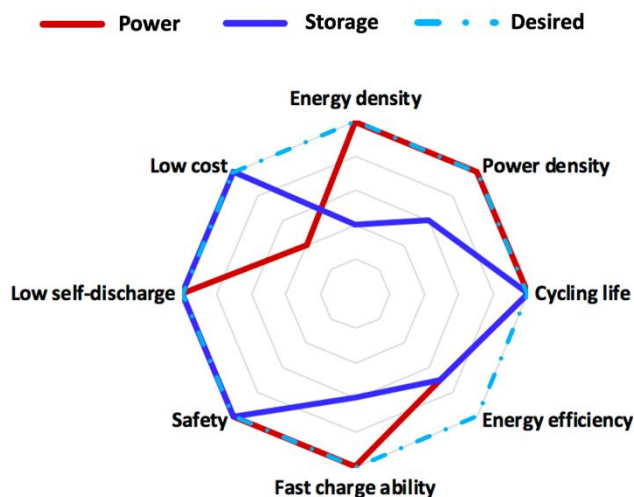
storage (PHS)<sup>5</sup> and compressed air,<sup>6</sup> kinetic energy by flywheels,<sup>7</sup> thermal energy by molten salts,<sup>8</sup> and chemical energy by secondary batteries<sup>9</sup> or by chemicals, *e.g.*, H<sub>2</sub> production.<sup>10</sup> On the other hand, electricity can be stored directly by superconducting magnetic energy storage (SMES) as infinitely flowing electric current<sup>11</sup> or by capacitors as electrostatic energy.<sup>12</sup> Currently, over 94% of the global storage capacity is undertaken by PHS,<sup>13</sup> which inconveniently counts on specific geographical features to generate a good hydraulic head between water reservoirs, up and down. Among storage solutions, batteries are the most attractive because they are modular and adaptable for homes, communities, and the grid.<sup>14</sup>

Batteries, in particular, Li-ion batteries (LIBs), are ubiquitous in portable electronics, power tools, and recently for electrified transportation, *e.g.*, e-bikes, and electric vehicles (EVs).<sup>15</sup> Yet the consensus is that the current LIB technology is unfit for storage purposes mainly due to the cost and safety issues. Electrochemical capacitors and other commercialized batteries, including lead-acid and nickel-metal hydride (Ni-MH), despite approaching their technological maturity and demonstrating their relevance for niche markets, have yet to address the massive demand of energy storage. The battery community has the mission to invent alternative battery technologies specifically for storage purposes.

Based on different applications, batteries can be classified into power batteries and storage batteries. As for power batteries for dispatchable uses, the goal of future development is crystal clear, which is to circumvent the anxieties of EVs, which include limited driving ranges, long charge times, insufficient battery longevity, and safety risks. The market relevance of power batteries is mostly defined by the driving

Department of Chemistry, Oregon State University, Corvallis, Oregon, United States  
97331-4003  
E-mail: [david.ji@oregonstate.edu](mailto:david.ji@oregonstate.edu)

range of EVs, where the current goal is set to 300 miles for the North America market, whereas the driving-range requirements may be less demanding in Asia and Europe. As the caveat, the extension of the driving range should not be at the expense of safety, where, however, there may exist a trade-off for nickel-rich cathode materials.<sup>16–18</sup> In the near future, it is unlikely that any battery technologies may advance to the level to subvert lithium-based batteries as the market-dominating power batteries.



**Fig. 1** Radar chart shows the wanted performance in comparison with the ideal cases, where red for power batteries; blue for storage batteries, and the dashed light blue line of the octagon marks the ideal scenarios.

On the other hand, the paths toward market-winning storage batteries are distinct from that of power batteries. In the radar chart (Fig. 1), the two solid curves sketch the wanted deliverables of power batteries and storage batteries compared to the ideal scenarios. As a most conspicuous difference, the evaluation metrics for storage batteries are relaxed on energy density and often on power density and fast rechargeability, all of which are, nevertheless, indispensable for good power batteries. Note that for certain applications, *e.g.*, for storing electricity from wind farms, storage batteries may be required to function at a rate, *e.g.*, 2C, *i.e.*, charge or discharge completed within 30 mins. Instead, the top priority of storage batteries is the cost—the levelized energy cost (LEC).<sup>19</sup> In contrast to power batteries, battery research on storage batteries is unchained from pursuing the ever-higher energy density, and thus the era when one battery type fits all has reached its end. Therefore, there will emerge an expansive paradigm of storage batteries.

## Cost Considerations

### Levelized Energy Cost

LEC is the expense of every kWh delivered by a storage facility as the output during the entire lifetime of the facility. Here, I take electricity

arbitrage, potentially by homeowners for revenue-generating, as an example to illustrate LEC via the following equation:

$$LEC = \frac{C_{cc} + C_m + C_e}{n * E * EE * DoD} \quad (1)$$

where  $C_{cc}$  is the capital cost, including installation fees,  $C_m$  is maintenance and operation cost,  $C_e$  is the total expense of electricity purchasing,  $n$  is the total number of cycles during the device's lifetime,  $E$  is the maximum energy that a battery can store,  $EE$  is the energy efficiency, *i.e.*, the round-trip efficiency of a charge/discharge cycle, and  $DoD$  is the average depth of discharge in each cycle. To break even, the electricity price by which the homeowners sell to the grid, *e.g.*, as the peak-hour price of electricity, cannot be lower than the LEC. Note that the estimated inflation rate should be included, which is missing in this equation.

In order to attain the minimal LEC, the numerator and the denominator terms in Equation (1) should be minimized and maximized, respectively. First, it is pivotal to note that the capital cost,  $C_{cc}$ , can be highly volatile, which has been evident for the market of lithium, nickel, and cobalt compounds.<sup>20</sup> In storage batteries, earth-abundant elements and common commodity materials<sup>21</sup> should be engaged,<sup>22</sup> and rare elements and expensive materials need to be avoided in the design of battery chemistries. Moreover, the economy of scale should be applicable to storage battery chemistries, where the battery manufacturing cost, including the environmental impacts, are sustainably low. Note that for most batteries, the maintenance and operation cost,  $C_m$ , may be nearly nil at a small scale, *e.g.*, a home module, where this cost may be more applicable to flow batteries, which rely on pumps, where the replacement of these pumps every 5 to 7 years<sup>23</sup> may demand professional service, resulting in  $C_m$ . For the minimal  $C_e$ , ideally, battery modules are connected by the internet of things (IoT), which will smartly store low-price electricity from solar or wind that is generated during 'inconvenient' hours when the demand is abyss low. In Equation (1), a bonus of cost that is not considered is the value reclaimed by recycling the decommissioned batteries.<sup>24,25</sup> Recycling of lead-containing compounds is how lead-acid batteries stay competitive to date.

Indeed, boosted electrochemical performance of the same battery chemistry will lower the LEC, where the approach is to maximize the product of  $n$ ,  $E$ ,  $EE$ , and  $DoD$ —the total delivered energy,  $E_T$ , of the device over the lifetime. Note that in the literature, batteries are typically evaluated in deep cycles with 100%  $DoD$ . However, cycling in intermediate  $DoD$  ranges, *e.g.*, from 40% to 80%, may significantly enhance the longevity of batteries.<sup>26</sup> For metal batteries, the  $E_T$  of the device may be maximized if the most suitable range of  $DoD$  is identified for the metal anodes.

According to a report of Sandia National Laboratories, the markets of grid storage applications are really diverse, where there are five categories, *i.e.*, electric supply, ancillary services, utility customers, grid system support, and renewables integration.<sup>27</sup> The above illustration is by no means comprehensive because the rate of return, *i.e.*, profit, can be very sensitive to different applications.<sup>28</sup>

Before LEC can be quantitatively determined for a battery technology, the storage battery chemistries and their constituent materials have to be evaluated by conventional metrics, gravimetric and volumetric, particularly at the stage of basic research. Gravimetric metrics, such as specific capacity, rate capability, and

specific energy/power are widely employed to evaluate the performance of battery electrodes in fundamental research. Volumetric metrics may be seen as unimportant for storage purposes; however, volumetric properties directly determine the amount of inactive materials used, such as electrolyte, separator, and packaging. For example, when the energy density is a half, the cost for all these inactive materials doubles.

Furthermore, storage batteries are only relevant if they can be scaled up, which means that the battery chemistries and the electrode materials must be conducive for materials and device engineering. Battery chemistries may behave very differently when the batteries adopt practically relevant conditions, particularly low electrolyte/electrode mass ratios and high loadings of active mass, such as Li-S batteries.<sup>29,30</sup>

### Liability Cost and Electrolytes

The most significant cost risk that is not covered in the above Equation (1) is the potential liability, often unaffordable to a manufacturer. The liability concern comes from the sheer scale of storage battery installation in the future, *e.g.*, for loading levelling. In order to best serve the societal needs, the battery storage eventually needs to deliver power at the gigawatt (GW) scale safely, where the scale is on par with the power that one PHS facility or a nuclear power plant delivers. By simple estimation, if the power density of a battery is 200 W kg<sup>-1</sup>, and the density of this battery is 2.0 kg L<sup>-1</sup>, to deliver power at one GW, the volume of batteries will take 2500 m<sup>3</sup>, when not accounting for the space needed for operation, *e.g.*, service and venting. Furthermore, the coming 5G era demands safe UPS solutions for data centers and server farms more than ever, where currently gel (sealed) lead-acid batteries are the widely trusted safe option.

Now, let us regard batteries not as an electronic device but as a reactor that holds a wet synthetic reaction. Usually, to design a wet synthetic reaction, a chemist should do the due diligence to select a reaction medium, *i.e.*, a solvent, where such a medium defines the chemical environments for the reaction as well as affects the yield, the reaction rate, and the safety of the reaction. In batteries, it is the electrolyte that serves as the reaction medium via the electrode-electrolyte interfaces, sometimes through the solid electrolyte interphase (SEI),<sup>31,32</sup> and most importantly, the battery safety directly relates to its electrolyte.<sup>33,34</sup> Regarding the safety of batteries, the pivotal question is which type(s) of electrolytes the storage batteries should employ. Currently, there are four primary types of electrolytes: (1) Aprotic organic electrolytes, (2) Ionic liquid (IL) electrolytes, (3) Solid-state electrolytes, and (4) Aqueous electrolytes. The first three electrolytes afford wider electrochemical windows than the aqueous electrolytes, where they allow the operation of highly reducing anode materials, *e.g.*, lithiated carbonaceous anodes in LIBs and lithium metal in Li-S and Li-O<sub>2</sub> batteries. Organic electrolytes are what the current LIBs use, and the LIB community is considering IL electrolytes<sup>35</sup> and solid-state electrolytes.<sup>36</sup>

Among these electrolytes, it seems that conventional carbonate-based organic electrolytes are not aligned with the high safety requirements for large-scale storage. Although the safety of LIBs that use such electrolytes has been managed at the scale of EVs by battery management systems (BMS), it is unlikely that such electrolytes could circumvent the demand of energy storage at the

GW scale.<sup>37</sup> The risk will be hair-raising if a GW facility adopts flammable batteries that are vulnerable to natural disasters and accidental thermal runaway of cells. Unfortunately, to date, due to the lack of suitable alternative storage batteries, LIBs have been installed for commercial storage purposes, and frequent reports of accidents of these facilities have caused a serious public safety concern.

However, it is essential to note that not all organic solvents are flammable, *e.g.*, if fire retardants are employed as electrolyte solvents.<sup>38,39</sup> Recent studies reported that high salt concentrations in such fire-extinguishing solvents allow good performance of the carbonaceous anode in different batteries.<sup>40,41</sup> However, like IL electrolytes, non-flammability of electrolytes may not necessarily equal “non-exploding” as it is the thermal stability of the electrolytes and the flammability of the released gas molecules that are most relevant to the explosion risk.<sup>42,43</sup> This same concern applies to an emerging class of electrolytes—deep eutectic solvents (DES), which have shown utilities mainly in flow batteries.<sup>44,45</sup> It is the limited thermal stability of the hydrogen bond donors of such electrolytes that raises the concern.<sup>46</sup>

Recently, efforts have been flooded to solid-state electrolytes to solve challenges of lithium metal batteries, including safety.<sup>47–49</sup> Without solubility in solid-state electrolytes, polysulfide shuttling in Li-S batteries is certainly prevented; however, the Li-dendrite formation and the resulting short-circuit were still observed with solid-state electrolytes.<sup>50</sup> Furthermore, it was reported that solid-state electrolytes, particularly oxides, and molten lithium could react violently at relatively high temperatures, which negates the promise of safety benefits of this type of electrolytes.<sup>51</sup> As another challenge, the electrodes’ volumetric change may cause contact failures between the solid-state electrolytes and electrodes, where this issue is more severe for large batteries but less so for miniaturized batteries.<sup>52</sup> Ultimately, let alone the safety considerations, the prospect of IL and solid-state electrolytes is gloomy for the usage in storage batteries, considering the high cost of these electrolytes. To date, most work on solid-state electrolytes has been on Li-based batteries. Yet solid-state electrolytes may be an interesting research topic for aqueous metal batteries, *e.g.*, Zn-metal batteries, given cost-effective electrolytes are identified.<sup>53</sup>

It is widely believed that aqueous batteries are the most relevant for storage purposes with the consideration predominantly on the glamour of their safety, where the “decomposed” aqueous electrolytes, mainly water vapor, are not flammable or explodable. Furthermore, it is very likely that aqueous batteries, albeit of a modest energy density, can afford the most competitive LEC.

Let’s look at the commercial aqueous batteries first. Valve-regulated lead-acid batteries (VRLA), originally invented in 1934,<sup>54</sup> is a strong competitor to the storage market as currently, most data centers employ VRLA as UPS batteries.<sup>55,56</sup> It is unclear why Ni-MH batteries have not been widely employed for energy storage. Note that Ni-MH cells were commercialized nearly simultaneously as LIBs were; nevertheless, the latter has received relentless effort for optimization, but the attention that Ni-MH batteries have secured has not been phenomenal, at least from academia. On the other hand, there exist some inherent challenges of Ni-MH batteries, *e.g.*, the use of rare-earth elements,<sup>57</sup> the relatively faster self-discharge,

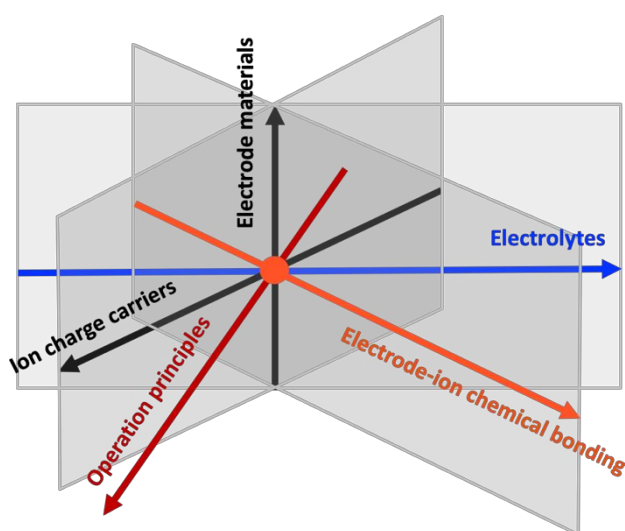
and the safety concern based on the fact that the anode of Ni-MH batteries is simply a hydrogen-storage material.<sup>58</sup>

For future aqueous batteries to be competitive, their LEC needs to be lower than Lead Acid and Ni-MH batteries. Recently, the effort has been devoted to aqueous LIBs.<sup>59–61</sup> In particular, the operation window of aqueous electrolytes has been widened using highly concentrated aqueous electrolytes, *i.e.*, water-in-salt electrolyte (WiSE).<sup>62,63</sup> However, it remains a question whether the LEC of aqueous LIBs will be competitive. For the sake of lowering the LEC, it is necessary to move beyond lithium, which will be discussed in a later section on ion charge carriers.

Nevertheless, aqueous batteries are not always innocent when examining their potential safety faults. The oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) on the sides of cathode and anode, respectively, must be suppressed because the accumulation of H<sub>2</sub> and O<sub>2</sub> may possibly cause cell damages although explosion is rare for aqueous batteries.<sup>64</sup> HER or OER also causes poor Coulombic efficiency (CE) and fast self-discharge. Aqueous electrolytes if acidic or basic can be corrosive to the electrodes and the current collectors as well, where the piecemeal dissolution of electrode active mass as a function of time causes capacity fading.<sup>65</sup>

## Five Dimensions of Storage Battery Chemistries

Batteries are the reactors that decouple redox reactions, where the reactants do not get to meet each other directly, and the 'transactions' of charge and mass transfers between the reactants are completed via the transports through two charge conduction media: the external circuit passing electrons and the internal electrolyte migrating ions, *i.e.*, mass. When looking at such redox reactions holistically, electrodes alone cannot represent the reactants or products, which also entail the ion charge carriers and sometimes the solvent molecules of electrolytes.



**Fig. 2** Five dimensions of considerations construct a new paradigm of storage battery chemistries. The permutations of the five dimensions can generate 10 research planes, where three of them are shown

here as examples. The knowledge of LIBs is built in the plane defined by Electrode materials × Electrolytes.

As shown in **Fig. 2**, the five dimensions conceptually constitute a paradigm for the design of storage battery chemistries: electrode materials, electrolytes, ion charge carriers, electrode-ion chemical bonding,<sup>66</sup> and operation principles. Any two dimensions define a unique plane of research, where there are 10 such planes. In retrospect, the development of LIBs has been on the plane set by two dimensions: electrode materials and electrolytes, where the Li<sup>+</sup> is the default choice of the ion charge carrier, the electrode-ion interactions are taken as purely ionic, and the battery is in a cation rocking-chair configuration.<sup>67,68</sup> In this article, I will not detail the discussion about electrolytes and electrodes, and the interested readers are referred to prior review articles for in-depth information on these two dimensions of different battery technologies (For example Ref.69–71). Herein, I will underscore the other three dimensions of considerations that touch on the nature of chemical reactions in batteries, where the reactants and reaction medium coexist symbiotically. Mainly, this article puts a conspicuous focus on the chemical bonding between the ion charge carriers and the electrode hosts. Of note, the four basic battery operation principles are proposed here for the first time, which is aimed to streamline the futuristic design of battery device configurations. I will detail the discussion on the anion storage electrode materials. For the last section, I will share my perspectives on some critical issues of aqueous metal batteries.

The primary objective of this article is to elicit the attention of the community on balanced and holistic considerations toward future storage batteries. The many dimensions of considerations certainly sketch an intricate space, which explains the difficulty of inventing a practically relevant storage battery technology,<sup>72</sup> but suggests vast opportunities on new battery chemistries to be explored. This article attempts to sort out this complexity in a conceptual framework, which foreshadows a roadmap to the future paradigm of storage batteries.

## Ionic Charge Carriers

### LIBs Unfolded via Electrode Materials

The history of LIB research is rich in research philosophy and methodologies. There has been over four decades of strenuous work on LIBs, where the most effort has been focused on the design and optimizing electrode materials and electrolytes with Li-ion taken as the default ion charge carrier. A suite of discoveries have brought this technology to the current stage, including that Harris studied the electrodeposition in a variety of solvents that would be employed in electrolytes of LIBs;<sup>73</sup> Whittingham discovered the topotactic intercalation of Li-ions in layered Li<sub>x</sub>TiS<sub>2</sub>;<sup>74,75</sup> Goodenough and coworkers reported that Li-ions could be reversibly removed from Li<sub>x</sub>CoO<sub>2</sub>;<sup>76</sup> Yazami and Touzain tested electrochemical lithium intercalation in graphite.<sup>77</sup> The later game-changers of LIBs were mainly the electrode materials, *i.e.*, spinel LiMn<sub>2</sub>O<sub>4</sub>,<sup>78</sup> olivine LiFePO<sub>4</sub>,<sup>79,80</sup> nickel-rich oxides,<sup>81–83</sup> Li-rich metal oxides,<sup>84,85</sup> and silicon anodes.<sup>86,87</sup>

LIBs have been evolving to attain a higher energy density for EV applications, where the technical approaches have been to widen the potential difference between anode and cathode and to increase the capacity of both electrodes. For a higher cathode's potential, compounds, such as  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$ ,<sup>88</sup>  $\text{LiCoPO}_4$ ,<sup>89</sup> have been scrutinized. To raise the cathode capacity, one strategy is to extract Li-ions more completely from the  $\text{LiMO}_2$  compounds,<sup>90</sup> and another approach is to activate the anionic redox reactivity of oxygen atoms in  $\text{Li}_2\text{MO}_3$ .<sup>85,91,92</sup> In fact, the ultimate anionic redox cathode may be  $\text{Li}_2\text{S}$ ,<sup>93,94</sup>  $\text{Li}_2\text{O}_2$ ,<sup>95</sup> and even  $\text{LiI}$ ,<sup>96</sup> where during battery charge, it is anions of these salts as redox centers that get oxidized into sulfur solid,  $\text{O}_2$  gas, and  $\text{I}_2$  solid, respectively.

A plethora of materials have been explored to increase the anode capacity, where most of them are conversion-reaction ones, including metal oxides,<sup>97,98</sup> metal sulfides,<sup>99,100</sup> alloying electrodes,<sup>101–103</sup> and organic solids.<sup>104–106</sup> However, the choice of commercial LIB anode has 'stubbornly' remained as carbon-based materials, among which graphite,<sup>77</sup> soft carbon,<sup>107</sup> hard carbon,<sup>108</sup> have all been investigated. Recently, Li metal anode (LMA) has been celebrating its 'renaissance' despite its early commercial failure in the late 1980s.<sup>109</sup> Yet the daunting challenge is to reach a CE of 99.95% so that 60% of LMA remains active after 1000 cycles. Indeed, the use of LMA is probably the only viable path to reach an energy density of 500 Wh/kg for secondary batteries.<sup>110</sup>

In hindsight, the odyssey of LIBs has been a gradation of electrode materials that are sequenced by the diminishing prospect of achieving high electrochemical performance. This list adds new members of 'mainstream' electrodes, from ionic and electronic dual conductors, *e.g.*,  $\text{LiCoO}_2$ , to electronic insulators, *e.g.*,  $\text{LiFePO}_4$ , from 2D ion-diffusion electrodes, *e.g.*,  $\text{LiTiS}_2$ , to non-2D diffusion materials, *e.g.*,  $\text{LiMn}_2\text{O}_4$ , from topotactic intercalation electrodes, *e.g.*, transition metal sulfides and oxides, to conversion/alloying-reaction electrodes, *e.g.*, silicon and sulfur, and to plating electrodes, *i.e.*, LMA.<sup>110</sup>

The progress made on LIBs has significantly extended the depth of understanding and the landscape of electrode materials and electrolytes, in particular, the structure-performance correlations. The community has learned many correlations that serve as design principles of new electrode materials later, *i.e.*, inductive effect,<sup>111</sup> nanoconfinement effect,<sup>112–114</sup> shortening diffusion pathways,<sup>115,116</sup> widening the ion diffusion channels,<sup>117,118</sup> electrode coating,<sup>119</sup> doping,<sup>120</sup> defects,<sup>121</sup> redox mediators,<sup>122</sup> solvent-in-salt electrolytes,<sup>123,124</sup> to name a few. Advanced *ex situ* and *in situ* characterization tools,<sup>125–128</sup> as well as computation studies<sup>129–131</sup> have significantly advanced the development of LIBs as well. All knowledge accumulated from the research on LIBs has provided the source of inspiration and a toolbox for the ongoing studies on storage batteries.

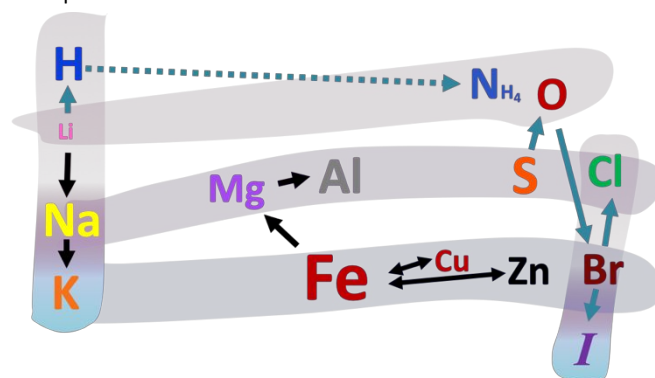
### The Diffusion of Attention on the Periodic Table

#### Metal Ion Charge Carriers

During the past decade, research on storage battery chemistries has evolved rapidly along the third dimension of considerations—ion charge carriers—additional to the electrode materials and electrolytes. Interestingly, it has been a stochastic "walk" of the battery community stepping on different elements as ion charge

carriers, as shown in **Fig. 3**. With  $\text{Li}^+$  as the starting point, attention has gone to  $\text{Na}^{+132,133}$  and recently to  $\text{K}^{+134,135}$  along the alkali metal group due to their earth abundance. Note that  $\text{Na}^+$  was seriously considered as a charge carrier nearly simultaneously with  $\text{Li}^+$  in the 1980s.<sup>136,137</sup> Phenomenal progress has been made in promoting the electrochemical properties, *e.g.*, capacity,<sup>138,139</sup> rate capability,<sup>140,141</sup> and cycling life<sup>142</sup> for Na-ion batteries (NIBs)<sup>143</sup> and K-ion batteries (KIBs).<sup>144</sup> Often, electrode materials known from the prior studies in LIBs have been employed as model materials; however, the community has been frequently surprised by the different performance revealed on the same electrode materials with charge carriers other than Li-ion.<sup>145,146</sup>  $\text{Ca}^{2+}$  was touched on as well for ion-transfer batteries;<sup>147</sup> however, reversible Ca plating has yet to be demonstrated.<sup>148</sup> Most recently, we reported that  $\text{Cu}^{2+}$  can be employed as a charge carrier for an aqueous sulfur electrode, where  $\text{Cu}^{2+}$  itself is redox active in forming  $\text{Cu}_2\text{S}$ .<sup>149</sup> To exploit the redox reactivity of charge carriers may represent a promising direction for the design of storage batteries.

For metal batteries, charge carriers are selected often because their corresponding metals are employed as anodes, where the interests have been hovering on Mg,<sup>150,151</sup> Al,<sup>152,153</sup> and Zn,<sup>154–156</sup> besides the alkali metal batteries.<sup>157</sup> Recently, Fe metal-based batteries originally invented by Edison<sup>158,159</sup> have started to attract attention again with alkaline Fe- $\text{O}_2$  batteries,<sup>160</sup> and a battery with an insertion cathode of Prussian blue analog in our recent study, for example.<sup>161</sup>



**Fig. 3** A map of ion charge carriers covered in battery research, where they are arranged resembling where they are in the periodic table, where small fonts of letters indicate their low earth abundance.

It is critical to note that the usage of divalent charge carriers does not lead to a doubled capacity of the electrodes. The capacity of an electrode is determined by the number of charges transferred, which relates to the changes of oxidation states of the redox centers within the electrodes, *e.g.*, the center elements or the redox-active ligands. This is reflected by the fact that the same electrodes often exhibit even lower capacity values when hosting multivalent ions than monovalent ions. The high charge density of multivalent ions induces strong electrostatic interactions with the hosts, thus being electrostatically "sticky", which causes irreversible structural changes of electrodes.<sup>162,163</sup>

Furthermore, the utility of metal batteries is ultimately evaluated by cycle life and the energy density, which are dictated by the

reversibility, *i.e.*, CE, of the metal anodes. CV measurements suggest the reversible behavior of Mg plating/stripping with a CE near unity.<sup>164,165</sup> It was reported that the CE of Al plating is 95% from a molten NaAlCl<sub>4</sub> electrolyte at a current density below 1 mA/cm<sup>2</sup>.<sup>166</sup> However, the more accurate CE values of Mg anode and Al anode from chronopotentiometry, *i.e.*, galvanostatic charge/discharge (GCD) tests, have yet to be reported. Recently, the measurement of average CE of Li plating/stripping has caught attention, which employs the following equation:<sup>167,168</sup>

$$CE = \frac{n * Q_c + Q_s}{n * Q_c + Q_T} \quad (2)$$

where the anode mass corresponding to  $Q_c$  is repeatedly stripped/plated for  $n$  cycles from/onto the initially plated metal anode of  $Q_T$  on the current collector that is typically several times of  $Q_c$ , and  $Q_s$  represents the remaining metal anode on the current collector that can be measured in the last complete stripping after  $n$  cycles. We employed this method to calculate the average CE of Fe anode plating/plating as 90.7% in an aqueous electrolyte of 0.5 M FeSO<sub>4</sub>.<sup>161</sup>

From the epic history of LIBs, it seems that the bottleneck of various metal batteries is the dearth of cathodically stable electrolytes. The LIB field is fortunate to have identified the alkyl carbonates for the carbonaceous anode, particularly ethylene carbonate (EC), which could decompose to “seal” the “lithium reservoirs” of graphitic anodes, thus kinetically prohibiting rapid parasitic reactions. However, for all metal batteries, the metal anodes are exposed squarely to the electrolytes, where to find the electrolytes that facilitate reversible plating/stripping is a top priority of metal batteries. Some exciting progress has been made with new electrolytes.<sup>169,170</sup>

#### Nonmetal Ion Charge Carriers

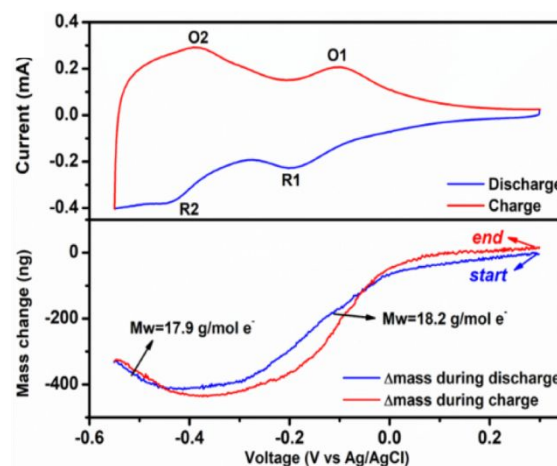
To date, most battery chemistries use metal-ion charge carriers, and non-metal cations have received little attention. Recently, renewed efforts have been devoted to hydrogen-containing cations, including H<sup>+</sup> and NH<sub>4</sub><sup>+</sup>. The usage of protons as charge carriers should be dated back to 1859 when Planté invented lead-acid batteries. The discharge of lead-acid batteries, indeed, uses protons to convert PbO<sub>2</sub> to PbSO<sub>4</sub> in a “conversion” reaction. In Ni-MH batteries and in the graphite hydrogen-insertion electrodes, where alkaline electrolytes are employed, it should be stressed that it is not protons but hydride ions (H<sup>-</sup>) that serve as the charge carrier in the hydride anodes.<sup>171,172</sup> On the other hand, interestingly, as for the NiOOH cathode of Ni-MH batteries, it does take in protons to form Ni(OH)<sub>2</sub> during battery discharge.<sup>173,174</sup>

Proton is the lightest and smallest ion charge carrier one can possibly find for batteries, where its measured radius is ~0.89 fm or ~2.1 fm, using muon or e<sup>-</sup> spectroscopy, respectively.<sup>175</sup> It is often expected that hosting protons in electrodes would cause the negligible strain of the electrodes, where the longevity of proton batteries would be superior to that of existing batteries. Plus, the rate capability of proton batteries that transport tiny protons should be superlative. Indeed, proton facilitates the operation of some aqueous pseudocapacitors. In 1971, Trasatti and Buzzanca reported the pseudocapacitive behavior of RuO<sub>2</sub> in an acidic electrolyte.<sup>176</sup> The reaction mechanism has been described as RuO<sub>2</sub> + δH<sup>+</sup> + δe<sup>-</sup> ↔ RuO<sub>2</sub>δ(OH)<sub>δ</sub>. In 1976, Schöllhorn and Besenhard investigated proton

insertion to form H<sub>0.5</sub>MnO<sub>3</sub>.<sup>177</sup> Recently, similar electrochemical proton incorporation has been reported for other metal oxides, including TiO<sub>2</sub>,<sup>178</sup> MnO<sub>2</sub>,<sup>179</sup> WO<sub>3</sub>,<sup>180</sup> MoO<sub>3</sub>,<sup>181</sup> and MXene.<sup>182</sup>

The high-rate proton-storage behavior was later attributed to the crystal water molecules in electrodes. In 1995, Zheng *et al.* observed that hydrous RuO<sub>2</sub> exhibits enhanced pseudocapacitive properties than its non-hydrous counterpart.<sup>183</sup> As another example, it is well known that WO<sub>3</sub> hydrate shows faster electrochromic performance than its non-hydrous version.<sup>184</sup> Unfortunately, these electrode materials are not suitable platforms to demonstrate the power of the Grotthuss mechanism due to a lack of the percolating hydrogen-bonding network inside the electrodes.

In aqueous electrolytes, protons combine with water molecules, forming hydroniums; therefore, hydronium has been considered as a battery charge carrier, *e.g.*, for organic molecular solid electrodes.<sup>185</sup> H<sub>3</sub>O<sup>+</sup> as a charge carrier is of a medium ionic size, 100 ± 10 pm, which is very close to that of Na<sup>+</sup>, 102 pm, with the coordination number (CN) six.<sup>186</sup> However, it is often a question whether proton or hydronium serves as the charge carrier within electrodes. To address this question, my group employed an electrochemical quartz crystal microbalance (EQCM) to quantify the mass changes of an electrode material of WO<sub>3</sub>·0.89H<sub>2</sub>O in an acidic electrolyte.<sup>187</sup> As Fig. 4 shows, during the initial cathodic process, the electrode surrenders mass at the rate of 18 g/mole of e<sup>-</sup>, which indicates water molecules are squeezed out of the electrode's structure. At the deep DOD, there is mass gain at a rate of 18 g/mole of e<sup>-</sup>, where at this time, hydroniums are inserted back. Interestingly, lattice water molecules may transport in the opposite or the same direction compared to proton as a charge carrier, and thus lattice water molecules in electrodes are not spectators in electrochemical processes using an aqueous electrolyte. However, in nonaqueous electrolytes, ‘free’ protons may serve as the charge carrier. Sjödin and coworkers reported an all-organic proton battery, where the poly(3,4-ethylenedioxythiophene) (PEDOT)-based electrodes operate on quinone/hydroquinone redox reactions.<sup>188</sup>



**Fig. 4** CV curves of the WO<sub>3</sub>·0.89H<sub>2</sub>O electrode at a scan rate of 3 mV/s (top) and the *in situ* EQCM results of WO<sub>3</sub>·0.89H<sub>2</sub>O (bottom). Blue: cathodic scan; red: anodic scan.<sup>187</sup> Reproduced with permission of ref. 187. Copyright 2018 American Chemical Society.

Topotactic insertion of  $\text{NH}_4^+$  into a solid electrode, *i.e.*,  $\text{TaS}_2$ , was reported by Whittingham in 1974.<sup>189</sup> Recently, Huggins and Cui studied the reversible storage of  $\text{NH}_4^+$  in Prussian blue analogs.<sup>190</sup> Gogotsi and coworkers reported the electrochemical properties of a MXene electrode with  $\text{NH}_4^+$  as the charge carrier.<sup>191</sup> We first reported a full cell design of an  $\text{NH}_4$ -ion battery.<sup>192</sup> We studied the remarkable fit of  $\text{NH}_4^+$  as a charge carrier for Prussian blue analog electrodes in terms of long cycle life.<sup>193</sup> Indeed,  $\text{NH}_4^+$  with an ionic radius of 1.48 Å (CN=6), larger than  $\text{K}^+$ ,  $\text{Na}^+$ , and Li, matches the voids of Prussian blue analogs better, and the inserted  $\text{NH}_4^+$  is not hydrated. Furthermore,  $\text{NH}_4^+$  is a molecular ion, which may form covalent-ionic bonding with its electrode hosts. This will be highlighted in a later section of electrode-ion chemical bonding.

Anions are no newcomers for their function of compensating for the charge neutrality in electrochemical reactions. For Li-S batteries that cannot detain polysulfide ions in the cathode, the polysulfide ions,  $\text{S}_x^{2-}$  ( $3 < x < 8$ ), essentially serve as the redox-active charge carriers.<sup>194</sup>  $\text{Br}^-$  and  $\text{I}^-$  ions are widely employed in flow batteries<sup>195</sup> and redox-mediated supercapacitors,<sup>196</sup> respectively. Most recently, "atomic plating" of both Br and Cl inside the galleries of graphite from LiBr and LiCl mixed with graphite as solid has been realized in the environment of WiSE.<sup>197</sup> I will expand the discussion related to anion hosting in the section of battery operation principles.

By an odyssey from Li-ion to all these different ion charge carriers, the community may have gained the impression that it is not the electrode materials alone that decides the electrochemical properties of electrodes but the coupling of electrodes and the charge carriers that collectively shape the electrochemical behavior of the electrode systems.

## Electrode-Ion Chemical Bonding

### Varying Strengths of Chemical Bonding

Based on examples of different battery systems, the fourth dimension of storage battery design has surfaced: the chemical bonding between the electrode materials and the ion charge carriers. On the one hand, the formation or breaking of the electrode-ion chemical bonding drives the changes of Gibbs free energy of a battery system and the associated cell voltage. On the other hand, such chemical bonding may profoundly affect the kinetic behaviors of electrodes as well.<sup>198</sup>

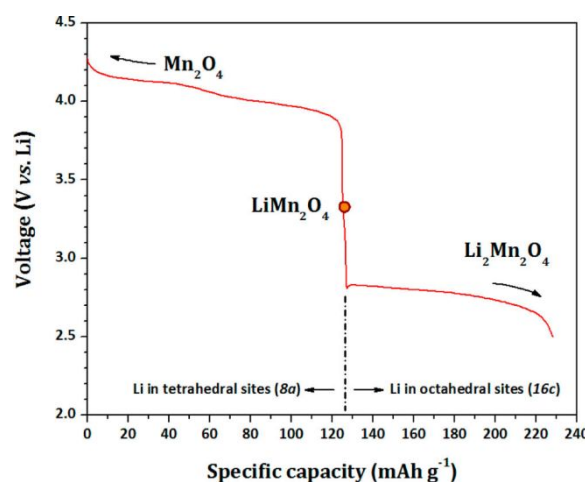
As for thermodynamics, let's look at carbon anode first. In electrochemical cells, Li- or K-ions can be reversibly inserted into graphite anode to form binary Li- or K-graphite intercalation compounds (GICs),<sup>199,200</sup> whereas binary Na-GICs do not even exist. Yet switching the electrode from graphite to hard carbon<sup>201</sup> or soft carbon,<sup>202</sup> a good capacity above 200 mAh/g can be readily obtained for Na-ion storage. What is different between graphite and these nongraphitic carbons? We conducted neutron total scattering and the associated pair distribution function (PDF)<sup>203</sup> studies on hard carbon and soft carbon, where the results suggested that there exist a great number of defects in these nongraphitic carbons.<sup>204,205</sup> Greaney and coworkers computed the binding energies between Na atoms and the representative defect sites, which theoretically suggests that the defect sites bind Na atoms more strongly than basal graphene sites, thus being favorable to contribute capacity for Na

storage.<sup>206</sup> Such defective sites may include point defects, *e.g.*, monovacancy, divacancy, and Stone-Wales defects; edges, *i.e.*, zigzag and armchair sites; even graphene sites with curvatures. Greaney and coworkers reported the following equation to calculate the formation energy of Na-C binary compounds:<sup>207</sup>

$$\Delta H = \frac{E_{\text{Na}_x + \text{C}_N} - (xE_{\text{NaBCC}} + E_{\text{C}_N})}{x} \quad (3)$$

where  $N$  is the number of carbon atoms in the system,  $x$  is the number of sodium atoms incorporated,  $E_{\text{Na}_x + \text{C}_N}$  denotes the energy of the Na-C system,  $E_{\text{C}_N}$  is about the energy of the carbon structure, and  $E_{\text{NaBCC}}$  refers to the cohesive energy for each atom on Na metal surface. A positive  $\Delta H$  from Equation (3) would suggest sodium plating on the carbon surface instead of Na insertion into carbon; conversely, if  $\Delta H$  is negative, Na can be inserted into the carbon electrode. In Equation (3), the entropy changes and the overpotentials are not considered. It is evident that weak Na-C interactions with a small  $E_{\text{Na}_x + \text{C}_N}$  would fail the formation of Na-C compounds. Goddard III and coworkers compared the calculated binding energies of different alkali metals with graphene and found that the binding energy is the weakest for Na, akin to that of Mg.<sup>208</sup>

Another example is a cathode material of LIBs, spinel  $\text{Li}_x\text{Mn}_2\text{O}_4$ . During the electrochemical extraction of Li-ions from  $\text{Li}_2\text{Mn}_2\text{O}_4$ , the potential of the M(IV)/M(III) couple would abruptly rise by over 1 V when  $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$  ( $1 > x > 0$ ) transitions to  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $1 > x > 0$ ), as shown in Fig. 5.<sup>209</sup> Interestingly, at this transition the remaining Li-ions in  $\text{LiMn}_2\text{O}_4$  would move from the roomy octahedral sites to the cramped tetrahedral sites. The higher operation potential certainly relates to enhanced ionic bonding due to the much closer Li-O proximity in the tetrahedral sites. Cairns and coworkers suggested the existence of partial Li-O-Mn covalency based on their  $^7\text{Li}$  NMR measurements, which provides an alternative perspective to understand the high operation potential.<sup>210</sup>

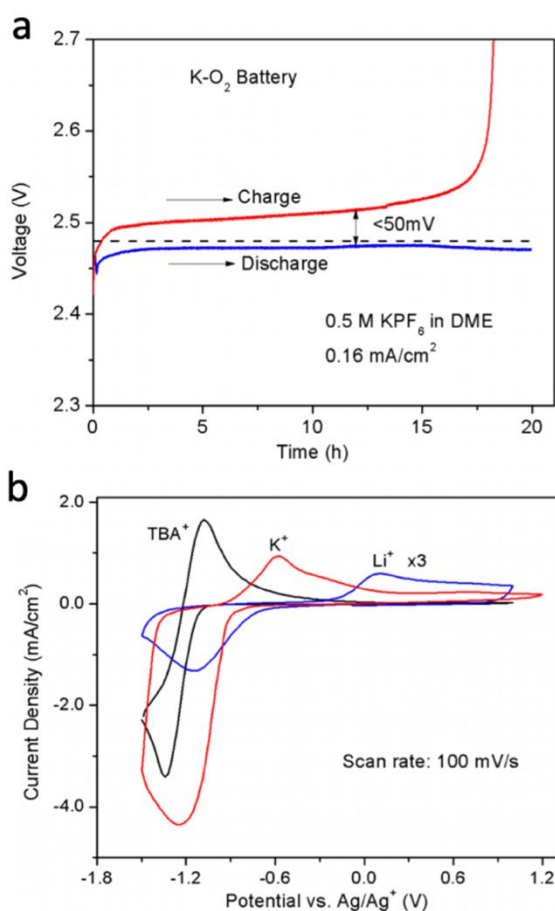


**Fig. 5** The voltage curve for  $\text{Li}^+$  insertion and extraction of  $\text{Li}_x\text{Mn}_2\text{O}_4$ .<sup>209</sup> Reproduced with permission of ref. 209 Copyright 2013 American Chemical Society.

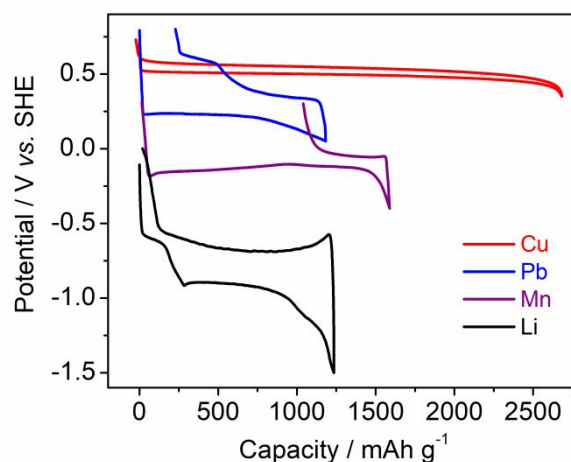
Pearson's Hard and Soft Acids and Bases (HSAB) theory<sup>211</sup> could shed light on the empirical trends observed for molecular battery electrodes, gaseous or solid. One example of the gaseous electrodes is the  $\text{O}_2$  electrode in  $\text{K-O}_2$  batteries, firstly reported by Wu and coworkers,<sup>212</sup> where the discharge product of  $\text{O}_2$  is potassium superoxide,  $\text{KO}_2$ , unlike the peroxide discharge products of  $\text{Na}_2\text{O}_2$



and  $\text{Li}_2\text{O}_2$  in  $\text{Na-O}_2$ <sup>213</sup> and  $\text{Li-O}_2$  batteries,<sup>214,215</sup> respectively. This may be explained by the HSAB theory, where the “softer”  $\text{K}^+$  prefers to bind “soft”  $\text{O}_2^-$  to form  $\text{K-O}_2$ , whereas the harder  $\text{Li}^+$  or  $\text{Na}^+$  favors to interact with the harder peroxide  $\text{O}_2^{2-}$ , resulting in the formation of  $\text{Li}_2\text{O}_2$  or  $\text{Na}_2\text{O}_2$ . Interestingly, by forming metal superoxide, the polarization of the GCD profiles of  $\text{K-O}_2$  cells is very small (Fig. 6a), much less than that of the  $\text{Na-O}_2$  and  $\text{Li-O}_2$  batteries. Wu and coworkers further reported that the overpotential for the reversible formation of superoxide with a bulky alkyl ammonium cation, tetrabutylammonium ( $\text{TBA}^+$ ),  $\text{TBA-O}_2$ , is even smaller than that of  $\text{K-O}_2$ , where  $\text{TBA}^+$  happens to be softer than  $\text{K}^+$  (Fig. 6b). The trend begs the question of whether the decreased overpotential correlates to the increased softness of the cations and the increased covalency between the binding constituents of the resulting compounds, which may elicit further studies.



**Fig. 6 a.** GCD potential profiles of the first discharge–charge cycle of a  $\text{K-O}_2$  battery in an electrolyte of 0.5 M  $\text{KPF}_6$  in 1,2-dimethoxyethane. The  $\text{K}$  metal electrode was replaced by a fresh one after the first discharge process. **b.** CV curves for oxygen reduction and oxidation on a glassy carbon electrode in oxygen-saturated acetonitrile containing 0.1 M  $\text{TBAPF}_6$ ,  $\text{LiClO}_4$ , or  $\text{KPF}_6$  (three-electrode cell setup). Current density for the  $\text{LiClO}_4$  electrolyte was enlarged three times for clarity. A good reversibility of the  $\text{O}_2/\text{O}_2^-$  couple can be observed with tetrabutylammonium cation ( $\text{TBA}^+$ ) due to its large size and thus low charge density.<sup>212</sup> Reproduced with permission of ref. 212 Copyright 2013 American Chemical Society.



**Fig. 7** The GCD profiles of sulfur electrodes with  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Li}^+$  as charge carriers.<sup>149</sup> Reproduced with permission of ref. 149 Copyright 2019 Wiley.

The impacts of the HSAB theory on molecular electrodes were recently exemplified in our studies by the solid sulfur electrode that operates with  $\text{Cu}^{2+}$  as the charge carrier in an aqueous electrolyte.<sup>149</sup> Fig. 7 shows the GCD profiles of sulfur electrodes using  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Li}^+$  as charge carriers. The  $\text{Cu-S}$  electrode system exhibits the highest potential, greater than  $\text{Li}_2\text{S}$  by 1.3 V. The strong binding between the soft Lewis acids of  $\text{Cu}^{2+}/\text{Cu}^+$  and a soft Lewis base of  $\text{S}^{2-}$  avails the formation of  $\text{CuS}$  and  $\text{Cu}_2\text{S}$  as the intermediate and the final discharge products, respectively. The  $\text{Cu-S}$  system demonstrates a record-high capacity of 3044  $\text{mAh/g}$  or 609  $\text{mAh/g}$  based on the mass of sulfur or  $\text{Cu}_2\text{S}$ , respectively, where  $\text{Cu}^{2+}$  serves as the redox center as well. Intriguingly, the extent of polarization for the  $\text{Cu-S}$  electrode, *i.e.*, at 0.05 V, is only  $\sim 10\%$  that of the  $\text{Li-S}$  electrodes. A similar question here is whether the smaller extent of polarization relates to the higher covalency between  $\text{Cu}^{2+}/\text{Cu}^+$  and  $\text{S}^{2-}$  than that between  $\text{Li}^+$  and  $\text{S}^{2-}$ .

As a remote example of the HSAB theory, the soft-soft acid-base interaction also promotes the reversibility of a redox-mediated electrochemical capacitor, where its cathode operation is based on the oxidation of  $\text{Br}^-$  to  $\text{Br}_3^-$ . However,  $\text{Br}_3^-$  diffuses to the anode side, thus causing rapid self-discharge. Stucky and coworkers addressed this challenge by precipitating  $\text{Br}_3^-$  inside the nanopores of an activated carbon electrode by using a soft cation of  $\text{TBA}^+$  as a complexing agent.<sup>216</sup> The resulting  $\text{TBABr}_3$  infiltrated in the activated carbon seems insoluble in the aqueous electrolyte, which solves the self-discharge problem, and an ion-exchange-membrane separator is not necessary.

### Covalent-Ionic Pseudocapacitance

Kinetics of chemical reactions is an intricate subject. By recognizing the chemical-reaction nature of Faradaic processes in batteries, it appears that to understand pseudocapacitance may entail a picture larger than just the electrodes or solely the ion charge carriers. Thus, it may be efficacious to look for the correlations between the electrode-ion interactions and the rate behavior of batteries or pseudocapacitors. Unfortunately, the understanding along this line

is rudimentary, which, however, shows the marked opportunities to design fast Faradaic processes for future energy storage.

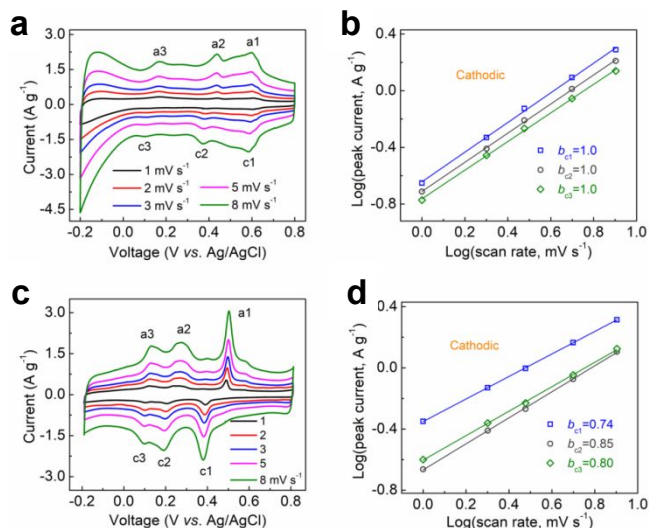
First, let's briefly summarize the evolving models of pseudocapacitance that have been built upon the properties of electrodes. Pseudocapacitance was originally defined for surface/near-surface storage of ion charges, where these charges, unlike those in electrical double layer capacitors (EDLCs), migrate across the EDL and continue to move through the near-surface regions of the Faradaic electrodes.<sup>217–219</sup> From early observations of pseudocapacitance, the ratio of the change of charge acceptance/loss,  $\Delta q$ , and the change of the electrode potential,  $\Delta V$ , is largely constant, where  $\Delta q/\Delta V$  coincides the definition of the capacitance of EDLCs. Therefore, in the early literature of pseudocapacitance, the rectangular shape of CV curves or the linear sloping GCD profiles were considered the prominent features of pseudocapacitance,<sup>220</sup> and even to date, linear GCD profiles are often deemed as pseudocapacitive performance.

Later, the definition of pseudocapacitance evolved to reflect the diffusion-related behavior that is either "capacitive" (also known as non-diffusion controlled or activation controlled) or diffusion controlled. A well-known equation of  $i = av^b$  can be used to describe the extent by which the Faradaic reaction is diffusion controlled, where  $i$  is the current of CV tests,  $a$  is a coefficient,  $v$  is the potential scan rate of the CV tests, and the exponent,  $b$ , is 0.5 or 1.0 if the reaction is completely diffusion controlled or fully capacitive, respectively.<sup>221,222</sup>

If pseudocapacitance were an exclusively surface phenomenon, the capacitance would be a function of the specific surface area of the electrode materials. Over a decade ago, Dunn and coworkers began to report pseudocapacitive behavior of metal oxide electrodes with relatively low surface areas.<sup>222,223</sup> The majority of the stored ions in these electrodes must be well beneath the surface of the electrode particles, and these materials exhibit high  $b$  values close to 1.0, a strong characteristic of non-diffusion-controlled behavior. Through a series of seminal reports, Dunn and coworkers formulated a new model of pseudocapacitance that encompasses intercalation pseudocapacitance, where pseudocapacitance no longer has to be a surface phenomenon.<sup>224,225</sup>

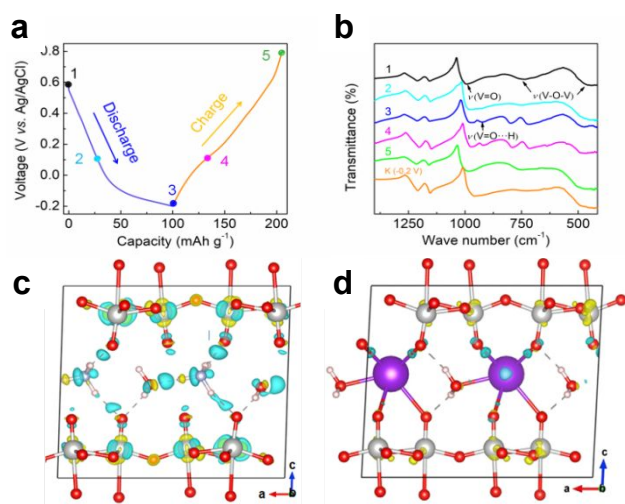
Until recently, the correlations of pseudocapacitance have been attributed to the properties of electrode materials, where limited attention had been paid to the identities of ion charge carriers because Li-ion was often taken as the default charge carrier like in LIB studies. Our recent study attempted to change this situation.<sup>226</sup> We compared the  $\text{NH}_4^+$ - and  $\text{K}^+$ -hosting behaviors of a bilayered  $\text{V}_2\text{O}_5$  electrode. Their storage mechanisms in the  $\text{V}_2\text{O}_5$  structure are via intercalation based on the relatively low specific surface area of  $\text{V}_2\text{O}_5$ , *i.e.*,  $37 \text{ m}^2/\text{g}$  and the fact that the lattice of  $\text{V}_2\text{O}_5$  uniformly shrinks or expands upon ion insertion and deinsertion, respectively. Despite using the same electrode, the same concentration of the electrolyte, and the same anion of the salt, there exist interesting disparities between hosting  $\text{NH}_4^+$  and  $\text{K}^+$ . Firstly,  $\text{V}_2\text{O}_5$  electrode exhibits a much larger capacity of  $\text{NH}_4^+$  storage,  $100 \text{ mAh/g}$ , than that of  $\text{K}^+$ ,  $60 \text{ mAh/g}$ . Secondly, the hosting of  $\text{NH}_4^+$  gives rise to much faster rate performance than that of  $\text{K}^+$ . For  $\text{NH}_4^+$ , the pairs of cathodic peaks and anodic peaks are nearly vertically aligned with small overpotentials (Fig. 8a), where this scenario was defined by B. E. Conway as "kinetic reversibility", which occurs when the potential

scan rate,  $v$ , is slower than the reaction rate constant,  $k_0$ .<sup>12,227</sup> In stark contrast, the peaks of redox pairs for the  $\text{K}^+$  storage, particularly the most right pair, are well separated with wide gaps and overpotentials (Fig. 8c), a characteristic of kinetic irreversibility. Note that there are two known scenarios for kinetic reversibility: (1) Chemisorption of redox species on electrodes,<sup>227</sup> (2) Extremely thin-film electrodes.<sup>228</sup> Additionally, the  $b$  values of  $i = av^b$  for  $\text{NH}_4^+$  storage is unity for different peaks, whereas it is about 0.8 for  $\text{K}^+$  (Fig. 8b,d)



**Fig. 8** a. c. CV curves from 1 to  $8 \text{ mV s}^{-1}$  for  $\text{NH}_4^+$  and  $\text{K}^+$  storage, respectively. b. d. The  $b$  values from the logarithm of the cathodic peak current vs. the logarithm of scan rate.<sup>219</sup> Reproduced with permission of ref. 219 Copyright 2019 Elsevier.

The model of intercalation pseudocapacitance could not explain well the different kinetic behaviors between  $\text{K}^+$  and  $\text{NH}_4^+$  as charge carriers. We tentatively attribute such difference to their different flavors of electrode-ion chemical bonding. *Ex situ* Fourier-transform infrared (FTIR) spectroscopic results reveal that the bonding between the inserted  $\text{NH}_4^+$  and  $\text{V}_2\text{O}_5$  causes the split of V-O vibration peaks, attributing to some covalency, juxtaposed to no splitting for  $\text{K}^+$  (Fig. 9a,b). DFT calculations suggest a charge transfer (CT) of  $0.17 e^-$  from  $\text{V}_2\text{O}_5$  to every inserted  $\text{NH}_4^+$ . The charge density isosurfaces of the  $\text{NH}_4^+\text{-V}_2\text{O}_5$  depict delocalized charge distribution in sharp contrast to the localized ionic picture of the  $\text{K}^+$  case (Fig. 9c,d). I posit that the difference relates to the fact that  $\text{NH}_4^+$  as a molecular ion with  $\sigma^*$  orbitals is a better electron acceptor than  $\text{K}^+$  in forming a donor-acceptor bond or a covalent-ionic bonding.<sup>229,230</sup> The interaction between  $\text{NH}_4^+$  and bilayered  $\text{V}_2\text{O}_5$  can be essentially viewed as chemisorption taking place inside the lattice of the electrode. I dub this type of pseudocapacitance as chemisorption-involved insertion pseudocapacitance, or covalent-ionic pseudocapacitance, or CI pseudocapacitance.



**Fig. 9** a. The first GCD profiles of VO300 in the  $(\text{NH}_4)_2\text{SO}_4$  electrolyte. b. *Ex situ* FTIR spectra at selected SOC. The bottom spectrum was collected after potassiation to  $-0.2$  V vs. Ag/AgCl. c.d. Plots of charge density difference resulting from the host/guest interaction. From the reduced  $\text{V}_2\text{O}_5$  electrode in panel (c), a small amount of charge is transferred from V (the yellow lobes on the Vanadium) through the bonded O=V bond, accumulating charges in a  $\text{H}\cdots\text{O}=\text{V}$  bond (blue cloud). Panel (d) shows the lack of CT for the insertion of potassium atoms (purple). The charge density isosurfaces are  $\pm 0.005$   $e/\text{\AA}^3$  with blue surfaces for bounding electron-accumulated regions and yellow surfaces for regions of electron depletion.<sup>226</sup> Reproduced with permission of ref 226 Copyright 2019 Elsevier.

Furthermore, the ion transport of molecular ions inside electrode may be very different from that of metal ions, where metal ions would slide or hop inside the lattices of electrodes for transporting, whereas  $\text{NH}_4^+$  may swing or rotate to transport as in a “monkey-bar-walking” fashion, oriented by the formation of the hydrogen bond between individual hydrogen atoms of  $\text{NH}_4^+$  with oxo-oxygens of the  $\text{V}_2\text{O}_5$  lattice.

Molecular ions as charge carriers represent a fascinating underexplored area, where the values in such studies will not only share new understandings for the battery design but serve as powerful reactors to prepare new compounds that cannot be fabricated otherwise. Our recent study on the reversible insertion of methyl viologen ( $\text{MV}^{2+}$ ) into a molecular solid of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) demonstrates the impacts of nuances from the electrode-ion chemical bonding on the electrode structures and the fast electrochemical reactions.<sup>231</sup> This study serves as an example to solicit systems of supramolecular chemistry<sup>232</sup> for energy storage, and also highlights an electrochemical approach to prepare new supramolecular structures.

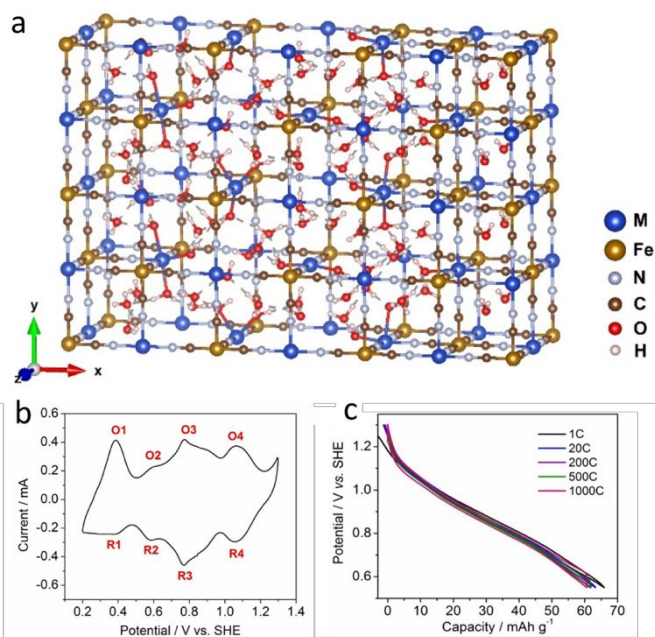
### Grotthuss Pseudocapacitance

In 1806, *von* Grotthuss posited that electrical conduction in water is via “succession of decomposition and recombination of the elements of water”, where water is “decomposed and recomposed at once”.<sup>233,234</sup> Recent theoretical studies further revealed that proton

conduction is a structural diffusion event through the breaking and forming, in concert, of the O-H covalent bond and  $\text{H}^+\cdots\text{OH}_2$  hydrogen bond *via*  $\text{H}_5\text{O}_2^+$ , the Zundel ion.<sup>235–237</sup> Namely, when a proton approaches one end of the water chain, with the Domino-falling-like bond vibrations taking place instantaneously, the other end of the water chain kicks out a proton to complete the proton conduction.

However, it is critical to note that the prerequisite of the Grotthuss mechanism is the ion-molecule chemical bonding that is much stronger than the *van der Waals* forces, and the conventional ion-dipole interactions, where such ion-molecule bonding may include hydrogen bond (HB)<sup>238</sup>, *e.g.*,  $\text{H}^+\cdots\text{OH}_2$ , Li-bond,<sup>239</sup> and bonds with  $\sigma$  holes, *e.g.*, halogen bond (XB).<sup>240–242</sup> Compared to H-bond, Li-bond is more ionic with a smaller extent of CT.<sup>243,244</sup>

The Grotthuss conduction differs from the vehicle-like transport, *i.e.*, the molecular diffusion, where with the vehicular fashion an ion “escorted” by a solvation shell moves by pushing through other solvent molecules, thus engaging significant energy barriers. Understandably, the diffusion-free Grotthuss conduction is faster than the vehicular conduction, which explains the higher conductivity of HCl solution than that of NaCl with the same solute concentration.



**Fig. 10** a. DFT calculations of the water orientations in a  $3\times 1\times 1$  super cell of CuFe-TBA. b. CV curve of the CuFe-TBA electrode for (de)insertion of proton, c. GCD profiles of CuFe-TBA at 1, 20, 200, 500 and 1000 C rate ( $1\text{C} = 65$   $\text{mA g}^{-1}$ )<sup>245</sup> Reproduced with permission of ref. 245 Copyright 2019 Springer Nature.

In order to employ the Grotthuss proton conduction in battery electrodes, it is critical to have water ‘canals’ built inside the electrode structures so as to generate a percolating H-bonding network. Unfortunately, most prior studies fall short of facilitating this percolating hydrogen bonding network. Recently, our collaborative research reported an example of the Grotthuss proton storage in a defective and hydrated Prussian blue analog—Turnbull’s blue,  $\text{Cu}[\text{Fe}(\text{CN})_6]_{0.63}\cdot 0.37\cdot 3.4\text{H}_2\text{O}$  (CuFe-TBA), as the electrode.<sup>245</sup>

Structural characterization and density functional theory (DFT) calculations collectively suggest the percolation of a hydrogen-bonding network inside the electrode structure (Fig. 10a). Interestingly the CuFe-TBA electrode also exhibits the fast kinetic reversibility, revealed by its CV curves displaying vertically aligned redox peaks (Fig. 10b). Furthermore, with an active mass loading of  $1.5 \text{ mg cm}^{-2}$ , upon increasing the current rate from 1 C to 1000 C, the GCD profiles are nearly identical without obvious overpotentials (Fig. 10c). These results unequivocally demonstrate the power of Grotthuss conduction in promoting the rate capability of Faradaic reactions. The Grotthuss proton storage is a unique Faradaic process, where it is distinct from the intercalation pseudocapacitance or the surface EDLC. Here, I tentatively name it as Grotthuss pseudocapacitance.

### Conjecture of the Correlation between Covalent-Ionic Bonding and Pseudocapacitance

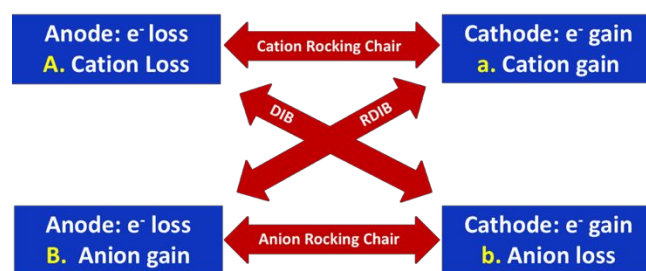
From the above examples of capacitive  $\text{NH}_4^+$  storage and proton Grotthuss pseudocapacitance plus the electrode systems of TBA- $\text{O}_2$ ,  $\text{K-O}_2$ , and Cu-S, I posit that covalent-ionic bonding between the charge-compensating ion and the electrode is one root cause of capacitive or non-diffusion-controlled kinetic behavior of Faradaic electrodes, *i.e.*, the pseudocapacitance. Such covalent-ionic bonding of the Lewis donor-acceptor characteristic may take place on the surface of electrode materials, known as chemisorption, or in the lattice of a crystalline or amorphous material. However, the boundaries of bonding strengths for this correlation to be valid are unclear. For example, if a completely covalent bonding were formed between the electrode structure and the inserted ion, the rate capability must be poor as the ions could not move at all. Thus, it is postulated that there exists an extent of covalency or a value of CT that corresponds to the maximum kinetic behavior, and this CT value may vary depending on the unique properties of electrodes and ions.

### Additional Opportunities Related to Chemical Bonding in Batteries

Note that the electrode-ion interactions should include the interplays between the lattice solvent *e.g.*, lattice water, in the electrode structure and the inserted ions, where such interactions are often described as shielding of ions.<sup>155,246</sup> Besides the electrode-ion interplays, the inserted ions may interact among themselves. It is expected that the inserted ions would only repulse each other. However, when there is CT from the electrode to ions, the inserted ions may form covalent or metallic bonds between themselves.<sup>247</sup> In the recent work by Wang and coworkers, the ratio of intercalants over carbon atoms in  $\text{C}_{3.5}[\text{Br}_{0.5}\text{Cl}_{0.5}]$ , a Stage-I GIC, is unprecedented. This coincides with the near-neutral oxidation states of  $\text{Br}^{0.05}$  and  $\text{Cl}^{0.25}$  due to the near-unity CT, and the deduced conclusion that these ions not only exert little repulsion between each other within the graphite host but form covalent bonds to form molecules or even polymers.<sup>197</sup> Besides the electrode-ion interactions and ion-ion interactions, the interplays between the lattice water molecules themselves can be instrumental. The Grotthuss proton conduction in the water-rich Turnbull's blue electrode is an exceptional example, which shows the values of the percolating hydrogen bonding network inside the electrode to the high rate capability.<sup>245</sup>

One important implication of CT to ion charge carriers is that the inserted ions themselves serve as redox centers, thus being an extra venue for electronic charge storage. The higher  $\text{NH}_4^+$  storage capacity than  $\text{K}^+$  in the bilayered  $\text{V}_2\text{O}_5$  electrode seems aligned with this implication. The Cu-S electrode system highlighted earlier also showcases the benefits of such redox-active ion charge carriers (RIC).<sup>149</sup>

### Four Basic Operation Principles of Batteries



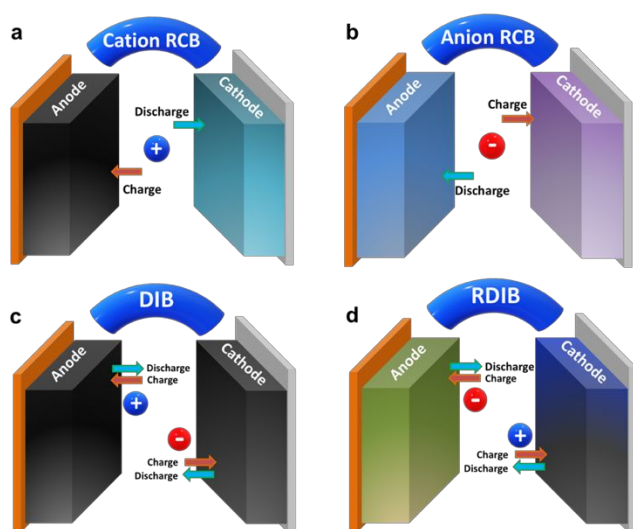
**Fig. 11** Schematic shows how four fundamental principles of battery operation are constructed. **A** pairs with **a** to form a Cation RCB; **B** couples with **b** to build an Anion RCB; **A** pairs with **b**, which leads to a DIB; **B** couples with **a** to be an RDIB.

One basic rule of Faradaic electrochemical reactions, spontaneous or not, is that the products of electrochemical reactions are charge neutral. The exception is on the surface of electrode particles, where the charges are responsible for the energy difference between the chemical potential,  $\mu$ , and electrochemical potential,  $\bar{\mu}$ , of the electrode surface. The charge-neutrality rule requires both anode and cathode of a battery stay neutral over cycling upon losing or gaining electrons in redox reactions. Therefore, when electrons migrate from anode to cathode or *vice versa*, the concomitant ion migration in the electrolyte must compensate for the charge neutrality of electrodes no matter whether cations or anions or both are matriculated as charge carriers.

Let me use a discharge process to illustrate the construction of the four battery operation principles that are derived from the charge-neutrality rule. As for the anode that surrenders electrons, there are two scenarios to stay neutral: **(A)** The anode evicts cations of the same quantity of charges into the electrolyte, and **(B)** The anode incorporates electrolyte-born anions. Regarding the cathode that gains electrons, similarly, the two routes are: **(a)** The cathode harvests electrolyte-born cations, and **(b)** The cathode expels anions into the electrolyte.

The permutations of **A**, **B** coupling with **a**, **b** lead to four basic battery operation principles, as shown by the linking double-headed arrows in Fig. 11. The **(A, a)** batteries, *e.g.*, LIBs, NIBs, and KIBs, are cation rocking-chair batteries (RCB) or, with more pictorial precision, "pendulum" batteries, where during cycling, cation charge carriers commute between the anode and cathode (Fig. 12a).<sup>248</sup> More precisely, during discharge of a cation RCB, anode releases cations into the anode side of the electrolyte, and cathode takes in cations from the cathode side of the electrolyte simultaneously. To be more inclusive, when metals are employed as the anode, I consider such metal batteries as cation RCBs, *e.g.*, Li batteries,<sup>249</sup> Na batteries,<sup>250</sup>

Mg batteries,<sup>251</sup> Zn batteries,<sup>154,252</sup> and Fe batteries.<sup>161</sup> Nevertheless, the ionic charge carrier in an RCB is not necessarily a cation, where the commuting ion can be an anion in the **(B, b)** RCB. Studies of **(B, b)** anion RCBs can be dated to 1970s,<sup>253</sup> and this area recently has garnered renewed interests **(Fig. 12b)**.<sup>254,255</sup> Note that during operation of any RCBs, cation- or anion-based, the salt concentration in the electrolyte stays constant; therefore, in these batteries, the usage of electrolytes can be minimized and the separator can be made ultra-thin.



**Fig. 12** Schematics of four types of battery configurations. **a.** Cation RCB, **b.** Anion RCB, **c.** DIB, and **d.** RDIB.<sup>256</sup>

When **A, B** and **a, b** are cross-linked, as depicted in **Figure 11**, the **(A, b)** and **(B, a)** batteries employ both cation and anion as charge carriers during operation. The **(A, b)** battery is known as DIB, where its charge process “feeds” the anode and the cathode with cations and anions, respectively **(Fig. 12c)**.<sup>257</sup> Note that EDLCs operate exactly in the same fashion as DIB does. In the **(B, a)** batteries, the assignments of charge carrier for the electrodes are the opposite— anions for the anode and cations for the cathode, which was, thus, named as reverse dual-ion batteries (RDIB) in our recent report **(Fig. 12d)**.<sup>256</sup> The migration paths of cations and anions in DIBs and RDIBs resemble a playing accordion, where during operation, the anions and cations are either simultaneously dumped into the electrolyte or concurrently matriculated by the electrodes. Of note, when DIBs (and RDIB) operate, the electrolyte is initially the sole source of ionic charge carriers, thus making the electrolyte a part of battery’s active mass.<sup>258</sup> Therefore, the electrolyte with a sufficient number of ions is indispensable for the operation of these batteries, and “capacity” of the electrolyte is linearly proportional to its salt concentration, which substantially affects the cell energy density. Remarkably, three of four battery types— anion RCB, DIB, and RDIB—engage the anion storage, by (de)insertion, in one or both electrodes to reach the charge neutrality.

Although the battery community had favored metal ions as charge carriers as the norms; yet the first reported ion-insertion

electrode was an acceptor-type GIC by Rüdorff and Hoffmann in 1938, where they studied the electrochemical intercalation of  $\text{HSO}_4^-$  anions into graphite in an “ion transfer cell”.<sup>259</sup> Since then, acceptor-type GICs have remained at the central stage of anion intercalation chemistry.<sup>260</sup> In 1989, a patent was issued on the first DIB or dual-graphite battery, where redox-amphoteric graphite serves as both cathode and anode.<sup>261</sup> This invention may have been inspired by the reports on the reversible formation of donor-type Li-GICs, a newcomer after anion-GICs.<sup>262</sup> It is worth noting that the conducting polymer community has studied electrochemical doping of anions in polymer matrices since the 1980s, and the electrolytes used were typically aqueous ones.<sup>263,264</sup>

The challenge of acceptor-type GICs as the anion-hosting cathode is that their formation takes place at highly oxidizing potentials, *i.e.*, 4.5 to 5.5 V vs.  $\text{Li}^+/\text{Li}$ , where most solvents in the aprotic electrolytes would be oxidized. As one approach, the community worked on new electrolytes to address this challenge. Trulove and coworkers employed IL electrolytes to improve the reversibility of the graphite cathode.<sup>265</sup> More recent studies could reversibly cycle graphite cathode using IL electrolytes.<sup>266–268</sup> Ethyl methyl sulfone and an electrolyte with a fluorinated solvent can also survive above 5.0 V vs.  $\text{Li}^+/\text{Li}$ .<sup>269,270</sup> Tang and coworkers used a higher concentration of nonaqueous electrolytes, which shows stable cycling of graphite in graphite-Al DIB.<sup>271,272</sup>

The usage of electrolytes of high salt concentrations and IL electrolytes lowers the anion-insertion potential in graphite compared to the dilute electrolytes.<sup>273</sup> To explain this phenomenon, the logic to formulate the Equation (3) is used to generate the following Equation (4), where the entropy changes and overpotentials are, again, not considered:

$$\Delta H = \frac{E_{(xA^- + c_N)} - E_{C_N} + x\Delta H_{\text{desolv. } A^-} + x\Delta H_{\text{desolv. } \text{Li}^+} + xE_{\text{LiBCC}}}{x} \quad (4)$$

where graphite is employed as the cathode (A) and the plating/stripping of Li is the anode in a Carbon || Li half-cell of DIBs,  $\Delta H$  is the enthalpy change of the half-cell,  $E_{C_N}$  is the cathode energy before anion insertion occurs, where there are  $N$  carbon atoms in the system,  $E_{(xA^- + c_N)}$  is the energy of the anion-inserted cathode, where  $x$  is the number of anion incorporated,  $E_{\text{LiBCC}}$  is the change of cohesive energy of Li metal for adding one lithium atom on the surface, and  $\Delta H_{\text{desolv. } A^-}$  and  $\Delta H_{\text{desolv. } \text{Li}^+}$  represent the desolvation energies of anions and  $\text{Li}^+$  ions, respectively. For the graphite cathode, the high operation potential is due to the fact that  $\Delta H$  is too negative, where  $\Delta H \approx -n \cdot F \cdot \text{emf}$ , where  $n$  is the number of charges transferred,  $F$  is the Faraday constant, and  $\text{emf}$  is the electromotive force, *i.e.*, the thermodynamic cell voltage. In order to render  $\Delta H$  less negative, one can practice the following: decreasing the absolute difference of ( $E_{(xA^- + c_N)} - E_{C_N}$ ), and/or increasing the absolute values of desolvation energies,  $\Delta H_{\text{desolv. } A^-}$  and/or  $\Delta H_{\text{desolv. } \text{Li}^+}$ . For a higher concentration of the salt in the solvent or in ILs, the desolvation energies of both cations and anions may be increased due to the increased population of cation-anion pairs more strongly bonded than the ion-solvent species. This argument should be applicable to the WISE as well.

Another approach to stabilize the graphite cathode is to grow artificial SEI on graphite’s surface, where Wu and coworkers formed

such SEI by discharging graphite at low potentials in an organic carbonate electrolyte.<sup>274</sup>

The attention on anion-hosting cathode has shifted to non-graphitic materials. Upon compromising the long-range order of graphite, it was reported that soft carbon, *e.g.*, MCMC, could deliver a good capacity, whereas the capacity of amorphous carbon, *i.e.*, hard carbon, is low, most likely due to its structure being too tortuous for molecular ions to migrate through.<sup>275</sup> More recently, it is found that molecular solids and metal-organic frameworks (MOF) could reversibly store anions.<sup>276,277,278,279</sup> Their capacities are not necessarily higher than graphite; however, their operation potentials are much lower than graphite, within the stable range of aprotic electrolytes.

Interestingly when the operation potential of anion storage is sufficiently low, anion-storage electrodes become relevant to be used as a battery anode to pair with cation-deficient cathode materials, thus forming an RDIB. We reported the first RDIB with ferrocene encapsulated in activated carbon as the low-potential anode.<sup>249</sup> The use of anion-hosting anode is a hallmark for battery design because such a device configuration has the luxury to select a cathode from a great number of cation-deficient cathode materials reported for LIBs during the past four decades. Nevertheless, in prior studies, cation-deficient cathode materials had to be coupled with metallic anode materials, *e.g.*, Li, Na, K, and Mg, in nonaqueous electrolytes or Zn in aqueous electrolytes. These cells are 'half-cells' if the metal anode is not of finite mass compared to the cathode.

Over the past decades, the choice of electrodes for anion storage had been bound to the carbon-containing materials that are expected more structurally flexible, *e.g.*, graphite, soft carbon, polymers, and organic molecular solids. However, we recently discovered that a compact inorganic metal oxide, *i.e.*, Mn<sub>3</sub>O<sub>4</sub>, could reversibly host anions of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> from their aqueous electrolytes and deliver a good capacity value and stable cycling.<sup>280</sup> The anion insertion transforms the crystalline structure of Mn<sub>3</sub>O<sub>4</sub> partially amorphous; however, this phase change appears to be harmless for the reversibility. It is the author's opinion that oxidative anion storage is a common phenomenon of electrochemical reactions, where many yet-to-be-explored materials may exhibit reversible properties, high capacity, and long cycling life.

In the DIB field, most studies have employed nonaqueous electrolytes. Nonaqueous electrolytes allow the usage of a broad spectrum of energetic anode materials; whereas, aqueous electrolytes require anode to operate without significant HER. However, compared to nonaqueous electrolytes, aqueous electrolytes exhibit higher solubility toward many salts, and the concentration can be sufficiently high for the aqueous electrolytes to become WiSE. An ultra-high concentration of the electrolytes has profound impacts on the performance of DIBs because the chemical environment of such electrolytes is very different for water molecules and salt ions compared to that in dilute aqueous electrolytes and nonaqueous electrolytes.

One example is that the concentrations of electrolytes could dramatically shift the cation or anion insertion potentials in the electrode materials. In 2015, Wang, Xu, and coworkers reported a WiSE, where a near-saturation salt concentration increases the cation-insertion potential.<sup>62</sup> Recently, my group reported that higher electrolyte concentrations lower the anion-incorporation potential

of electrodes.<sup>256</sup> In fact, these up or down potential shifts depend on the activity coefficients of cations and anions in the Nernst equation with calculations shown below:

Electrode (ox) + Cation<sup>n+</sup> + ne<sup>-</sup> → Electrode (red)

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{c_{\text{cation}} * \gamma_{\text{cation}}} \quad (5)$$

Electrode (ox) + ne<sup>-</sup> → Electrode (red) + Anion<sup>n-</sup>

$$E = E^\circ - \frac{RT}{nF} \ln (c_{\text{anion}} * \gamma_{\text{anion}}) \quad (6)$$

where  $E^\circ$ ,  $R$ ,  $T$ ,  $n$ ,  $F$ ,  $c_{\text{cation}}$ ,  $\gamma_{\text{cation}}$ ,  $c_{\text{anion}}$ , and  $\gamma_{\text{anion}}$  are the standard potential, gas constant (8.3145 J·K<sup>-1</sup>·mol<sup>-1</sup>), the absolute temperature (298 K), the number of electrons transferred, Faraday constant (96485 J·V<sup>-1</sup>·mol<sup>-1</sup>), cation concentration, cation activity coefficient, anion concentration, and anion activity coefficient, respectively. The shifts of the operation potentials of either cation or anion insertion relate to the activity coefficients that are orders of magnitude higher in WiSE than in dilute ones.<sup>256</sup>

In advancing the performance of DIBs, the capacity and operation potential of the anode are critical for the energy density of DIBs. To this end, anode materials other than graphite have been investigated, including alloying electrodes such as Al,<sup>281</sup> Sn,<sup>282</sup> and LMAI.<sup>283,284</sup> The DIB setup sets free the choice of anode materials, where anode investigated for NIBs and KIBs are all relevant as suitable anode materials for DIBs beyond lithium.<sup>285,286,287</sup>

### Opportunities in the Anion-Insertion Redox Battery Chemistry

Anion storage represents remarkable opportunities in designing new battery chemistries. Nevertheless, I consider the 'plating' of small halide atoms such as fluoride and chloride as the Holy Grail of this research area. Electrochemical conversion by reduction or oxidation from ions to their neutral elemental phases is plating, which is best known for metals but rarely reported for nonmetals. The best electrode is 'no electrode' with zero mass and volume taken, which is simply a current collector for plating. The electrode-free approach was exemplified by the anode-free lithium batteries.<sup>288</sup> The recent breakthrough of insertion of Br<sup>0.05</sup> and Cl<sup>0.25</sup> into the galleries of graphite, by Wang and coworkers showcased the power of 'plating' of nonmetals in achieving a high energy density of batteries.<sup>197</sup> Of note, such 'plating' is at the atomic scale, where nearly-neutral atoms of Br<sup>0.05</sup> and Cl<sup>0.25</sup> are fastened under the protection of stacking graphene sheets as the extended current collector. However, it would be challenging to plate bulk Cl and Br phases in their molecular phases, which are gaseous and liquid, respectively. My group recently plated a solid iodine electrode from a WiSE that contains superhalides of [ZnI<sub>x</sub>(H<sub>2</sub>O)<sub>4-x</sub>]<sup>2-x</sup>.<sup>289</sup>

Next to 'plating', it would be insertion chemistries of light anions in high-capacity electrode hosts that are more interesting for the sake of a greater energy density. To this end, one may want to consider the concentrations of electrolytes as well, where the mass of anions should either be considered when calculating the specific capacity of the cathode or when estimating the energy density of the full cells. For DIBs (and RDIBs), it seems that highly concentrated electrolytes, aprotic or aqueous, are more attractive due to their higher specific 'capacity' values. Furthermore, if saturated electrolytes are employed, it is pivotal to understand that during charge of DIBs or discharge of RDIBs, WiSE may no longer stay as WiSE due to the matriculation of ions when forming the ion-inserted

electrodes. To maintain the high concentrations of electrolytes, we proposed that a certain mass of electrolyte salt(s) can be pre-mixed with either of the electrodes before operation of batteries.<sup>256</sup> Upon the usage of electrolyte-born ions, the solid salt helps maintain the high concentrations of the electrolytes via dissolution.

In summary, the four basic battery operation principles particularly the anion-hosting mechanisms in electrodes provide a panoramic view on the design of battery chemistries at the full reaction's scale.

## Perspectives on Aqueous Metal Batteries

As discussed above, considering both factors of cost and safety, it appears to be most realistic that the future GW battery storage facilities deploy aqueous batteries. Among aqueous storage batteries, metal batteries are the most attractive due to the usage of high-capacity metal anodes. There are primarily two types of metal batteries: The first is cation RCB that use a cation-deficient insertion cathode; the second is DIB that employs an anion-insertion or anion-plating cathode. For all metal batteries, the challenge of capacity fading for the cathode may not be a showstopper, which can be tackled with novel electrolytes; however, it is the performance of the metal anodes that eventually determines the future of a metal battery. Close attention should be paid to the long-standing challenges of metal anodes: HER and irregular plating morphology, *e.g.*, dendrites.

The storage battery community could learn much from the recent progress in promoting the CE and addressing the dendrite formation of LMA.<sup>290</sup> For example, in Zn batteries, the parasitic reaction on the surface of zinc metal anode (ZMA) arises from the reactions with water, *i.e.*, HER. To mitigate HER, one can decrease the concentration of water near the surface of ZMA, which renders water less reactive cathodically, or one can raise ZMA's oxidation potential, which turns ZMA less reactive anodically, where a Zn-based WiSE, *e.g.*, 30 m ZnCl<sub>2</sub>, which we first reported for Zn batteries, could accomplish both tasks to a large extent.<sup>291</sup> Furthermore, based on the Sand's law, a higher concentration of salts in the electrolytes delays Sand's extinction, thus inhibiting the formation of tip-grown morphologies, often described as dendrites.<sup>290</sup> Another parameter that should be monitored is the pH value of the aqueous electrolytes, where an acidic environment accelerates HER on the surface of ZMA. All these considerations are applicable to other aqueous metal batteries, including Fe batteries. Three dimensional (3D) architectures of current collectors may play a role in stabilizing the performance of metal anodes, which certainly helps mitigate the dendrite problem.<sup>292</sup>

Aqueous electrolytes are rarely spectators in aqueous batteries as for affecting the performance of electrodes. HER of electrolytes not only lowers CE of metal anodes, leads to fast self-discharge and capacity fading, dries up the electrolytes, but causes safety concerns. To evaluate CE of metal anodes' plating/stripping processes in aqueous electrolytes, it is pivotal to cover a wide range of current rates or current densities (in units of mA/g or mA/cm<sup>2</sup>, respectively). A high current rate/density can mask the negative impacts of HER and suggest overestimated CE values of the metal anodes because the kinetics of HER are largely consistent regardless of the adopted current rate/density of plating and stripping. High current

rate/density can reveal the reversibility of the metal anode that does not consider the reactivity of the electrolytes. However, to investigate the metal anode for its practicality in a battery, one must consider the reactions between the metal anodes and the electrolytes.

Note that a long cycle life of electrodes implies their stable performance at the cell scale, where aqueous electrolytes' stability in contacts with the electrodes should be considered. The suggestion here is to differentiate the usage of the terms of 'cyclability' and 'cycle life', where the former is about electrodes' reversibility alone, which can be revealed at high rates, and the latter is about the ensemble of the electrode and the electrolyte, where the cycle life should ideally be marked with the number of days taken for the cycling measurements.

Another challenge associated with aqueous metal batteries pertains to the corrosiveness of the electrolytes to cathode materials as well as to current collectors. If the cathode slowly dissolves in the aqueous electrolytes, the cycle life of such electrodes is a function of time. In addition, high-potential cathodes may cause OER of water. However, at a high current rate/density, cathode materials that dissolve or cause OER may still deliver a large number of cycles with minimal capacity fading, where the duration of such cycling tests may not be long. To reveal the true cycle life of cathode in aqueous metal batteries, again, it is crucial to note how many days used for cycling.

To inhibit the reactivity of water, *i.e.*, HER and OER, inorganic SEI from the decomposition of the electrolyte salts may be instrumental, where the aim is to achieve similar kinetic stability in aqueous systems as that seen on carbon anodes of LIBs. Alternatively, it is highly promising is to tune the strength of O-H bonds of water by constructing conducive chemical environments to stabilize water molecules. Both approaches may have tremendous impacts on the future of aqueous batteries.

The choice of current collectors in aqueous batteries is not trivial, where few current collector materials are very stable in aqueous electrolytes.<sup>293</sup> Al affords greater overpotentials of HER for Li-ion-based electrolytes; however, caution should be taken when using Al as the negative current collector because Al can reduce some charge carriers, *e.g.*, Zn<sup>2+</sup> and Fe<sup>2+</sup>. Titanium is more inert on the anode side; however, it is relatively expensive. An excessive mass of metal anode itself can be employed as the anode current collector. Graphite paper or cloth seems to be a suitable current collector for both anode and cathode, albeit the anion-insertion into graphite should be concerned on the cathode side.

To date, most studies for aqueous batteries were done in coin cells. Coin cells exert a large pressure, and the used active mass of electrodes in coin cells is typically small. Such conditions are suitable to test electrodes' performance, but often reveal little about the electrolyte's reactivity toward electrodes. The author expects that future studies will report more pouch cell results when the focus is about new electrolytes for metal anodes. Note that pouch cells may swell when gas evolves in the cells. Such information will be vital for the community to evaluate new battery chemistries.

Lastly, a rarely discussed concern of Zn batteries relates to the rarity of zinc, where Zn is only four times more abundant as Li in the Earth crust. According to the International Energy Agency, the world needs 266 GW of energy storage by 2030 to combat global warming. Bloomberg New Energy Finance estimates that the global energy

storage will hit 942 GW by 2040. If we estimate the power density of Zn batteries as 200 W/kg and assume that all 942 GW of storage is undertaken by Zn batteries, which is unlikely, it will need 4.71 million metric tons of Zn batteries. If we estimate half of the battery mass comes from Zn metal or Zn ions, we will need 2.36 million metric tons of Zn. The good news is that in 2018 alone, the global production of zinc is over 13 million metric tons, and in addition, Zn used in batteries can be recycled. In this situation, the consumption of Zn for Zn batteries would constitute 1.8% of the total global Zn production by 2040 if we assume that the annual global Zn production is maintained at 13 million metric tons for the next 20 years. Therefore, it is most likely that the global installation of Zn batteries will not face the shortage of the Zn supply despite its relative rarity.

## Conclusions and Perspectives

In this new paradigm of storage batteries, to invent the market-winning storage batteries, a roadmap that encompasses considerations toward minimizing the LEC will be highly valuable to the community. Practically relevant innovations in the storage battery field should present progress aligned with lowering the cost and/or enhancing the electrochemical performance for a lowered LEC. The energy-density-oriented research philosophy that has served well for LIBs no longer can effectively guide the progress in storage batteries. The development of storage batteries may require a holistic view on the chemical-reaction nature of batteries, where one is allowed to consider most aspects of a chemical reaction: the reactants and the reaction medium. From a purview, five dimensions of battery chemistries: electrodes, ion charge carriers, electrode-ion chemical bonding, electrolytes, and basic operation principles should be considered in designing a new battery chemistry.

This article emphasized some empirical trends of electrochemical properties of battery electrodes as a function of the chemical bonding between the electrodes and the inserted ions. In the author's opinion, the ion-electrode chemical bonding will serve as one powerful search engine to discover new battery chemistries and better understand existing ones. For the pursuit of marketing-winning battery chemistries, the boundaries that set for specific ion battery types should be removed. Instead, the field may find suitable storage battery chemistries faster by elucidating the implications in thermodynamics and kinetics of electrochemical processes associated with the interplays between the electrodes and the ion charge carriers.

It is expected the community will move beyond focusing on the materials alone and will address the nature of Faradaic processes in batteries from a holistic perspective of chemical reactions. Chemical reactions take place by providing amenable chemical environments for reactants, where such reactants in batteries are electrode structures, ions, and sometimes electrolyte solvent molecules. To define the chemical environments, one should select the reaction medium, which is the electrolyte in batteries. Inspired by the recent breakthroughs made with new electrolytes of WISE, the battery field will continue to make more discoveries that relate to innovations of electrolytes. Another observation is that the focus of the battery field has gradually extended beyond the regimes of solid-state chemistry/physics. It moves to interdisciplinary areas, where attention focuses on the design of electrolytes and the interface with

the electrodes. Future foci may be the reactivity of all reactants in the new chemical environments defined by the electrolytes. For example, the reactivity of water becomes tunable within WISE. To this end, the effort is in high needs to curtail the reactivity of the solvent of electrolytes. In aqueous electrolytes, to address HER and OER represents a more urgent task than to offer a new electrode structure if that is indifferent to the extent of HER and OER. The reactivity of electrolytes directly pertains to the reversibility of batteries, *i.e.*, the cycle life, and the rate of self-discharge—the properties that determine whether a battery is commercially relevant.

Batteries are nothing but reactors of chemical reactions. One should not only design the chemical reactions but also choose the reactor configurations that best reveal the energy and power of the chemical reactions. The four basic battery operation principles are the types of reactors to enable different battery chemistries. The field will witness the looming revolution on the diversity of the battery configurations. Despite the novelties and new ideas to be explored, the community needs a universal guideline of battery performance evaluation, which is indispensable toward finding a suite of practically relevant battery chemistries. Basic research may not need to deliver commercialization-related milestones. Claims, such as energy density, power density, and cycle life, however, need to be aligned with lowering the LEC.

The GW batteries will need novel designs of battery devices, which may be larger than non-aqueous batteries. To date, there have been many different battery designs, including coin cells, cylindrical cells, pouch cells, and micro/thin-film batteries, and printable batteries.<sup>294,295</sup> The industry of aqueous storage batteries can solicit the expertise from the lead-acid batteries.

In summary, the research on storage batteries will witness a paradigm shift from approaches of materials science to considerations of chemical science.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

X.J. is thankful to U.S. National Science Foundation Award No 1551693 for the financial support. X.J. thanks Mr. Woonchul Shin for his assistance in formatting the references and obtaining permissions of reproducing figures published in journals.



*Prof. Xiulei Ji graduated from Jilin University with a B.Sc. in chemistry in 2003. He obtained his Ph.D. degree from the University of Waterloo in 2009. He was an NSERC Postdoctoral Fellow at the University of California, Santa Barbara from 2010 to 2012. Dr. Ji is currently an Associate Professor at the Department of Chemistry, Oregon State University. His*



research interests are design principles of electrochemical energy storage, and materials chemistry in batteries and pseudocapacitors.

## Notes and references

- G. Crabtree, *Nature*, 2015, **526**, S92–S92.
- Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, **111**, 3577–3613.
- G. M. Crawley ed., *Energy Storage*, World Scientific, Singapore, 2017.
- 35x25: A Vision for Energy Storage*, Energy Storage Association, 2017.
- E. Barbour, I. A. G. Wilson, J. Radcliffe, Y. Ding and Y. Li, *Renew. Sustain. Energy Rev.*, 2016, **61**, 421–432.
- H. Lund and G. Salgi, *Energy Convers. Manag.*, 2009, **50**, 1172–1179.
- B. Bolund, H. Bernhoff and M. Leijon, *Renew. Sustain. Energy Rev.*, 2007, **11**, 235–258.
- U. Herrmann, B. Kelly and H. Price, *Energy*, 2004, **29**, 883–893.
- M. Aneke and M. Wang, *Appl. Energy*, 2016, **179**, 350–377.
- J. A. Turner, *Science*, 2004, **305**, 972–974.
- W. Buckles and W. V. Hassenzahl, *IEEE Power Eng. Rev.*, 2000, **20**, 16–20.
- B. E. Conway, *J. Electrochem. Soc.*, 1991, **138**, 1539–1548.
- The world's water battery: Pumped hydropower storage and the clean energy transition, International Hydropower Association
- B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 2011, **334**, 928–935.
- M. Li, J. Lu, Z. Chen and K. Amine, *Adv. Mater.*, 2018, **30**, 1800561.
- Y.-K. Sun, *ACS Energy Lett.*, 2019, **4**, 1042–1044.
- M. Bianchini, M. Roca-Ayats, P. Hartmann, T. Brezesinski and J. Janek, *Angew. Chem. Int. Ed.*, 2019, **58**, 10434–10458.
- S. Sharifi-Asl, J. Lu, K. Amine and R. Shahbazian-Yassar, *Adv. Energy Mater.*, 2019, **9**, 1900551.
- S. Chu and A. Majumdar, *Nature*, 2012, **488**, 294–303.
- GEVO 2018, <https://www.iea.org/gevo2018/>
- N. Nitta and G. Yushin, *Part. Part. Syst. Charact.*, 2014, **31**, 317–336.
- P. C. K. Vesborg and T. F. Jaramillo, *RSC Adv.*, 2012, **2**, 7933–7947.
- M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli and M. Saleem, *J. Electrochem. Soc.*, 2011, **158**, R55–R79.
- A. M. Bernardes, D. C. R. Espinosa and J. A. S. Tenório, *J. Power Sources*, 2004, **130**, 291–298.
- Y. Shi, G. Chen and Z. Chen, *Green Chem.*, 2018, **20**, 851–862.
- D. E. Turney, J. W. Gallaway, G. G. Yadav, R. Ramirez, M. Nyce, S. Banerjee, Y. K. Chen-Wiegart, J. Wang, M. J. D'Ambrose, S. Kolhekar, J. Huang and X. Wei, *Chem. Mater.*, 2017, **29**, 4819–4832.
- J. M. Eyer and G. P. Corey, *Energy storage for the electricity grid: benefits and market potential assessment guide: a study for the DOE Energy Storage Systems Program*, Sandia Report, 2010.
- D. M. Davies, M. G. Verde, O. Mnyshenko, Y. R. Chen, R. Rajeev, Y. S. Meng and G. Elliott, *Nat. Energy*, 2019, **4**, 42–50.
- J. Lochala, D. Liu, B. Wu, C. Robinson and J. Xiao, *ACS Appl. Mater. Interfaces*, 2017, **9**, 24407–24421.
- J. Chen, W. A. Henderson, H. Pan, B. R. Perdue, R. Cao, J. Z. Hu, C. Wan, K. S. Han, K. T. Mueller, J.-G. Zhang, Y. Shao and J. Liu, *Adv. Mater.*, 2017, **17**, 3061–3067.
- E. Peled, *J. Electrochem. Soc.*, 1979, **126**, 2047–2051.
- L. Suo, D. Oh, Y. Lin, Z. Zhuo, O. Borodin, T. Gao, F. Wang, A. Kushima, Z. Wang, H.-C. Kim, Y. Qi, W. Yang, F. Pan, J. Li, K. Xu and C. Wang, *J. Am. Chem. Soc.*, 2017, **139**, 18670–18680.
- F. La Mantia, M. Pasta, H. D. Deshazer, B. E. Logan and Y. Cui, *Nano Lett.*, 2011, **11**, 1810–1813.
- C. Ashtiani, *ECS Transactions*, 2008, **11**, 1–11.
- M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–629.
- Z. Gao, H. Sun, L. Fu, F. Ye, Y. Zhang, W. Luo and Y. Huang, *Adv. Mater.*, 2018, **30**, 1705702.
- N. Williard, W. He, C. Hendricks and M. Pecht, *Energies*, 2013, **6**, 4682–4695.
- X. Wang, E. Yasukawa and S. Kasuya, *J. Electrochem. Soc.*, 2001, **148**, A1066–A1071.
- K. Xu, S. Zhang, J. L. Allen and T. R. Jow, *J. Electrochem. Soc.*, 2002, **149**, A1079–A1082.
- J. Wang, Y. Yamada, K. Sodeyama, E. Watanabe, K. Takada, Y. Tateyama and A. Yamada, *Nat. Energy*, 2018, **3**, 22–29.
- Z. Zeng, V. Murugesan, K. S. Han, X. Jiang, Y. Cao, L. Xiao, X. Ai, H. Yang, J.-G. Zhang, M. L. Sushko and J. Liu, *Nat. Energy*, 2018, **3**, 674–681.
- A. Basile, M. Hilder, F. Makhlooghiyazad, C. Pozo-Gonzalo, D. R. MacFarlane, P. C. Howlett and M. Forsyth, *Adv. Energy Mater.*, 2018, **8**, 1703491.
- M. Ue, H. Tokuda, T. Kawai, M. Yanagidate and Y. Otake, *ECS Trans.*, 2009, **16**, 173–181.
- K. Takechi, Y. Kato and Y. Hase, *Adv. Mater.*, 2015, **27**, 2501–2506.
- C. Zhang, L. Zhang, Y. Ding, X. Guo and G. Yu, *ACS Energy Lett.*, 2018, **3**, 2875–2883.
- N. Delgado-Mellado, M. Larriba, P. Navarro, V. Rigual, M. Ayuso, J. García and F. Rodríguez, *J. Mol. Liq.*, 2018, **260**, 37–43.
- X.-B. Cheng, C.-Z. Zhao, Y.-X. Yao, H. Liu and Q. Zhang, *Chem*, 2019, **5**, 74–96.
- R. Murugan, V. Thangadurai and W. Weppner, *Angew. Chem. Int. Ed.*, 2007, **46**, 7778–7781.
- X. Han, Y. Gong, K. K. Fu, X. He, G. T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rubloff, Y. Mo, V. Thangadurai, E. D. Wachsman and L. Hu, *Nat. Mater.*, 2017, **16**, 572–579.
- K. Ishiguro, Y. Nakata, M. Matsui, I. Uechi, Y. Takeda, O. Yamamoto and N. Imanishi, *J. Electrochem. Soc.*, 2013, **160**, A1690–A1693.
- H. Chung and B. Kang, *Chem. Mater.*, 2017, **29**, 8611–8619.
- L. Xu, S. Tang, Y. Cheng, K. Wang, J. Liang, C. Liu, Y.-C. Cao, F. Wei and L. Mai, *Joule*, 2018, **2**, 1991–2015.
- J. Fu, J. Zhang, X. Song, H. Zarrin, X. Tian, J. Qiao, L. Rasen, K. Li and Z. Chen, *Energy Environ. Sci.*, 2016, **9**, 663–670.
- P. T. Moseley, *J. Power Sources* 2000, **88**, 71–77.
- I. González, A. Ramiro, M. Calderón, A. J. Calderón and J. F. González, *Int. J. Hydrog. Energy*, 2012, **37**, 11090–11103.
- S. McCluer. Battery Technology for Data Centers and Network Rooms: Lead-Acid Battery Options. APC Schneider Electric White paper # 30.
- Y. Li, D. Han, S. Han, X. Zhu, L. Hu, Z. Zhang and Y. Liu, *Int. J. Hydrog. Energy*, 2009, **34**, 1399–1404.
- Y. Liu, H. Pan, M. Gao and Q. Wang, *J. Mater. Chem.*, 2011, **21**, 4743–4755.
- W. Li, J. R. Dahn and D. S. Wainwright, *Science*, 1994, **264**, 1115–1118.
- J.-Y. Luo, W.-J. Cui, P. He and Y.-Y. Xia, *Nat. Chem.*, 2010, **2**, 760–765.
- Y. Wang, J. Yi and Y. Xia, *Adv. Energy Mater.*, 2012, **2**, 830–840.
- L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang and K. Xu, *Science*, 2015, **350**, 938–943.
- C. Yang, J. Chen, T. Qing, X. Fan, W. Sun, A. von Cresce, M. S.

- Ding, O. Borodin, J. Vatamanu, M. A. Schroeder, N. Eidson, C. Wang and K. Xu, *Joule*, 2017, **1**, 122–132.
- 64 D. Pavlov, in *Lead-Acid Batteries: Science and Technology (Second Edition)*, ed. D. Pavlov, Elsevier, Amsterdam, 2017, 593–620.
- 65 L. Zhang, I. A. Rodríguez-Pérez, H. Jiang, C. Zhang, D. P. Leonard, Q. Guo, W. Wang, S. Han, L. Wang and X. Ji, *Adv. Funct. Mater.*, 2019, **29**, 1902653.
- 66 L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, Cornell University Press, 1960.
- 67 M. M. Thackeray, C. Wolverton and E. D. Isaacs, *Energy Environ. Sci.*, 2012, **5**, 7854–7863.
- 68 C. Liu, F. Li, L.-P. Ma and H.-M. Cheng, *Adv. Mater.*, 2010, **22**, E28–E62.
- 69 K. Xu, *Chem. Rev.*, 2004, **104**, 4303–4418.
- 70 J. W. Choi and D. Aurbach, *Nat. Rev. Mater.*, 2016, **1**, 16013.
- 71 C.-X. Zu and H. Li, *Energy Environ. Sci.*, 2011, **4**, 2614–2624.
- 72 M. Winter, B. Barnett and K. Xu, *Chem. Rev.*, 2018, **118**, 11433–11456.
- 73 W. S. Harris, *Electrochemical Studies in Cyclic Esters*, A Thesis, 1958.
- 74 M. S. Whittingham, *Science*, 1976, **192**, 1126–1127.
- 75 N. Pereira, G. G. Amatucci, M. S. Whittingham and R. Hamlen, *J. Power Sources*, 2015, **280**, 18–22.
- 76 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, 1980, **15**, 783–789.
- 77 R. Yazami and Ph. Touzain, *J. Power Sources*, 1983, **9**, 365–371.
- 78 M. M. Thackeray, W. I. F. David, P. G. Bruce and J. B. Goodenough, *Mater. Res. Bull.*, 1983, **18**, 461–472.
- 79 A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *Electrochem. Soc. Meeting Abstracts*, 1996, **96-1**, 73.
- 80 A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**, 1188–1194.
- 81 Y.-K. Sun, S.-T. Myung, B.-C. Park, J. Prakash, I. Belharouak and K. Amine, *Nat. Mater.*, 2009, **8**, 320–324.
- 82 J. Kim, H. Lee, H. Cha, M. Yoon, M. Park and J. Cho, *Adv. Energy Mater.*, 2018, **8**, 1702028.
- 83 N. Yabuuchi and T. Ohzuku, *J. Power Sources*, 2003, **119–121**, 171–174.
- 84 M. M. Thackeray, S.-H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek and S. A. Hackney, *J. Mater. Chem.*, 2007, **17**, 3112–3125.
- 85 J. Hong, W. E. Gent, P. Xiao, K. Lim, D.-H. Seo, J. Wu, P. M. Csernica, C. J. Takacs, D. Nordlund, C.-J. Sun, K. H. Stone, D. Passarello, W. Yang, D. Prendergast, G. Ceder, M. F. Toney and W. C. Chueh, *Nat. Mater.*, 2019, **18**, 256.
- 86 H. Li, X. Huang, L. Chen, G. Zhou, Z. Zhang, D. Yu, Y. Jun Mo and N. Pei, *Solid State Ion.*, 2000, **135**, 181–191.
- 87 C. K. Chan, H. Peng, G. Liu, K. Mcllwrath, X. F. Zhang, R. A. Huggins and Y. Cui, *Nat. Nanotechnol.*, 2008, **3**, 31–35.
- 88 Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao and J. R. Dahn, *J. Electrochem. Soc.*, 1997, **144**, 205–213.
- 89 K. Amine, H. Yasuda and M. Yamachi, *Electrochem. Solid-State Lett.*, 2000, **3**, 178–179.
- 90 J.-N. Zhang, Q. Li, C. Ouyang, X. Yu, M. Ge, X. Huang, E. Hu, C. Ma, S. Li, R. Xiao, W. Yang, Y. Chu, Y. Liu, H. Yu, X.-Q. Yang, X. Huang, L. Chen and H. Li, *Nat. Energy*, 2019, **4**, 594–603.
- 91 E. McCalla, A. M. Abakumov, M. Saubanère, D. Foix, E. J. Berg, G. Rousse, M.-L. Doublet, D. Gonbeau, P. Novák, G. V. Tendeloo, R. Dominko and J.-M. Tarascon, *Science*, 2015, **350**, 1516–1521.
- 92 C. S. Johnson, N. Li, C. Lefief, J. T. Vaughey and M. M. Thackeray, *Chem. Mater.*, 2008, **20**, 6095–6106.
- 93 H. Danuta, U. Juliusz, *US Patent No. 3043896A*, 1962.
- 94 H. Yamin and E. Peled, *J. Power Sources*, 1983, **9**, 281–287.
- 95 S. H. Oh, R. Black, E. Pomerantseva, J.-H. Lee and L. F. Nazar, *Nat. Chem.*, 2012, **4**, 1004–1010.
- 96 J. B. Phipps, T. G. Hayes, P. M. Skarstad and D. F. Untereker, *Solid State Ion.*, 1986, **18–19**, 1073–1077.
- 97 M. M. Thackeray, W. I. F. David and J. B. Goodenough, *J. Solid State Chem.*, 1984, **55**, 280–286.
- 98 P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J.-M. Tarascon, *Nature*, 2000, **407**, 496–499.
- 99 Y. Miki, D. Nakazato, H. Ikuta, T. Uchida and M. Wakihara, *J. Power Sources*, 1995, **54**, 508–510.
- 100 T. Stephenson, Z. Li, B. Olsen and D. Mitlin, *Energy Environ. Sci.*, 2013, **7**, 209–231.
- 101 M. N. Obrovac, L. Christensen, D. B. Le and J. R. Dahn, *J. Electrochem. Soc.*, 2007, **154**, A849–A855.
- 102 A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala and G. Yushin, *Nat. Mater.*, 2010, **9**, 353–358.
- 103 J. M. Mosby and A. L. Prieto, *J. Am. Chem. Soc.*, 2008, **130**, 10656–10661.
- 104 X. Han, C. Chang, L. Yuan, T. Sun and J. Sun, *Adv. Mater.*, 2007, **19**, 1616–1621.
- 105 H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J.-M. Tarascon, *ChemSusChem*, 2008, **1**, 348–355.
- 106 Y. Lu, X. Hou, L. Miao, L. Li, R. Shi, L. Liu and J. Chen, *Angew. Chem. Int. Ed.*, 2019, **58**, 7020–7024.
- 107 R. Fong, U. von Sacken and J. R. Dahn, *J. Electrochem. Soc.*, 1990, **137**, 2009–2013.
- 108 J. R. Dahn, T. Zheng, Y. Liu and J. S. Xue, *Science*, 1995, **270**, 590–593.
- 109 K. Nakajima, *Mainichi Dly. News*, 1989, **1**.
- 110 J. Liu, Z. Bao, Y. Cui, E. J. Dufek, J. B. Goodenough, P. Khalifah, Q. Li, B. Y. Liaw, P. Liu, A. Manthiram, Y. S. Meng, V. R. Subramanian, M. F. Toney, V. V. Viswanathan, M. S. Whittingham, J. Xiao, W. Xu, J. Yang, X.-Q. Yang and J.-G. Zhang, *Nat. Energy*, 2019, **4**, 180–186.
- 111 A. K. Paclhi, K. S. Nanjunclawamy, C. Masquelier, S. Okada, and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**, 1609–1613.
- 112 C. Zhu, R. E. Usiskin, Y. Yu and J. Maier, *Science*, 2017, **358**, eaao2808.
- 113 H. Huang, S.-C. Yin and L. F. Nazar, *Electrochem. Solid-State Lett.*, 2001, **4**, A170–A172.
- 114 J. Lu, Z. Chen, Z. Ma, F. Pan, L. A. Curtiss and K. Amine, *Nat. Nanotechnol.*, 2016, **11**, 1031–1038.
- 115 J. K. Shon, H. S. Lee, G. O. Park, J. Yoon, E. Park, G. S. Park, S. S. Kong, M. Jin, J.-M. Choi, H. Chang, S. Doo, J. M. Kim, W.-S. Yoon, C. Pak, H. Kim and G. D. Stucky, *Nat. Commun.*, 2016, **7**, 11049.
- 116 X. Ji, K. T. Lee and L. F. Nazar, *Nat. Mater.*, 2009, **8**, 500.
- 117 Y. Zhao, C. Han, J. Yang, J. Su, X. Xu, S. Li, L. Xu, R. Fang, H. Jiang, X. Zou, B. Song, L. Mai and Q. Zhang, *Adv. Mater.*, 2015, **15**, 2180–2185.
- 118 H. J. Lee, J. Shin and J. W. Choi, *Adv. Mater.*, 2018, **30**, 1705851.
- 119 X. Meng, X.-Q. Yang and X. Sun, *Adv. Mater.*, 2012, **24**, 3589–3615.
- 120 P. S. Herle, B. Ellis, N. Coombs and L. F. Nazar, *Nat. Mater.*, 2004, **3**, 147.
- 121 M. S. Islam, D. J. Driscoll, C. A. J. Fisher and P. R. Slater, *Chem. Mater.*, 2005, **17**, 5085–5092.
- 122 Y. Chen, S. A. Freunberger, Z. Peng, O. Fontaine and P. G. Bruce, *Nat. Chem.*, 2013, **5**, 489–494.
- 123 C. A. Angell, C. Liu and E. Sanchez, *Nature*, 1993, **362**, 137.
- 124 L. Suo, Y.-S. Hu, H. Li, M. Armand and L. Chen, *Nat. Commun.*, 2013, **4**, 1481.
- 125 W. Li, M. Li, Y. Hu, J. Lu, A. Lushington, R. Li, T. Wu, T.-K. Sham and X. Sun, *Small Methods*, 2018, **2**, 1700341.
- 126 Y. Li, Y. Li, A. Pei, K. Yan, Y. Sun, C.-L. Wu, L.-M. Joubert, R.

- Chin, A. L. Koh, Y. Yu, J. Perrino, B. Butz, S. Chu and Y. Cui, *Science*, 2017, **358**, 506–510.
- 127 M. D. Levi, G. Salitra, N. Levy, D. Aurbach and J. Maier, *Nat. Mater.*, 2009, **8**, 872–875.
- 128 J. Y. Huang, L. Zhong, C. M. Wang, J. P. Sullivan, W. Xu, L. Q. Zhang, S. X. Mao, N. S. Hudak, X. H. Liu, A. Subramanian, H. Fan, L. Qi, A. Kushima and J. Li, *Science*, 2010, **330**, 1515–1520.
- 129 J. Newman, K. E. Thomas, H. Hafezi and D. R. Wheeler, *J. Power Sources*, 2003, **119–121**, 838–843.
- 130 M. Doyle, T. F. Fuller and J. Newman, *J. Electrochem. Soc.*, 1993, **140**, 1526–1533.
- 131 A. Urban, D.-H. Seo and G. Ceder, *Npj Comput. Mater.*, 2016, **2**, 16002.
- 132 H. Pan, Y.-S. Hu and L. Chen, *Energy Environ. Sci.*, 2013, **6**, 2338–2360.
- 133 N. Yabuuchi, K. Kubota, M. Dahbi and S. Komaba, *Chem. Rev.*, 2014, **114**, 11636–11682.
- 134 A. Eftekhari, *J. Power Sources*, 2004, **126**, 221–228.
- 135 A. Eftekhari, Z. Jian and X. Ji, *ACS Appl. Mater. Interfaces*, 2017, **9**, 4404–4419.
- 136 C. Delmas, *Adv. Energy Mater.*, 2018, **8**, 1703137.
- 137 C. Delmas, J.-J. Braconnier, C. Fouassier and P. Hagemuller, *Solid State Ion.*, 1981, **3–4**, 165–169.
- 138 J. Ding, H. Wang, Z. Li, A. Kohandehghan, K. Cui, Z. Xu, B. Zehri, X. Tan, E. M. Lotfabad, B. C. Olsen and D. Mitlin, *ACS Nano*, 2013, **7**, 11004–11015.
- 139 C. Zhao, Q. Wang, Y. Lu, B. Li, L. Chen and Y.-S. Hu, *Sci. Bull.*, 2018, **63**, 1125–1129.
- 140 Z. Li, Z. Jian, X. Wang, I. A. Rodríguez-Pérez, C. Bommier and X. Ji, *Chem. Commun.*, 2017, **53**, 2610–2613.
- 141 D. S. Charles, M. Feyngenson, K. Page, J. Neufeind, W. Xu and X. Teng, *Nat. Commun.*, 2017, **8**, 15520.
- 142 L. Jiang, Y. Lu, C. Zhao, L. Liu, J. Zhang, Q. Zhang, X. Shen, J. Zhao, X. Yu, H. Li, X. Huang, L. Chen and Y.-S. Hu, *Nat. Energy*, 2019, **4**, 495–503.
- 143 Y.-S. Hu, S. Komaba, M. Forsyth, C. Johnson and T. Rojo, *Small Methods*, 2019, **3**, 1900184.
- 144 X. Wu, D. P. Leonard and X. Ji, *Chem. Mater.*, 2017, **29**, 5031–5042.
- 145 P. Ge and M. Foulletier, *Solid State Ion.*, 1988, **28–30**, 1172–1175.
- 146 L. Xue, H. Gao, W. Zhou, S. Xin, K. Park, Y. Li and J. B. Goodenough, *Adv. Mater.*, 2016, **28**, 9608–9612.
- 147 A. L. Lipson, B. Pan, S. H. Lapidus, C. Liao, J. T. Vaughey and B. J. Ingram, *Chem. Mater.*, 2015, **27**, 8442–8447.
- 148 D. Aurbach, R. Skaletsky and Y. Gofer, *J. Electrochem. Soc.*, 1991, **138**, 3536–3545.
- 149 X. Wu, A. Markir, L. Ma, Y. Xu, H. Jiang, D. P. Leonard, W. Shin, T. Wu, J. Lu and X. Ji, *Angew. Chem. Int. Ed.*, 2019, **58**, 12640–12645.
- 150 D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich and E. Levi, *Nature*, 2000, **407**, 724–727.
- 151 J. Muldoon, C. B. Bucur and T. Gregory, *Chem. Rev.*, 2014, **114**, 11683–11720.
- 152 S. Licht and D. Peramunage, *J. Electrochem. Soc.*, 1993, **140**, L4–L6.
- 153 M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang and H. Dai, *Nature*, 2015, **520**, 324–328.
- 154 H. Pan, Y. Shao, P. Yan, Y. Cheng, K. S. Han, Z. Nie, C. Wang, J. Yang, X. Li, P. Bhattacharya, K. T. Mueller and J. Liu, *Nat. Energy*, 2016, **1**, 16039.
- 155 D. Kundu, B. D. Adams, V. Duffort, S. H. Vajargah and L. F. Nazar, *Nat. Energy*, 2016, **1**, 16119.
- 156 F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J. A. Dura, K. Xu and C. Wang, *Nat. Mater.*, 2018, **17**, 543–549.
- 157 M. D. Tikekar, S. Choudhury, Z. Tu and L. A. Archer, *Nat. Energy*, 2016, **1**, 16114.
- 158 S. U. Falk and A. J. Salkind, *Alkaline Storage Batteries*, John Wiley, New York, 1969.
- 159 A. K. Manohar, S. Malkhandi, B. Yang, C. Yang, G. K. S. Prakash and S. R. Narayanan, *J. Electrochem. Soc.*, 2012, **159**, A1209–A1214.
- 160 X. Yu and A. Manthiram, *ACS Energy Lett.*, 2017, **2**, 1050–1055.
- 161 X. Wu, A. Markir, Y. Xu, C. Zhang, D. P. Leonard, W. Shin and X. Ji, *Adv. Funct. Mater.*, 2019, **29**, 1900911.
- 162 R. Attias, M. Salama, B. Hirsch, Y. Goffer and D. Aurbach, *Joule*, 2019, **3**, 27–52.
- 163 I. A. Rodríguez-Pérez, Y. Yuan, C. Bommier, X. Wang, L. Ma, D. P. Leonard, M. M. Lerner, R. G. Carter, T. Wu, P. A. Greaney, J. Lu and X. Ji, *J. Am. Chem. Soc.*, 2017, **139**, 13031–13037.
- 164 O. Mizrahi, N. Amir, E. Pollak, O. Chusid, V. Marks, H. Gottlieb, L. Larush, E. Zinigrad and D. Aurbach, *J. Electrochem. Soc.*, 2008, **155**, A103–A109.
- 165 D. Aurbach, H. Gizbar, A. Schechter, O. Chusid, H. E. Gottlieb, Y. Gofer and I. Goldberg, *J. Electrochem. Soc.*, 2002, **149**, A115–A121.
- 166 X.-G. Sun, Z. Zhang, H. Y. Guan, C. A. Bridges, Y. Fang, Y.-S. Hu, G. M. Veith and S. Dai, *J. Mater. Chem. A*, 2017, **5**, 6589–6596.
- 167 B. D. Adams, J. Zheng, X. Ren, W. Xu and J.-G. Zhang, *Adv. Energy Mater.*, 2018, **8**, 1702097.
- 168 G.-T. Kim, G. B. Appetecchi, M. Montanino, F. Alessandrini and S. Passerini, *ECS Trans.*, 2010, **25**, 127–138.
- 169 I. Shterenberg, M. Salama, H. D. Yoo, Y. Gofer, J.-B. Park, Y.-K. Sun and D. Aurbach, *J. Electrochem. Soc.*, 2015, **162**, A7118–A7128.
- 170 K. A. See, K. W. Chapman, L. Zhu, K. M. Wiaderek, O. J. Borkiewicz, C. J. Barile, P. J. Chupas and A. A. Gewirth, *J. Am. Chem. Soc.*, 2016, **138**, 328–337.
- 171 D. Qu, *J. Power Sources*, 2008, **179**, 310–316.
- 172 M. C. Verbraeken, C. Cheung, E. Suard and J. T. S. Irvine, *Nat. Mater.*, 2015, **14**, 95–100.
- 173 Z. Mao, P. De Vidts, R. E. White and J. Newman, *J. Electrochem. Soc.*, 1994, **141**, 54–64.
- 174 H. Zhang, X. Yu and P. V. Braun, *Nat. Nanotechnol.*, 2011, **6**, 277–281.
- 175 R. Pohl, A. Antognini, F. Nez, F. D. Amaro, F. Biraben, J. M. R. Cardoso, D. S. Covita, A. Dax, S. Dhawan, L. M. P. Fernandes, A. Giesen, T. Graf, T. W. Hänsch, P. Indelicato, L. Julien, C.-Y. Kao, P. Knowles, E.-O. Le Bigot, Y.-W. Liu, J. A. M. Lopes, L. Ludhova, C. M. B. Monteiro, F. Mulhauser, T. Nebel, P. Rabinowitz, J. M. F. dos Santos, L. A. Schaller, K. Schuhmann, C. Schwob, D. Taqqu, J. F. C. A. Veloso and F. Kottmann, *Nature*, 2010, **466**, 213–216.
- 176 S. Trasatti and G. Buzzanca, *J. Electroanal. Chem. Interfacial Electrochem.*, 1971, **29**, A1–A5.
- 177 R. Schöllhorn, R. Kuhlmann and J. O. Besenhard, *Mater. Res. Bull.*, 1976, **11**, 83–90.
- 178 F. Fabregat-Santiago, E. M. Barea, J. Bisquert, G. K. Mor, K. Shankar and C. A. Grimes, *J. Am. Chem. Soc.*, 2008, **130**, 11312–11316.
- 179 S.-C. Pang, M. A. Anderson and T. W. Chapman, *J. Electrochem. Soc.*, 2000, **147**, 444–450.
- 180 J. B. Mitchell, W. C. Lo, A. Genc, J. LeBeau and V. Augustyn, *Chem. Mater.*, 2017, **29**, 3928–3937.
- 181 X. Wang, Y. Xie, K. Tang, C. Wang and C. Yan, *Angew. Chem. Int. Ed.*, 2018, **57**, 11569–11573.
- 182 S. Wang, X. Zhao, X. Yan, Z. Xiao, C. Liu, Y. Zhang and X. Yang, *Angew. Chem. Int. Ed.*, 2019, **58**, 205–210.
- 183 J. P. Zheng, P. J. Cygan and T. R. Jow, *J. Electrochem. Soc.*, 1995, **142**, 2699–2703.

- 184 Z. Xie, L. Gao, B. Liang, X. Wang, G. Chen, Z. Liu, J. Chao, D. Chen and G. Shen, *J. Mater. Chem.*, 2012, **22**, 19904–19910.
- 185 X. Wang, C. Bommier, Z. Jian, Z. Li, R. S. Chandrabose, I. A. Rodríguez-Pérez, P. A. Greaney and X. Ji, *Angew. Chem. Int. Ed.*, 2017, **56**, 2909–2913.
- 186 R. D. Shannon, *Acta Crystallogr. A*, 1976, **32**, 751–767.
- 187 H. Jiang, J. J. Hong, X. Wu, T. W. Surta, Y. Qi, S. Dong, Z. Li, D. P. Leonard, J. J. Holoubek, J. C. Wong, J. J. Razink, X. Zhang and X. Ji, *J. Am. Chem. Soc.*, 2018, **140**, 11556–11559.
- 188 R. Emanuelsson, M. Sterby, M. Strømme and M. Sjödin, *J. Am. Chem. Soc.*, 2017, **139**, 4828–4834.
- 189 M. S. Whittingham, *J. Chem. Soc., Chem. Commun.*, 1974, 328–329.
- 190 C. D. Wessells, M. T. McDowell, S. V. Peddada, M. Pasta, R. A. Huggins and Y. Cui, *ACS Nano*, 2012, **6**, 1688–1694.
- 191 M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum and Y. Gogotsi, *Science*, 2013, **341**, 1502–1505.
- 192 X. Wu, Y. Qi, J. J. Hong, Z. Li, A. S. Hernandez and X. Ji, *Angew. Chem. Int. Ed Engl.*, 2017, **56**, 13026–13030.
- 193 X. Wu, Y. Xu, H. Jiang, Z. Wei, J. J. Hong, A. S. Hernandez, F. Du and X. Ji, *ACS Appl. Energy Mater.*, 2018, **1**, 3077–3083.
- 194 L. Stuart, *US Patent No.* 4828942 1989.
- 195 C. Ponce de León, A. Frías-Ferrer, J. González-García, D. A. Szánto and F. C. Walsh, *J. Power Sources*, 2006, **160**, 716–732.
- 196 B. Wang, J. A. Maciá-Agulló, D. G. Prendiville, X. Zheng, D. Liu, Y. Zhang, S. W. Boettcher, X. Ji and G. D. Stucky, *J. Electrochem. Soc.*, 2014, **161**, A1090–A1093.
- 197 C. Yang, J. Chen, X. Ji, T. P. Pollard, X. Lü, C.-J. Sun, S. Hou, Q. Liu, C. Liu, T. Qing, Y. Wang, O. Borodin, Y. Ren, K. Xu and C. Wang, *Nature*, 2019, **569**, 245.
- 198 M. B. Armand, in *Materials for Advanced Batteries*, eds. D. W. Murphy, J. Broadhead and B. C. H. Steele, Springer US, Boston, 1980, 145–161.
- 199 D. Guerard and A. Herold, *Carbon*, 1975, **13**, 337–345.
- 200 Z. Jian, W. Luo and X. Ji, *J. Am. Chem. Soc.*, 2015, **137**, 11566–11569.
- 201 D. A. Stevens and J. R. Dahn, *J. Electrochem. Soc.*, 2000, **147**, 1271–1273.
- 202 M. M. Doeff, Y. Ma, S. J. Visco and L. C. D. Jonghe, *J. Electrochem. Soc.*, 1993, **140**, L169–L170.
- 203 S. J. L. Billinge and M. G. Kanatzidis, *Chem. Commun.*, 2004, **0**, 749–760.
- 204 C. Bommier, T. W. Surta, M. Dolgos and X. Ji, *Nano Lett.*, 2015, **15**, 5888–5892.
- 205 Z. Jian, C. Bommier, L. Luo, Z. Li, W. Wang, C. Wang, P. A. Greaney and X. Ji, *Chem. Mater.*, 2017, **29**, 2314–2320.
- 206 Z. Li, C. Bommier, Z. S. Chong, Z. Jian, T. W. Surta, X. Wang, Z. Xing, J. C. Neuefeind, W. F. Stickle, M. Dolgos, P. A. Greaney and X. Ji, *Adv. Energy Mater.*, 2017, **7**, 1602894.
- 207 C. Bommier, X. Ji and P. A. Greaney, *Chem. Mater.*, 2019, **31**, 658–677.
- 208 Y. Liu, B. V. Merinov and W. A. Goddard, *Proc. Natl. Acad. Sci.*, 2016, **113**, 3735–3739.
- 209 J. B. Goodenough and K.-S. Park, *J. Am. Chem. Soc.*, 2013, **135**, 1167–1176.
- 210 M. C. Tucker, L. Kroeck, J. A. Reimer and E. J. Cairns, *J. Electrochem. Soc.*, 2002, **149**, A1409–A1413.
- 211 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533–3539.
- 212 X. Ren and Y. Wu, *J. Am. Chem. Soc.*, 2013, **135**, 2923–2926.
- 213 P. Hartmann, C. L. Bender, M. Vračar, A. K. Dürr, A. Garsuch, J. Janek and P. Adelhelm, *Nat. Mater.*, 2013, **12**, 228–232.
- 214 T. Ogasawara, A. Débart, M. Holzapfel, P. Novák and P. G. Bruce, *J. Am. Chem. Soc.*, 2006, **128**, 1390–1393.
- 215 R. Black, B. Adams and L. F. Nazar, *Adv. Energy Mater.*, 2012, **2**, 801–815.
- 216 S. J. Yoo, B. Evanko, X. Wang, M. Romelczyk, A. Taylor, X. Ji, S. W. Boettcher and G. D. Stucky, *J. Am. Chem. Soc.*, 2017, **139**, 9985–9993.
- 217 B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Springer US, New York, 1999.
- 218 M. F. El-Kady, V. Strong, S. Dubin and R. B. Kaner, *Science*, 2012, **335**, 1326–1330.
- 219 C. Zhang, W. Lv, Y. Tao and Q.-H. Yang, *Energy Environ. Sci.*, 2015, **8**, 1390–1403.
- 220 H. Y. Lee and J. B. Goodenough, *J. Solid State Chem.*, 1999, **144**, 220–223.
- 221 H. Lindström, S. Södergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt and S.-E. Lindquist, *J. Phys. Chem. B*, 1997, **101**, 7717–7722.
- 222 J. Wang, J. Polleux, J. Lim and B. Dunn, *J. Phys. Chem. C*, 2007, **111**, 14925–14931.
- 223 T. Brezesinski, J. Wang, S. H. Tolbert and B. Dunn, *Nat. Mater.*, 2010, **9**, 146–151.
- 224 V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P.-L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon and B. Dunn, *Nat. Mater.*, 2013, **12**, 518–522.
- 225 H.-S. Kim, J. B. Cook, H. Lin, J. S. Ko, S. H. Tolbert, V. Ozolins and B. Dunn, *Nat. Mater.*, 2017, **16**, 454–460.
- 226 S. Dong, W. Shin, H. Jiang, X. Wu, Z. Li, J. Holoubek, W. F. Stickle, B. Key, C. Liu, J. Lu, P. Alex. Greaney, X. Zhang and X. Ji, *Chem*, 2019, **5**, 1537–1551.
- 227 H. Angerstein-Kozłowska, J. Klinger and B. E. Conway, *J. Electroanal. Chem. Interfacial Electrochem.*, 1977, **75**, 45–60.
- 228 A. J. Bard and L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, Wiley, New York, 2001.
- 229 B. D. Pelatt, J. F. Wager and D. A. Keszler, *J. Solid State Chem.*, 2019, **274**, 337–351.
- 230 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
- 231 Z. Wei, W. Shin, H. Jiang, X. Wu, W. F. Stickle, G. Chen, J. Lu, P. A. Greaney, F. Du and X. Ji, *Nat. Commun.*, 2019, **10**, 3227.
- 232 J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 89–112.
- 233 C. J. T. Grotthuss, *Ann Chim*, 1806, **LVIII**, 54–74.
- 234 B. Jaselskis and C. E. Moore, *Bull Hist Chem*, 2007, **32**, 10.
- 235 M. Thämer, L. D. Marco, K. Ramasesha, A. Mandal and A. Tokmakoff, *Science*, 2015, **350**, 78–82.
- 236 D. Marx, M. E. Tuckerman, J. Hutter and M. Parrinello, *Nature*, 1999, **397**, 601–604.
- 237 C. T. Wolke, J. A. Fournier, L. C. Dzugan, M. R. Fagiani, T. T. Odbadrakh, H. Knorke, K. D. Jordan, A. B. McCoy, K. R. Asmis and M. A. Johnson, *Science*, 2016, **354**, 1131–1135.
- 238 M. J. Minch, *J. Chem. Educ.*, 1999, **76**, 759.
- 239 D. N. Shigorin, *Spectrochim. Acta*, 1959, **14**, 198–212.
- 240 F. Guthrie, *J. Chem. Soc.*, 1863, **16**, 239–244.
- 241 O. Hassel and J. Hvoslef, *Acta Chem Scand*, 1954, **8**, 873.
- 242 A.-C. C. Carlsson, J. Gräfenstein, A. Budnjo, J. L. Laurila, J. Bergquist, A. Karim, R. Kleinmaier, U. Brath and M. Erdélyi, *J. Am. Chem. Soc.*, 2012, **134**, 5706–5715.
- 243 A. B. Sannigrahi, T. Kar, B. G. Niyogi, P. Hobza and P. v. R. Schleyer, *Chem. Rev.*, 1990, **90**, 1061–1076.
- 244 T.-Z. Hou, W.-T. Xu, X. Chen, H.-J. Peng, J.-Q. Huang and Q. Zhang, *Angew. Chem. Int. Ed.*, 2017, **56**, 8178–8182.
- 245 X. Wu, J. J. Hong, W. Shin, L. Ma, T. Liu, X. Bi, Y. Yuan, Y. Qi, T. W. Surta, W. Huang, J. Neuefeind, T. Wu, P. A. Greaney, J. Lu and X. Ji, *Nat. Energy*, 2019, **4**, 123–130.
- 246 P. Novák and J. Desilvestro, *J. Electrochem. Soc.*, 1993, **140**, 140–144.
- 247 K. Sato, M. Noguchi, A. Demachi, N. Oki and M. Endo, *Science*, 1994, **264**, 556–558.
- 248 M. Lazzari and B. Scrosati, *J. Electrochem. Soc.*, 1980, **127**, 773–774.

- 249 D. Lin, Y. Liu and Y. Cui, *Nat. Nanotechnol.*, 2017, **12**, 194–206.
- 250 Z. W. Seh, J. Sun, Y. Sun and Y. Cui, *ACS Cent. Sci.*, 2015, **1**, 449–455.
- 251 E. Levi, Y. Gofer and D. Aurbach, *Chem. Mater.*, 2010, **22**, 860–868.
- 252 Q. Zhao, W. Huang, Z. Luo, L. Liu, Y. Lu, Y. Li, L. Li, J. Hu, H. Ma and J. Chen, *Sci. Adv.*, 2018, **4**, eaao1761.
- 253 J. H. Kennedy and J. C. Hunter, *J. Electrochem. Soc.*, 1976, **123**, 10–14.
- 254 M. A. Reddy and M. Fichtner, *J. Mater. Chem.*, 2011, **21**, 17059–17062.
- 255 X. Zhao, Z. Zhao-Karger, D. Wang and M. Fichtner, *Angew. Chem. Int. Ed.*, 2013, **52**, 13621–13624.
- 256 X. Wu, Y. Xu, C. Zhang, D. P. Leonard, A. Markir, J. Lu and X. Ji, *J. Am. Chem. Soc.*, 2019, **141**, 6338–6344.
- 257 X. Zhou, Q. Liu, C. Jiang, B. Ji, X. Ji, Y. Tang and H.-M. Cheng, *Angew. Chem. Int. Ed.*, 2019, DOI:10.1002/anie.201814294.
- 258 J. R. Dahn and J. A. Seel, *J. Electrochem. Soc.*, 2000, **147**, 899–901.
- 259 W. Rüdorff and U. Hofmann, *Z. Für Anorg. Allg. Chem.*, 1938, **238**, 1–50.
- 260 M. Armand and P. Touzain, *Mater. Sci. Eng.*, 1977, **31**, 319–329.
- 261 F. P. McCullough, C. A. Levine, R. V. Snelgrove, *US Patent No. 4830938A*, 1989.
- 262 W. Rüdorff and E. Schulze, *Z. Für Anorg. Allg. Chem.*, 1954, **277**, 156–171.
- 263 W.-S. Huang, B. D. Humphrey and A. G. MacDiarmid, *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases*, 1986, **82**, 2385–2400.
- 264 P. Novák, K. Müller, K. S. V. Santhanam and O. Haas, *Chem. Rev.*, 1997, **97**, 207–282.
- 265 R. T. Carlin, H. C. D. Long, J. Fuller and P. C. Trulove, *J. Electrochem. Soc.*, 1994, **141**, L73–L76.
- 266 T. Placke, O. Fromm, S. F. Lux, P. Bieker, S. Rothermel, H.-W. Meyer, S. Passerini and M. Winter, *J. Electrochem. Soc.*, 2012, **159**, A1755–A1765.
- 267 T. Placke, A. Heckmann, R. Schmuck, P. Meister, K. Beltróp and M. Winter, *Joule*, 2018, **2**, 2528–2550.
- 268 J. Peng, N. Chen, R. He, Z. Wang, S. Dai and X. Jin, *Angew. Chem. Int. Ed.*, 2017, **56**, 1751–1755.
- 269 J. A. Seel and J. R. Dahn, *J. Electrochem. Soc.*, 2000, **147**, 892–898.
- 270 J. A. Read, A. V. Cresce, M. H. Ervin and K. Xu, *Energy Environ. Sci.*, 2014, **7**, 617–620.
- 271 X. Zhang, Y. Tang, F. Zhang and C.-S. Lee, *Adv. Energy Mater.*, 2016, **6**, 1502588.
- 272 X. Tong, F. Zhang, B. Ji, M. Sheng and Y. Tang, *Adv. Mater.*, 2016, **28**, 9979–9985.
- 273 I. A. Rodríguez-Pérez and X. Ji, *ACS Energy Lett.*, 2017, **2**, 1762–1770.
- 274 W.-H. Li, Q.-L. Ning, X.-T. Xi, B.-H. Hou, J.-Z. Guo, Y. Yang, B. Chen and X.-L. Wu, *Adv. Mater.*, 2019, **31**, 1804766.
- 275 T. Ishihara, M. Koga, H. Matsumoto and M. Yoshio, *Electrochem. Solid-State Lett.*, 2007, **10**, A74–A76.
- 276 I. A. Rodríguez-Pérez, Z. Jian, P. K. Waldenmaier, J. W. Palmisano, R. S. Chandrabose, X. Wang, M. M. Lerner, R. G. Carter and X. Ji, *ACS Energy Lett.*, 2016, **1**, 719–723.
- 277 I. A. Rodríguez-Pérez, C. Bommier, D. D. Fuller, D. P. Leonard, A. G. Williams and X. Ji, *ACS Appl. Mater. Interfaces*, 2018, **10**, 43311–43315.
- 278 M. L. Aubrey and J. R. Long, *J. Am. Chem. Soc.*, 2015, **137**, 13594–13602.
- 279 S. Dühnen, R. Nölle, J. Wrogemann, M. Winter and T. Placke, *J. Electrochem. Soc.*, 2019, **166**, A5474–A5482.
- 280 H. Jiang, Z. Wei, L. Ma, Y. Yuan, J. J. Hong, X. Wu, D. P. Leonard, J. Holoubek, J. J. Razink, W. F. Stickle, F. Du, T. Wu, J. Lu and X. Ji, *Angew. Chem. Int. Ed.*, 2019, **58**, 5286–5291.
- 281 X. Zhang, Y. Tang, F. Zhang and C.-S. Lee, *Adv. Energy Mater.*, 2016, **6**, 1502588.
- 282 M. Sheng, F. Zhang, B. Ji, X. Tong and Y. Tang, *Adv. Energy Mater.*, 2017, **7**, 1601963.
- 283 X.-T. Xi, W.-H. Li, B.-H. Hou, Y. Yang, Z.-Y. Gu and X.-L. Wu, *ACS Appl. Energy Mater.*, 2019, **2**, 201–206.
- 284 X.-T. Xi, X. Feng, X.-J. Nie, B.-H. Hou, W.-H. Li, X. Yang, A.-B. Yang, W.-D. Sun and X.-L. Wu, *Chem. Commun.*, 2019, **55**, 8406–8409.
- 285 L. Fan, Q. Liu, S. Chen, K. Lin, Z. Xu and B. Lu, *Small*, 2017, **13**, 1701011.
- 286 L. Fan, Q. Liu, S. Chen, Z. Xu and B. Lu, *Adv. Energy Mater.*, 2017, **7**, 1602778.
- 287 S. Dong, Z. Li, I. A. Rodríguez-Pérez, H. Jiang, J. Lu, X. Zhang and X. Ji, *Nano Energy*, 2017, **40**, 233–239.
- 288 R. Weber, M. Genovese, A. J. Louli, S. Hames, C. Martin, I. G. Hill and J. R. Dahn, *Nat. Energy*, 2019, **4**, 683–689.
- 289 J. J. Hong, L. Zhu, C. Chen, L. Tang, H. Jiang, B. Jin, T. C. Gallagher, Q. Guo, C. Fang and X. Ji, *Angew. Chem., Int. Ed.*, 2019, DOI: 10.1002/anie.201909324.
- 290 S. Li, M. Jiang, Y. Xie, H. Xu, J. Jia and J. Li, *Adv. Mater.*, 2018, **30**, 1706375.
- 291 C. Zhang, J. Holoubek, X. Wu, A. Daniyar, L. Zhu, C. Chen, D. P. Leonard, I. A. Rodríguez-Pérez, J.-X. Jiang, C. Fang and X. Ji, *Chem. Commun.*, 2018, **54**, 14097–14099.
- 292 J. F. Parker, C. N. Chervin, I. R. Pala, M. Machler, M. F. Burz, J. W. Long and D. R. Rolison, *Science*, 2017, **356**, 415–418.
- 293 Y. Yamada, K. Usui, K. Sodeyama, S. Ko, Y. Tateyama and A. Yamada, *Nat. Energy*, 2016, **1**, 16129.
- 294 P. Zhang, F. Wang, M. Yu, X. Zhuang and X. Feng, *Chem. Soc. Rev.*, 2018, **47**, 7426–7451.
- 295 M. Yu and X. Feng, *Joule*, 2019, **3**, 338–360.

The societal energy income should ideally come from cost-effective ‘farming’ of renewable sources, *e.g.*, solar, wind, tidal, and geothermal. Energy storage facilities are the ‘banks’ of energy, where the currency is electricity. From energy banks, customers, *e.g.*, electric vehicles, can “cash” out energy anytime and anywhere, and into these banks, people can invest their energy surplus or saving through the smart internet of things. However, we have yet to reach this sustainable energy economy that demands ubiquitous and localized storage solutions.

Storage batteries represent the most promising solution to fill the gap in storage needs for the future. Such battery facilities may be installed at the gigawatt-scale that the world has never seen. Storage batteries must be competitive in its levelized energy cost compared to the utility electricity price, and these batteries must be safe without facing liability cost. As of now, the battery field may have entered a new research paradigm that entails more holistic considerations. This article enlists five dimensions of factors, including electrode materials, ion charge carriers, electrolytes, electrode-ion interactions, and battery operation principles. I introduce empirical trends that exemplify the relevance of these considerations. These seemingly intricate considerations are different aspects of chemical reactions taking place in a compartmentalized reactor.