Water in rechargeable multivalent-ion batteries : an electrochemical Pandora's box

Manalastas, William, Jr.; Kumar, Sonal; Verma, Vivek; Zhang, Liping; Yuan, Du; Srinivasan, Madhavi

2018

Manalastas, W., Jr., Kumar, S., Verma, V., Zhang, L., Yuan, D., & Srinivasan, M. (2019). Water in rechargeable multivalent-ion batteries : an electrochemical Pandora's box. *ChemSusChem*, 12(2), 379-396. doi:10.1002/cssc.201801523

<https://hdl.handle.net/10356/140527>

<https://doi.org/10.1002/cssc.201801523>

This is the accepted version of the following article: Manalastas, W., Jr., Kumar, S., Verma, V., Zhang, L., Yuan, D., & Srinivasan, M. (2019). Water in rechargeable multivalent-ion batteries : an electrochemical Pandora's box. *ChemSusChem*, 12(2), 379-396. doi:10.1002/cssc.201801523, which has been published in final form at <https://doi.org/10.1002/cssc.201801523>. This article may be used for non-commercial purposes in accordance with the Wiley Self-Archiving Policy [<https://authorservices.wiley.com/authorresources/Journal-Authors/licensing/self-archiving.html>].

Water in Rechargeable Multivalent-Ion Batteries: An Electrochemical Pandora's Box

William Manalastas, Jr.,^{*,[a]} Sonal Kumar,^[a] Vivek Verma,^[a] Liping Zhang,^[b] Du Yuan,^[b] and Madhavi Srinivasan^{*,[a, b]}

Chemsuschem@copyright 2019 Wiley. This is the peer reviewed version of the following article: Manalastas, W. J., Kumar, S., Verma, V., Zhang, L., Yuan, D., & Srinivasan, M. (2019). Water in rechargeable multivalent-ion batteries: an electrochemical Pandora's box. Chemsuschem, 12(2), 379-396, which has been published in final form at <https://doi.org/10.1002/cssc.201801523>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions

Multivalent-ion batteries built on water-based electrolytes represent energy storage at suitable price points, competitive performance, and enhanced safety. However, to comply with modern energy-density requirements, the battery must be reversible within an operating voltage window greater than 1.23 V or the electrochemical stability limits of free water. Taking advantage of its powerful solvation and catalytic activities, adding water to electrolyte preparations can unlock a

wider gamut of liquid mixtures compared with strictly nonaqueous systems. However, a point-by-point sweep of all potential formulations is arduous and ineffective without some form of systematic rationalization. The present Review consolidates recent progress, pitfalls, limits, and insights critical to expediting aqueous electrolyte designs to boost multivalent-ion battery outputs.

1. Introduction

The electromobility revolution has set off an explosion in demand for rechargeable Li-ion batteries in electric vehicle (EV) applications. Global EV sales skyrocketed from 10 000 in 2010 to 774 000 in 2016, as a result of better economies-of-scale, preferential taxation, and a stepwise jump in EV mileages (Figure 1).^[1] Among these factors, what prompted broad con-

Figure 1. Optimal (dashed lines) and worst (dotted lines) price-to-performance metrics for several battery technologies in the market, assuming a vehicular battery compartment with a maximum size of 300 dm³. Reproduced from ref. [1a] with permission from Macmillan Publishers Ltd.: Nature Energy, copyright 2018.

sumer overtures towards EV technology ultimately were battery energy densities augmented from 90 to 250 Wh kg⁻¹ over the same period.^[1a] The nascent market has, in turn, prompted juggernaut manufacturers, such as American Gigafactory

(Tesla), Japanese Panasonic, Korean LG Chem and Samsung SDI, Chinese Build Your Dreams Ltd. (BYD), and Contemporary Amperex Technology Ltd. (CATL), to make colossal facility commitments to scaling mature lithium-ion chemistries.^[2] Battery safety remains a core issue, however, because rising demands for ever more powerful batteries also exacerbate catastrophic EV autoimmolation hazards.^[3]

Whereas upgrading batteries is a perennial affair of materials screening for low-voltage anodes/high-voltage cathodes and powder nanosizing, the electrolytes of choice in high-performance lithium-ion batteries (LIBs) have conventionally been fluoro-containing salts dissolved in flammable organic solvents. Such organic electrolytes exhibit a favorable balance of ion-transport kinetics and operational voltage window, but, on the downside, in these systems: 1) low flash points amplify explosive thermal runaway risks; 2) any trace H₂O triggers a cascade of corrosive hydrolysis; 3) their natural bioremediation is limited; 4) the physicochemical energy density limits of current LIB configurations have almost been breached (currently at 770 Wh L⁻¹ vs. a theoretical maximum of 830 Wh L⁻¹);^[4] and 5) perhaps most fundamentally, the geopolitical constraints of highly coveted lithium and rare-earth-metal reserves needed for high-power LIBs are fast proving to be potential sources of international conflicts.^[5]

Beyond commercialized lithium-ion technology, aqueous batteries are now receiving rekindled interest for their safety, ease of scaling, and energy/power capabilities, which may surpass even those for nonaqueous systems.^[6] Clearly, developing water-compatible electrode materials and electrolytes of competitive caliber would greatly simplify processing, reduce manufacturing overheads, and expedite recycling efforts. However, because stored electrochemical energy is released as a product of voltage, current, and time, and the voltage stability of free water is severely limited, aqueous batteries inspire efforts to achieve high-energy batteries by drastically increasing charge capacity at moderate voltages, rather than by creating > 5 V cell systems.

One method is to replace the monovalent-ion shuttle with a multivalent-ion shuttle to effect multiple electron-transfer events per ion crossover. On a per ion basis, this would be a charge vector superior to that of elemental lithium.^[7] Indeed, transposing concepts from the aqueous lithium system to other water-based chemistries, recent reports have demonstrated remarkable breakthroughs with heavier elements, for example, Na,^[8] Mg,^[9] Al,^[10] K,^[11] Ca,^[12] Cu,^[13] Fe,^[14] Zn,^[15] Mn,^[16] Rb/Tl,^[17] and V.^[18] We aim to contribute insights to push these

[a] Dr. W. Manalastas, Jr., S. Kumar, V. Verma, Prof. M. Srinivasan
School of Materials Science and Engineering
Nanyang Technological University
11 Faculty Ave 639977, Singapore (Singapore)
E-mail: wmanalastas@ntu.edu.sg
madhavi@ntu.edu.sg

[b] Dr. L. Zhang, Dr. D. Yuan, Prof. M. Srinivasan
Energy Research Institute @ NTU
Nanyang Technological University
50 Nanyang Drive 637553, Singapore (Singapore)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/cssc.201801523>.

further, by focusing on low-cost, multivalent-ion (Mg, Ca, Zn, Al) battery development from an electrolyte point of view. The discussion is laid out as an analytical treatise to complement ongoing studies on novel multivalent-ion electrode materials.^[6d,19]

1.1. Fundamentals of battery electrolytes: Thermodynamics and kinetics

1.1.1. Thermodynamics: Predicting maximum voltage outputs

A battery operates by manipulating the transport of stored charge, externally through a load as electrons, performing useful work, and internally as ions to maintain electrostatic neutrality. If these charge-carrying conduits fail or are significantly impeded, the battery experiences either an acute rise in overpolarization effects and energy wasted as heat, or battery shutdown. Electrons in metallic contacts are more labile, in general, than ions migrating through an electrolyte medium; hence battery efficiencies are heavily dictated by electrolyte performance.

Each electron carries energy proportional to an established voltage difference, that is, through the pairing of a high-potential positive electrode (cathode) and a low-potential negative electrode (anode). Between the two electrodes, it is crucial for

William Manalastas, Jr. is a research fellow at the Energy Storage Lab (Singapore) in the group of Prof. M. Srinivasan. Previously, he was a CIC Energigune Ph.D. Fellow (Spain), mentored under the ALISTORE European electrochemistry network by Dr. F. Aguesse and Prof. J. A. Kilner. His research focuses on superionic solid electrolytes and aqueous electrolytes for next-generation batteries.

Madhavi Srinivasan is currently Professor at the School of Materials Science and Engineering, Nanyang Technological University (NTU), Singapore. Her research interests involve enhancing the performance of energy-storage devices, such as lithium-ion batteries; supercapacitors; and advanced batteries, such as sodium-ion batteries and zinc-based batteries, with the help of multifunctional nanoscale materials to power printed electronics, to store energy from renewable sources, and for powering electric vehicles. Her focus is on the fabrication and investigation of nanoscale materials/architectures for next-generation electrochemical energy storage devices. She graduated from the Indian Institute of Technology (IIT, India) and wrote her Ph.D. dissertation on lithium-ion batteries at the National University of Singapore (Singapore).

the electrolyte to be able to withstand the oxidizing/reducing potential exerted at interfacial contacts against the electrode bulk material during operation. This electrolyte–electrode interplay is illustrated in Figure 2a.

Figure 2. a) Diagram of electrochemical reaction potentials for an ideal electrolyte versus an electrode pair. The typical voltage versus capacity curves exhibited during discharge of a redox half-cell (e.g., Cu^{2+} -based cathode in a Daniel cell, paired with a Zn-metal anode), expressed on logarithmic (b) and linear (c) scales. The tracing dots indicate how the energy density increases for paired half-cell compartments that both enable saturation concentrations much greater than that of E° conditions, that is, $[\text{ox}] > 1 \text{ M}$, provided that the battery is being operated in a regime of minimal polarization losses.

Essentially, a liquid electrolyte must have an electrolyte LUMO higher than the cathode HOMO and an electrolyte HOMO lower than the anode LUMO. This concept is homologous to band gap theory for periodic systems, such as polyelectrolytes and ceramic electrolytes, wherein the LUMO corresponds to the conduction-band minimum and the HOMO corresponds to the valence-band maximum. If these conditions are not satisfied, the electrolyte decomposes, which may disrupt the internal flow of ions.

The Nernst equation [Eqs. (1)–(3)] establishes the half-cell potential for the anode and cathode separately:

$$E_{\text{net}} = E_{\text{cathode}} - E_{\text{anode}} \quad (1)$$

$$E_{\text{cathode}} = E^\circ_{\text{cathode}} - \frac{RT}{nF} \ln \frac{[\text{red}]^a}{[\text{ox}]^x} \quad (2)$$

$$\Delta G_{\text{rxn}} = -nFE_{\text{net}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}} \quad (3)$$

in which E° is the standard half-cell reduction potential of an electrochemical redox pair of fixed 1 M concentrations with respect to the standard hydrogen electrode (SHE) at 298 K and 1 atm ($= 101\,325 \text{ Pa}$); R is the universal gas constant; T is the absolute temperature in Kelvin; n is the stoichiometric number of electrons exchanged per reaction; F is the Faraday constant, $[\text{red}]$ is the activity (estimated by concentration) of the re-

duced form of a soluble species; [ox] is the activity (estimated by concentration) of its oxidized form; a and x are exponential powers determined by the coefficients of [red] and [ox], respectively, in the redox half-reaction; and ΔG_{rxn} , ΔH_{rxn} , and ΔS_{rxn} are the net Gibbs free energy, enthalpy, and entropy of the reaction, respectively.

Equations (1) and (2) have a major implication: the maximum cell potential (E_{net}) is critically determined more by $E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$ rather than by the reactant concentrations. Although higher [ox] indeed establishes stronger reduction potentials, the maximum solubility of salts in aqueous media is typically only about an order of magnitude above 1 M (the standard conditions under which $E_{\text{cathode}}^{\circ}$ or E_{anode}° are obtained). Because [ox] exerts an influence on each half-cell potential on a logarithmic scale (Figure 2b), specifically engineering aqueous salt solutions that can stabilize higher [ox] at saturation is a strategy that can offset E_{cathode} or E_{anode} by only about 0.1 V at most.

This means that a battery constructed such that the electrolyte concentration varies as it is directly consumed over time and regenerated subsequently as part of the energy-storage mechanism (e.g., the Zn/Zn²⁺ and Cu²⁺/Cu compartments within a modified Zn/Cu Daniell cell)^[21] would display little voltage-output augmentation between a 1 M saturation electrolyte reservoir versus, for example, a 10 M saturation electrolyte reservoir. Nonetheless, because electrons transferred in redox reactions are cumulative, the charge capacity contribution to energy density jumps immensely, as shown by the integrated area highlighted in Figure 2c. This is the principle behind high-energy redox flow batteries.

This also means that for batteries employing solid-state electrodes with which free/solvated ions released from one electrode are stoichiometrically consumed by the other electrode (e.g., intercalation or conversion mechanisms with a single ion carrier, such as Li⁺), the electrolyte concentration is theoretically fixed for the duration of charge–discharge events. Therefore, the choice of electrolyte concentration injected into a battery assembly can be deterministic of its extended performance for the duration of its service lifetime.

Furthermore, if this solid-state electrode is a pure metal in equilibrium with its elemental cations as the anode, its contribution to the overall potential is maintained theoretically constant during battery discharge/charge. In contrast, a multielement host-material anode (e.g., metal oxides, phosphates, sulfides) in equilibrium with a foreign-element cation creates conditions under which the phase-transition dynamics of the two-component solid solution increases the anodic potential upon discharging, thereby inducing a voltage-output penalty (Scheme 1). Therefore, because metal anodes provide low anodic voltages and the largest specific charge capacities (Table 1) for each element, pure metals make ideal anodes for maximum battery energy densities.

Under general conditions, E_{net} can also be related to ΔG_{rxn} as in Equation (3), that is, the maximum output voltage for a battery redox pair can be modeled through thermodynamic databanks for standard reactions. However, caution must be exercised in basing conclusions for electrochemical reactions in

Scheme 1. Evolution in electrochemical half-cell potentials of the positive and negative electrodes from a charged to a discharged state, if the anode material is a) a metal or b) an intercalation-type host material.

Table 1. Theoretical reduction potentials and charge capacities of some representative metal ions at 25 °C.^[22]

Metal-ion/ metal redox couple	Approximate electrode reduction potential [V] (vs. SHE)	Theoretical capacity	
		Gravimetric [mAh g ⁻¹]	Volumetric [mAh cm ⁻³]
Li ⁺ /Li	−3.04	3861	2062
Ca ²⁺ /Ca	−2.87	1337	2060
Mg ²⁺ /Mg	−2.37	2205	3833
Zn ²⁺ /Zn	−0.76	820	5854
Al ³⁺ /Al	−1.66	2980	8046

fluid media from datasets obtained through first-principle simulations. In particular, because most accessible reports describe computations in a simulated vacuum environment or under 1 atm, or a continuous reaction field model, conclusions in one system may not necessarily apply to an analogous system (e.g., a nonaqueous battery model vs. an aqueous battery model using similar anode/cathode materials). An electrochemical cell in actual operation would have solvent-dependent solvation/desolvation effects with associated entropic implications, driving a key outcome in which the operational output voltage of a battery is strongly limited by the nature of electrolyte media: $E_{\text{operation}} = E_{\text{thermodynamic}} - E_{\text{resistances}}$; $E_{\text{operation}}$ is the actual battery output voltage, $E_{\text{thermodynamic}}$ is the theoretical battery output voltage, and $E_{\text{resistances}}$ includes voltage drops due to internal charge-transfer resistance, internal polarization resistance, and external contact wiring resistances.

1.1.2. Kinetics: Rate-limited degradation

Bulk water has an electrochemical stability window of about 1.23 V. Recently, however, reports of high-voltage aqueous batteries (2.5 to 4 V) have claimed the successful use of interfacial controls to isolate bulk water from electrochemical contact.^[6a, c, 8b, c, 9a, 23] This was achieved through the creation of an artificial solid–electrolyte interface (SEI) on the electrode surface, which passivates against proton/hydroxyl electrolytic decomposition, but allows cation-specific diffusion. As opposed to thermodynamic control, such formulations achieve the purpose of a wide voltage window by suppressing electrolyte de-

composition rates to marginal levels, but are not completely stopped.

It is known that water exhibits electrochemistry dependent on the nature of the surface with which it interacts. Upon incorporation into lead–acid batteries, water tolerates a 2.1 V nominal voltage window, despite a narrow thermodynamic stability window of 1.23 V. Thanks to the slow kinetics of water electrolysis on Pb electrodes, the emission of gaseous H₂ on the cathode and O₂ on the anode is markedly reduced; thus allowing the reactions given in Equations (4) and (5) to proceed appreciably within practicable discharging/charging timescales.

Negative electrode (anode):

Positive electrode (cathode):

Water can also directly participate in electrochemical equilibria. During discharge in a lead–acid battery, insulating PbSO₄ is produced on both the positive and negative plates, which, if allowed to stay dormant, coalesces and leads to clogged electrolyte pores and lost capacity. This is termed “sulfation” ■ ■ ■ sulfation? sulfidation? ■ ■ ■, and to alleviate this, modern lead–acid batteries use engineering controls, such as Pb grids, absorbed glass mats, gel electrolytes, high-frequency pulse programs, and/or chemical controls such as additives (Bi, C, H₃PO₃, SnSO₄, etc.),^[24] thereby exerting some degree of control over precipitation morphology and dispersion. Notably, water is a crucial component to make this reaction reversible, and there is direct participation of H⁺ ions in shifting equilibria: the negative plate becomes locally basic during charging, whereas the positive plate becomes locally acidic. Hence, to ensure sufficient “sacrificial” water, mass convection, and avoid electrolyte stratification during operation, the concentrated acid electrolyte must be reasonably diluted from saturation. In fact, converse to commercial LIB systems, higher power rate cycling and less concentrated electrolytes both directly contribute to longer cycle lives of lead–acid batteries.^[25]

1.2. Main differences between aqueous and nonaqueous systems

Considering its molecular size, water is exceptional. The simple composition (2H+1O atoms), dipole moment (1.86–3.0 D),^[26] and dielectric constant ($\epsilon \approx 80$)^[27] create a unique combination of stability, solvation, mobility, and acid/base interactions that is not mimicked by any one organic molecule.

As detailed in Table 2, for example, acetonitrile, ethylene carbonate, and DMSO are also effective solvents for many salts and nonpolar molecules; however, unlike water, they are all highly combustible in O₂ atmosphere. Furthermore, 1) acetonitrile exhibits a full solvation layering uniformly for all halide

Table 2. Structures and polarity values of some organic molecules.				
Name	Structure	Dipole moment [D]	Dielectric constant [ϵ]	Ref.
acetonitrile		3.9	37–39	[29]
ethylene carbonate		4.8–4.9	90	[30]
DMSO		4.0–4.3	47	[31]

anions, whereas water exhibits significant molecular clustering and ion-size-dependent limited solvation of halide anions,^[28] 2) ethylene carbonate scales comparatively with water in dielectric constant values, and yet is a disproportionately viscous solvent at room temperature, poorly supporting ionic mobility as a unitary salt matrix; and 3) DMSO displays Lewis acid/base behavior, but without the characteristic autodissociation dynamics found in water.

Another important aspect of water is the high resistance against salt ion pairing in aqueous solutions. The solubility product constants (K_{sp}),^[32] which are indicative of matrix contributions to overcome lattice energies, and hence, cation–anion propensities to segregate out of solution, are nontrivial for a wide variety of salts in water. Salt ion-pairing behavior in water is much lower than that in, for example, organic or ionic-liquid matrices, which typically give rise to ion triplet formation.^[33] Ion triplets can take the form of anion–cation–anion or cation–anion–cation units, and derive from cation–anion interactions dominating over solute–solvent interactions.^[34]

Within a battery, ion pairs and ion triplets are detrimental to cycling performances. Ion pairs remove charge carriers from internal circulation, whereas each negatively charged ion triplet drags one cation from the direction of the applied bias towards the opposite direction. In the case of metal-ion batteries, whenever the cationic contribution to the total current is less than unity, the battery is prone to polarization-induced losses in energy efficiency.^[35] A cationic transference number (the fraction of total charge carried by cations) of unity is thus desirable. Metal cations of simple inorganic salts in aqueous media typically display cationic transference numbers between 0.26 to 0.58, except for protons (≈ 0.8),^[36] whereas metal cations in ionic-liquid media exhibit 0.01 to 0.30, sometimes even reaching negative values under electropolarization.^[37]

Working models to explain ion-pairing and ion-triplet formation phenomena were established by Fuoss, Kraus, Bruce, and Vincent,^[38] who analyzed nonlinear drops in limiting molar conductivities near the infinite dilution limit and deviations from the Kohlrausch law. They also reasoned in the same studies that, owing to stability issues, solvents with dielectric constant of $\epsilon > 10$ had difficulty in supporting associates larger than that of ion triplets in solution; a value well below the threshold of liquid water, and hence, these larger species would be markedly reduced in aqueous batteries.

Conductivity-wise, aqueous electrolytes fall within 10–190 mS cm (at 25 °C) and nonaqueous electrolytes within

< 10 mScm (at 25 °C).^[39] Hence, the high ion mobility within aqueous electrolytes should further afford higher power densities relative to nonaqueous chemistries.

Despite benefits, battery systems with water as a major component may suffer from marked self-discharge and corrosion issues due to, on a case-to-case basis, the absence of a protective solid film of stable integrity, which simultaneously facilitates metal-ion transport, but effectively excludes electronic contact between the electrode surface and bulk water. Furthermore, aggressive volatile or soluble products are typically formed as water decomposes: $\text{H}^+_{(\text{aq})}/\text{OH}^-_{(\text{aq})}/\text{H}_{2(\text{g})}/\text{O}_{2(\text{g})}$. These products can attack the metal bulk, leading to a vicious cycle of progressive degradation.

2. Mechanisms Steering Metal-Ion Electrochemistry in Water

2.1. Effects of dissolved gases

Dissolved O_2 or CO_2 can interfere with the cycling stability of aqueous batteries, due to the redox power of the former and precipitate-forming ability of the latter (especially under high pH conditions). Recent studies have demonstrated improved electrode capacity retention and cycling stability in deaerated electrolytes, relative to that in untreated electrolytes.^[40] Beh et al. demonstrated that dissolved O_2 interfered with the electrochemical stability of dissociated salt species,^[40a] whereas Brousse et al. postulated its role in corroding current collectors.^[41] Li et al.^[41] Luo et al.^[42] et al. made a stepwise improvement in aqueous $\text{LiTi}_2(\text{PO}_4)_3/\text{Li}_2\text{SO}_4/\text{LiFePO}_4$ systems by eliminating oxygen, adjusting pH, and carbon-coating electrodes; this resulted in a jump from 50% capacity retention in the 100th cycle for an as-mixed system to 90% in the 1000th cycle for a pretreated system.^[40b] However, the benefits of deoxygenation are only of a temporary nature,^[19d] because operating beyond the thermodynamic window of aqueous solutions is still bound to generate in situ O_2 over time.

Nonetheless, Butler et al. evaluated four techniques for the immediate removal of dissolved oxygen from water: boiling at 1 atm, boiling under reduced pressure, purging with N_2 , and ultrasonication under reduced pressure.^[42] They found that nitrogen purging for 20–40 min at a flow rate of 25 mL s^{-1} was most effective, and allowed a reduction in O_2 concentrations from 8.5 to 0.2–0.4 ppm, whereas boiling was the least effective.

Adding sacrificial O_2 scavengers that follow an electrochemically irreversible reaction may also improve systems from untoward oxidation of electrodes, for example, persulfates, iodites, ferrous oxide, unsaturated hydrocarbons, sulfites, cobalt(II) amine complexes, benzoacrylates, cobalt-catalyzed nylon embedded in a plastic external casing (OxbarTM), carbonyl hydrazide (carbohydrazide), and hydrazine (hydrazine), as suggested in several patents.^[43] Such controlled-release formulations consume O_2 because they are produced in situ during electrochemical cycling, the basic concept for which has been demonstrated elsewhere earlier.^[44]

On the other hand, an interesting report on manganese–hydrogen batteries demonstrated the use of hydrogen gas as a viable anode active material, that is, through compartmentalized pressurization, H_2 could be maintained in solution (the Henry law) and redox chemistry coupled with an electrolytic manganese dioxide (EMD) resulted in electrodeposition/stripping.^[16] This feat inspired a novel approach for fabricating metal–air batteries, with gaseous molecules as the cathodically active material, for example, O_2 , Cl_2 , and F_2 . However, the effectiveness of such a system would be contingent on an excellent separator because any gas diffusion to the anolyte would spontaneously oxidize the negative electrode material, precluding its participation in battery cycling.^[19e,45]

2.2. Effects of pH

A Pourbaix diagram is a thermodynamic construct that describes the expected physical state of substances under conditions of a certain pH and applied electrochemical potential.^[46] Often expressed relative to the SHE, the predominance regions for each chemical species are constructed based on free energy and Nernstian considerations [Figure 3 and Eqs. (2) and (3)].

Herein, water electrolysis typically sets in at applied potentials that evolve with a negative slope versus pH (see blue dashed lines in Figure 3). Because a low pH signifies high $[\text{H}^+]$ activity and a high pH signifies low $[\text{H}^+]$, according to the Le Chatelier principle, starving a reaction of reactants (e.g., minimizing $[\text{H}^+]$ in $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) hinders equilibria from being perturbed to shift forward. Therefore, a common approach for facilitating metal-ion electrodeposition (a reduction process) to dominate over H_2 emission (another reduction process) is formulating high-pH electrolytes. This transposes the entire voltage stability regime of water to lower values on the SHE scale, and may enable a sustained activation of target redox centers and the desired output voltage.

However, excessive pH manipulation may lead to damaged electrode integrity, for example, active materials, separators, additives, or binders may dissolve due to increased $[\text{OH}^-]$. A high pH also limits the available choices for the positive electrode because ion currents are set in direct competition with O_2 evolution. Carbon coating can protect compounds from dissolution, for example, as applied in manganates^[41,47] and vanadates,^[48] but neutralizes any electrode overpotential advantages against water electrolysis, owing to heightened electronic conductivity at the electrolyte–electrode interface. As far as possible, therefore, an excellent selection of a working pH is still of primary preference to maintain system stability.

Meanwhile, Pourbaix diagrams are often expressed by truncating information related to substantial common ion effects, that is, if a metal is placed under extreme pH conditions, but saturated with its ions. In Figure 3, we highlight modifications in Pourbaix-type equilibria with varying metal-ion concentrations for elemental Mg, Ca, Zn, and Al.

Here, bulk metals are assumed to be of uniform composition and chemical activity of unity. Evidently, each multivalent element behaves differently in the absence of cathodic polariza-

Figure 3. Pourbaix diagrams of a) Mg, b) Ca, c) Zn, and d) Al metals at 25 °C, adapted according to data guidelines from refs. [46,49], and expressed according to varied molal concentrations (numbers in gray indicate exponents in powers of 10) of each ion in aqueous solution. The blue dashed lines indicate the region beyond which water electrolysis occurs. The red dotted lines indicate the potentials for direct metal to ion conversion with electron release ($M \rightarrow M^{n+} + ne^-$) without interference from H^+/OH^- ions.

tion at 25 °C. For Mg, saturated solutions precipitate oxides above a pH of 10.2, but Mg ions remain soluble as $MgOH^+$ at even higher pH for lower ion concentrations. For Ca, the boundary between Ca^{2+} and $CaOH^+$ predominance is dictated by pH alone, regardless of Ca-ion concentrations. For Zn, the

metal forms ZnO under basic conditions, which begins between pH 8.6 and 11 at Zn-ion concentrations as low as 10^{-6} M. For Al, Al_2O_3 is refractory for all concentrations between pH 4.9 and 9.1, and permanently passivated at all $pH > 3$ with increasing $[Al^{3+}]$. In general, the precipitation/passivation regions expand with higher concentration of multivalent ions (M^{n+}) in solution, except for calcium.

At low pH, all of these multivalent element metals would dissolve spontaneously in solution. The driving force for this metal (M) dissolution originates from redox coupling with the hydrogen evolution reaction (HER), as given by Equations (6) and (7):

or redox coupling with dissolved oxygen in solution, as given by Equations (8) and (9):

A smaller voltage difference established by each pair of half-reactions results in a lower driving force for metal corrosion. Based on the Pourbaix diagrams, these minima occur at pH 10.3 for Mg, pH 12.7 for Ca, pH 5.1 for Zn, and pH 2.6 for Al, and should therefore be the theoretical pH for maximum stability as metal anodes of batteries. The corresponding driving potential (ΔV) for proton-driven corrosion at these pH points are 1.7 V for Mg, 2.1 V for Ca, 0.4 V for Zn, and 1.5 V for Al, whereas the corresponding driving potentials (ΔV) for oxygen-driven corrosion at these pH points are 2.9 V for Mg, 3.4 V for Ca, 1.6 V for Zn, and 2.7 V for Al. Hence, any diffuse O_2 in solution is expected to react very strongly with any exposed nascent metal of these elements. Metallic zinc is thermodynamically the most stable in water among the listed examples, and metallic calcium is least stable.

At neutral and basic pH, near the metal surface, metal hydroxides can be dehydrated to precipitate oxide films. The Pilling–Bedworth (PB) ratio [Eq. (10)] predicts whether this oxide film evolves into an adherent, nonporous, and protective shield, which acutely cuts access to corrosion and facilitates release of protons and oxygen.^[50] The PB ratio computes for volume mismatches if a metal layer is converted into its metal oxide [Eq. (10)]. Essentially, a PB ratio less than one gives rise to a porous oxide film, a PB ratio between one and two is suggestive of an effective passivation layer, and a PB ratio greater than two induces oxide spalling, which creates open channels for H^+ and O_2 diffusion.^[51]

$$PB \text{ ratio} = \frac{\text{oxide volume per metal atom}}{\text{metal volume per metal atom}} = \frac{(M'_{\text{oxide}})(\rho_{\text{oxide}})}{n(M'_{\text{metal}})(\rho_{\text{metal}})} \quad (10)$$

in which M' is the atomic or molecular mass, ρ is density, and n is the number of metal atoms per formula unit of its metal oxide.

With the respective PB ratios of Ca (0.6), Mg (0.8), Zn (1.6), and Al (1.3),^[52] and referring back to Figure 3, the corrosion behavior of Zn and Al foils in a battery with only a few drops of electrolyte is therefore predicted to be mostly self-limiting, but not for Ca and Mg. Any Ca metal and Mg metal in pure water will convert spontaneously and completely into Ca(OH)_2 or CaOH^+ and MgO , Mg(OH)_2 , or MgOH^+ over time. Among the four elements, only pH manipulation in a Zn-based battery creates conditions under which $\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Zn}_{(\text{s})}$ can occur within the thermodynamic stability window of free water (see red dotted lines in Figure 3c). This is providing that the interfacial contact between metallic Zn and bulk H_2O forms a uniform ZnO layer, which acts as a metastable semipermeable membrane for Zn^{2+} ions (interstitial diffusion in a crystallographic oxygen-defect environment),^[53] blocking H^+/OH^- species, and results in a high band gap (≈ 3.3 V at 25°C),^[54] blocking electron crossover to water molecules. ■■ok?■■

2.3. Effects of salt concentration and additives

Nonetheless, following the same Le Chatelier argument outlined above, preaddition or presaturation of a solution with the ionic species of a metal may be a strategy for reducing corrosion under conditions at which the working pH cannot be restricted, for example, in the extreme acidic regions. For example, if Al foils are placed in solutions of $\text{Al(NO}_3)_3$ and AlCl_3 at different concentrations, the metal corrosion process is markedly delayed by months (Figure S1 in the Supporting Information). This is contrary to the situation if the same foils are immersed in solutions of pure HNO_3 or HCl , in which the reaction is much faster and occurs within a day. It is therefore important during the evaluation of Pourbaix diagrams to consider unspecified kinetics because any thermodynamically spontaneous process can occur at ultrafast or ultraslow rates, depending on the application timescale. In practice, alkaline Zn/MnO₂ battery manufacturers report saturating KOH electrolytes with ZnO prior to battery assembly, creating a more concentrated Zn-ion reservoir. This accentuates Zn-ion reduction over that of proton reduction, according to the reactions given by Equations (11) and (12), thereby suppressing catastrophic H_2 gassing and retarding Zn corrosion.^[55]

It is worth commenting further on how superconcentration can alter the properties of aqueous solutions. Water behaves as a solvent with acidity/basicity determinable by solute ions within the estimable range $-1.74 < \text{pH} < 15.74$ at room temperature. The limits consider exaggerated situations in which the entire volume of liquid water is saturated with protons (as H_3O^+) or hydroxyl (OH^-) ions in one-to-one pairing with molecular H_2O , neglecting counterion effects and the fact that

physical referencing against the SHE (H_2 at 1 atm) becomes moot near the extreme limits (below pH 0 and above pH 14).^[56] Surpassing the limits of this region, water behaves as a buffering solute,^[57] as evidenced by its deactivation of solid acids^[58] and superacids,^[56,59] and marked suppression of ion dissociation.^[59a,60] Thus, the thermodynamic onset for the electrolytic decomposition of water in acidic/basic media can be inferably modeled only between $-1.74 < \text{pH} < 15.74$.

Examples of superconcentrated solutions include a Clerici solution^[61] of $\text{Ti(HCO}_2)_2/\text{Ti(C}_3\text{H}_3\text{O}_4)_4$ with a salt/water molar ratio of 9:11,^[62] a surfactant-stabilized hydrochloric acid liquid (5.7 acid/1 H_2O),^[59a] 98 wt% sulfuric acid (9 acid/1 H_2O),^[63] and 52 wt% NaOH (1 base/2 H_2O).^[60,64]

Apart from providing a counterbalancing negative charge to cations, electrolyte cations/anions may exert a buffering effect. Here, the buffering capacity is determinable through the Henderson–Hasselbach equation and reported pK_a and K_{sp} values.^[65] However, it is important to note that the groups of Wessells and Dushina have already demonstrated that actual pH-manipulated electrochemical windows can deviate from this expected Hess behavior, especially at extreme pH values (cf. Figure S2 in the Supporting Information).^[118]

The hydration interactions and polarizabilities of each supporting cation or anion are also postulated to affect the composition of the electrical double layer at the solid–liquid interface, exerting an influence over the applied potentials at which metal-ion reactivity or water reactivity is initiated.^[66] If salts are dissolved to aqueous saturation, an apparent enhancement in the electrochemical stability of both water and electrode material may be observable. For instance, in the case of zinc hexacyanoferrate (ZnHCF) electrodes, electrochemical cycling in a ZnSO_4 electrolyte allows for long-term cycling with minimal degradation, compared with when cells are cycled with $\text{K}_3\text{Fe(CN)}_6$, Na_2SO_4 , and K_2SO_4 electrolytes.^[66d] In unsuitable electrolytes, metal-to-ligand transition bands in the electrolyte UV/Vis spectra arising from the dissolution of $[\text{Fe(CN)}_6]^{3-}$ from the electrode into the liquid demonstrate greater ZnHCF stability in a zinc-containing electrolyte (Figure 4).

Figure 4. UV/Vis spectra of electrolyte solutions before (full detail) and after cycling (inset) with $\text{Zn}_3[\text{Fe(CN)}_6]_2$ (ZnHCF electrodes): the aqueous electrolytes consist of $\text{K}_3\text{Fe(CN)}_6$ (black), Na_2SO_4 (red), K_2SO_4 (blue), and ZnSO_4 (green). The photographs show the electrolytes (in the same order from left to right) before (top) and after the addition of Fe^{2+} (middle) or Fe^{3+} (bottom) as indicators of ZnHCF decomposition. Reproduced with permission from ref. [66d] Wiley-VCH, copyright 2014.

Taking this further, the groups of Yamada and Xu[■] have shown that, by taking advantage of electrolytic decomposition of bulky anion moieties (e.g., ionic liquids), an extended electrochemical voltage window is sustainably attainable through kinetic passivation, enabling metallic electrodeposition/stripping even for the most electropositive element: Li. They further show that a certain concentration threshold is necessary for this effect to appear, as illustrated in the galvanostatic cycling curves in Figure 5, for a pair of $\text{LiCoO}_2/\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes. Although they term 21 M[■] ok?[■] LiTFSI as a water-in-salt preparation, the molar ratio of Li+TFSI to H_2O is still less than 1:1.

Figure 5. Effect of electrolyte concentration on the cyclability of a $\text{LiCoO}_2/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell by using a) a dilute solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)/ H_2O at 1.2 M[■] and b) a concentrated water-in-bisalt melt of $\text{N}(\text{SO}_2\text{CF}_3)_2\text{Li}/\text{N}(\text{SO}_2\text{CF}_3)_2\text{Li}$. Reproduced with permission from ref. [6a] Chemistry Society of Japan, copyright 2017.

Yamada[■] argues that this behavior is not evident with concentrated aqueous electrolytes of inorganic Li salts (e.g., LiNO_3 and Li_2SO_4) at room temperature, for example, due to low saturation points ($\text{LiNO}_3 < 20$ mol%, $\text{Li}_2\text{SO}_4 < 5$ mol%), and indeed the structural matrix of bulk water is only locally distorted at these levels of concentration, as discussed in detail in various reports.^[67] The evolution of Raman bands corresponding to alkali-metal-water interactions shows a steady increase in wavenumber with respect to increased salt concentration, which suggests a more polar hydration sphere enclosing the cation.^[67d] In the case of LiNO_3 , concentrations between 1.5 and 7 M exhibit ion pair dynamics dominated by solvent mediation, whereas concentrations greater than 7 M suggest the onset of contact ion pairing (Scheme 2).^[67d] Vollmar reported that varied extents of desolvation might occur in hydrated Mg, Ca, Zn, and Al ions upon forming ion pairs near

Scheme 2. Evolution in ion-pairing dynamics with increasing salt concentrations.

saturation thresholds, depending on the identities of both the cation and anion.^[68]

However, Zheng and co-workers later showed that a mild temperature elevation from 25 to 35 °C immensely raises the solubility of LiNO_3 in water from 12 (as per Yamada et al.) to 22 M.^{[67]■} They further showed that cheap LiNO_3 salts could be used to cycle aqueous batteries on a par with, or even better than, expensive LiTFSI-based ionic liquids, due to a polymer-like aggregation of $\text{Li}-\text{O}-\text{Li}-\dots$ atoms, which begins at a salt-to-water molar ratio of 1:2.5, affording an electrolyte stability window of 2.55 V (Figure 6). They demonstrated further, through molecular dynamics simulations and thermal titration experiments, that this extended stability could be attributable to thermodynamic effects by only 0.02 V at most, with kinetic factors accounting for the bulk of the electrochemically measured 0.7 V augmentation.

Figure 6. Enhancement of the electrochemical stability window of an aqueous LiNO_3 electrolyte through a superconcentration regime at 35 °C, enabling a polymer-like networking of $\text{Li}-\text{O}-\text{Li}-\dots$ atoms. Reproduced with permission from ref. [67e] Elsevier, copyright 2018.

Passivation is effected only on certain substrates, with platinum substrates conferring minimal protection against water decomposition (Figure 7). Specifically, this passivation evolves with increasing effectivity, according to the trend $\text{Pt} < \text{SUS}$ stainless steel $< \text{Li}_4\text{Ti}_5\text{O}_{12} < \text{Zn} < \text{Al}$.^[6a] However, the influence of the substrate on limiting the practical stability window of aqueous electrolytes is markedly reduced upon adding surfactants at the critical micellar concentration (CMC), as illustrated by an extended water stability window on Ti electrodes and even on Pt electrodes upon the addition of sodium dodecyl sulfate (SDS) to aqueous electrolytes (Figure 8 and Figure S3 in the Supporting Information), wherein Hou et al.^[69a] and Sun et al.^[69b] demonstrate the effect of SDS on aqueous solutions of $\text{Na}_2\text{SO}_4/\text{ZnSO}_4$ and $\text{Li}_2\text{SO}_4/\text{ZnSO}_4$, and, as briefly illustrated in the Supporting Information, AlCl_3 . It has been further reported by empirical studies of the hydrolysis of Al^{3+} ions that SDS suppresses hydrolytic multimers, which promotes the existence of only $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^{2+}$ in solution.^[70]

Other electrolyte additives suggested for inhibiting the HER include citric acid and tartaric acid, whereas electrode surface modifications for the same purpose with Bi_2O_3 , H_3BO_3 , $\text{Ca}(\text{OH})_2$, In_2O_3 , Ga_2O_3 , $\text{In}(\text{OH})_3$, $\text{In}_2(\text{SO}_4)_3$, SnO_2 , CdO , PbO , Ti_2O_3 , silicates, HgO , Al_2O_3 , and tetraphenylporphyrin have also been suggested.^[71]

Figure 7. a) Extending the effective electrochemical window by kinetic passivation, and b) stability window behavior of water-in-bisalt electrolytes on the surface of various working electrodes. Reproduced with permission from ref. [6a, b] Chemistry Society of Japan, copyright 2017.

Figure 8. Linear sweep voltammetry of an electrolyte consisting of a 1 M solution of $\text{ZnSO}_4/1 \text{ M Na}_2\text{SO}_4$ without SDS surfactant (blank electrolyte), and with SDS surfactant (at the CMC), obtained by using Ti grid electrodes versus Ag/AgCl at 10 mV s^{-1} , but referenced to the SHE, along with a magnified view of the cathodic scan between -2 and 0 V, and a magnified view of the anodic scan between 0 and 2.5 V. Reproduced with permission from ref. [69a] Royal Society of Chemistry, copyright 2016.

3. Trends in Enabling Aqueous Electrolytes for Multivalent-Ion Batteries

3.1. Magnesium ions

At the beginning of the year 2000, the elements most expected to provide electrochemistry that approximated Li were Na and Mg; the former is in the same elemental group and the latter due to inferences from the diagonal rule in the periodic table. Sodium is inferior to lithium, in terms of either how low the anode voltage can be pushed or specific capacities.

Magnesium promises a twofold multiplier in volumetric energy density (3833 mAh cm^{-3} theoretically for Mg vs. 2046 mAh cm^{-3} for Li metal). The metallic redox voltage of -2.36 V (vs. SHE), however, is problematic for electroplating in aqueous solutions, and hence, achieving rechargeable Mg-metal batteries. For this, a solid electrolyte, such as inorganic $\text{Mg}(\text{BH}_4)(\text{NH}_2)$, has proven that reversible Mg plating/stripping is possible, albeit with a dismal $<50\%$ roundtrip efficiency and operation at $>150^\circ\text{C}$, whereas polyethylene oxide–Mg salt composites have shown mostly anionic charge transport rather cationic.^[72]

Although $\text{Mg}(\text{ClO}_4)_2$, $\text{Mg}(\text{NO}_3)_2$, or $\text{Mg}(\text{C}_2\text{F}_6\text{NO}_4\text{S}_2)_2$ in glyme, THF, and acetonitrile solvents are commonly employed in electrochemical testing of high-voltage Mg cathodes, Canepa et al. noted caveats, stating that complex isolation setups were required for Mg electrochemistry at the stripping/depositing electrodes.^[74] On the other hand, most successful exploits in Mg-metal reversibility have reported the use of a solution of $\text{Mg}(\text{PF}_6)_6 \cdot (\text{CH}_3\text{CN})_6$ in mixtures of $\text{CH}_3\text{CN}/\text{THF}$,^[75] Grignard etheral complexes,^[76] carboranes, and borohydrides,^[77] but without addressing the problem of electrolyte corrosivity.

Recently, three breakthroughs have been made: 1) anode pretreatment with a thermally cyclized polyacrylonitrile in $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, to enable cycling in a $\text{Mg}/\text{V}_2\text{O}_5$ full cell in an aqueous carbonate-based electrolyte;^[9b] 2) water-activity tuning between the electrolyte and VOPO_4 -based intercalation electrode to unlock capacities of 80 mAh g^{-1} (vs. $<10 \text{ mAh g}^{-1}$ for mismatched electrolyte/electrode water activities);^[73a] and 3) a demonstration of the mechanism of self-corrosion of Mg anodes,^[73b] wherein contaminant metallic species, which plate at a higher potential than that of Mg, deposit locally upon loss of cathodic protection of the low-voltage Mg bulk, inducing focused current lines and accelerated self-corrosion. Complexing agents have been suggested to aid in arresting this process (Figure 9).

3.2. Calcium ions

Calcium plating had been presumed to be unviable due to the lack of a divalent-cation transport mechanism through a passivation layer that arises at Ca-metal/electrolyte interfaces.^[78] Palacin et al. were the first to engineer a Ca-based SEI that supported Ca^{2+} migration at a moderate temperature of 75°C .^[79] Since then, reversible Ca electrochemistry has been demonstrated to be possible in $\text{Ca}(\text{ClO}_4)_2$,^[79,80] $\text{Ca}(\text{C}_2\text{F}_6\text{NO}_4\text{S}_2)_2$,^[81] $\text{Ca}(\text{CF}_3\text{SO}_3)_2$,^[82] and $\text{Ca}(\text{BF}_4)_2$.^[79] In parallel, Ca^{2+} in organic sol-

Figure 9. Mechanism of self-corrosion in Mg anodes wherein even ppm-scale metallic impurities induce locally focused currents with deleterious electrochemical consequences. Reproduced with permission from ref. [73] under a Creative Commons Attribution 4.0 International License.

vents, namely, SOCl_2 , γ -butyrolactone, acetonitrile, DMF, propylene carbonate, ethylene carbonate, THF, and methyl formate, has shown no plating activity.^[72]

Intercalation chemistry has been demonstrated in superconcentrated aqueous $\text{Ca}(\text{NO}_3)_2$ systems.^[23,83] Shielding of the hard ion center by water molecules has been inferred to be essential for any Ca^{2+} intercalation to occur in oxide lattices. To date, the highest performance demonstrated has been for a polyimide/ $2.5 \text{ M Ca}(\text{NO}_3)_2/\text{Cu}$ hexacyanoferrate system operating at 10°C for 1000 cycles with 88% capacity retention (nominal energy density of 60 Wh kg^{-1}).^[12] There is also a movement to explore heavy Grignard reagents (RCaX ; R is alkyl or phenyl and X is iodide or bromide) as an alternative route of electrolyte design, but such reagents are highly reactive with water.^[84]

3.3. Zinc ions

Metallic zinc anodes undergo facile electrodeposition/stripping in both nonaqueous and aqueous electrolytes, developing a passivation layer during operation that is stable, but not refractory.^[85] The ease in assembly of alkaline Zn– MnO_2 systems, their relatively low cost, and reliable capacities have led to their widespread commercialization over the years, but mostly for primary battery usage only.

Whereas popular efforts to make metallic-Zn batteries rechargeable have resulted in a wide compilation of electrolytes based on halides, oxoanions, and molten salts,^[87] there have been three recent findings with key implications for long-term cycling.

First, high-pH ($\text{pH} > 12$) electrolytes tend to form thick insulating ZnO layers and favor Zn dendritic penetration of separators, as opposed to mild-pH electrolytes, for example, comparing galvanostatic cycling in 40% KOH electrolyte versus in $2 \text{ M ZnSO}_4 + 0.1 \text{ M MnSO}_4$ (Figure 10).^[15c] Extended cycling stabilities ($>90\%$ after >100 cycles) were demonstrated by various groups with metallic Zn anodes in electrolytes with $3 < \text{pH} < 7$.^[15a,20,88]

Figure 10. Cycling behavior of Zn/MnO₂ batteries with either 40% KOH electrolyte (red) or 2 M ZnSO₄ + 0.1 M MnSO₄ electrolyte (blue). Reproduced from ref. [15c] with permission from Macmillan Publishers Ltd.: Nature Energy, copyright 2016.

Hong et al. investigated cathodic overpotential dynamics and varying zincate concentrations (e.g., Zn(OH)₂), and found that a low zincate concentration and small cathodic overpotential restricted dendritic zinc propagation.^[89] Indeed, Garcia et al. demonstrated the possibility of eliminating Zn dendrites altogether, simply by using pulsed charging protocols.^[90] The general consensus is that Zn-dendrite formation in alkaline environments is stimulated through an interplay between dissolution-precipitation and mass-diffusion limitations of pore-trapped [OH⁻], and therefore, an [OH⁻] gradient [Eq. (13)].

In turn, competitive electrodeposition between Zn(OH)₄²⁻ and ZnO aggravates current-density focusing, according to the reactions given in Equations (14) and (15).

The [OH⁻] gradient is essentially a pH gradient and, with respect to the *E* versus pH diagram for Zn (Figure 3c), this means that the Nernst equilibria above metallic Zn_(s) is being perturbed nonuniformly by a fixed charging voltage. Hence, Zn plating is favored more in certain regions and less in certain regions, which favor dendrites.

On the other hand, findings by Trocoli and La Mantia on cycling copper hexacyanoferrate cathodes with Zn metal anodes in 20 mM ZnSO₄ suggested that overpotential kinetics in smooth Zn foils favored hydrogen evolution and local pH changes, resulting in orphaned ZnO, which was detrimental to battery cycling, but which could be mitigated by using rough Zn anodes.^[119] Furthermore, concentrated electrolyte formulations with bulky anions (e.g., 3 M Zn(CF₃SO₃)₂ and 1 M Zn(TFSI)₂ + 20 M LiTFSI) have been postulated to form close ion pairs of Zn-anion species, effectively suppressing the formation of [Zn(H₂O)₆]²⁺ complexes and H₂ evolution kinetics.^[15d,88c]

Second, Kundu et al. recently reported that the charge-transfer resistance for Zn²⁺ in a hydrated V₃O₇ lattice varies greatly between using a nonaqueous (0.25 M Zn(CF₃SO₃)₂ in acetonitrile) and an aqueous (1 M ZnSO₄ in H₂O) electrolyte.^[86] The former leads to a low cumulative charge storage of 150 mAh g⁻¹ compared with 375 mAh g⁻¹ for the latter, with stark contrast in capacity retentions (Figure 11). The irreversibility in nonaqueous electrolytes is attributed to an activation barrier that is not due to a slow Zn²⁺ solid-state diffusion process within the lattice, but due to interfacial desolvation penalties in crossing the electrolyte-electrode interface, wherein dan-

Figure 11. Cycling behavior of Zn/V₃O₇·*n*H₂O cells in 1 M ZnSO₄/H₂O electrolyte (a,b) and 0.25 M Zn(CF₃SO₃)/acetonitrile electrolyte (c,d). Reproduced from ref. [86] with permission from Macmillan Publishers Ltd.: Nature Energy, copyright 2018.

gling bonds at the V_2O_5 crystalline edge are facily charge compensated for by H_2O molecules sheathing Zn^{2+} ions, but not by $CF_3SO_3^-$ /acetonitrile. This dramatically lowers the activation energy and leads to at least a 10-fold reduction in charge-transfer resistance. Similar effects have been reported for β - MnO_2 and layered V_2O_5 , wherein co-intercalated water buffers the entry of hard Zn^{2+} ions or aids in a crystallographic transformation to layered structures that favor facile ion solid-state diffusion.^[88a,91]

Third, notably, evidence of the formation of $Zn_4(SO_4)(OH)_6 \cdot nH_2O$ (as opposed to Zn intercalation as the cathodic charge-storage mechanism) has been routinely detected through diffraction techniques, but there are disagreements in prior reports about whether this is initiated by a change in pH or not.^[92] On the other hand, proton co-intercalation has been detected for multiple-cation (Zn^{2+}/Li^+ or Zn^{2+}/Mn^{2+}) electrolytes, but not single-cation (Zn^{2+}) electrolytes.^[93] The use of multiple cation electrolytes has been further shown to promote the benefits of better cycling capacities and dendrite suppression.^[88c,92a,93a,94]

3.4. Aluminum ions

Battery electrolytes with Al^{3+} charge carriers can be divided into two classes: chlorides and non-chlorides; the former encompasses most of the current literature. The most remarkable of these, to date, are $AlCl_3$ in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) and $AlCl_3$ in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) systems, which are Lewis acidic or basic, depending on the prepared ratio between $AlCl_3$ and the large organic moiety (EMIM or BMIM). The reported mechanisms for Al^{3+} electrochemical activities vary widely, with four main propositions.

The first mechanism is attributed to chloride-facilitated casing corrosion, that is, a working electrode of V_2O_5 deposited upon a stainless-steel substrate demonstrates remarkable redox peaks during cyclic voltammetry in the presence of $AlCl_3$ /[EMIM]Cl, whereas replacing the substrate with Pt led to zero electrochemical activity.^[95] Subsequent energy-dispersive X-ray spectroscopy (EDAX) analysis of the separator material for the former indicated ion transfer of Fe and Cr elements to the separator material (Figure 12), which was consistent with a scenario for stainless-steel corrosion.^[95]

The second mechanism attributes ion currents to Al^{3+} surface deposition and/or deep lattice intercalation with $AlCl_3$ or $Al_2(SO_4)/Zn(CH_3COO)_2$ aqueous electrolytes. Holland et al. initially found poor specific capacities for TiO_2 particles (actual 10 mA h g^{-1} vs. theoretical 335 mA h g^{-1}), leading them to propose that the reaction $TiO_2 + xAl^{3+} + 3xe^- \rightleftharpoons Al_xTiO_2$ occurs only on surface sites.^[10] Lahan and Das later demonstrated this low specific capacity to be an artefact of poor electronic percolation within the active material,^[96] that is, they were able to achieve an enhanced capacity (52 mA h g^{-1}) by compositing TiO_2 nanoparticles with conductivity-enhancing graphite, and confirmed lattice changes to match with Al_2TiO_5 and $Al_2Ti_7O_{15}$ phases through XRD and TEM analyses.^[96]

Figure 12. Cyclic voltammograms of V_2O_5 /Al cells with 1.2:1 (mol/mol) $AlCl_3$ /[EMIM]Cl on a) stainless-steel cathode substrate, and b) Pt cathode substrate. c) EDAX results for the separator material in a), showing evidence of Fe/Cr from stainless-steel corrosion. Reproduced with permission from ref. [95] The Electrochemical Society, copyright 2013.

The third mechanism rationalizes that Al^{3+} redox shifts to proceed through halometalate disproportionation ($4Al_2Cl_7^- + 3e^- \rightarrow Al + 7AlCl_4^-$), as demonstrated by Muñoz-Torrero et al. on three different substrates: stainless steel, aluminum, and expanded graphite.^[97] They showed the marked tendency of electrodepositing an Al "buffer" layer and flakes over prolonged cycling over these three substrates (Figure 13). They further demonstrated that a 3D electrode morphology promoted better power densities for charge/discharge, and that ease of Al nucleation on the substrate was key to maintaining low polarization effects (i.e., $\approx 100\text{ mV}$ in the case of stainless steel). In particular, for a graphite cathode, the solubility limit of $AlCl_3$ in [EMIM]Cl has been demonstrated to limit the anode capacity.^[98] Reversible Al-graphite batteries with [EMIM]Cl,^[99] urea,^[100] or $NaAlCl_4$ melt^[101] electrolytes have also been reported, and operate on the same principle.

The fourth mechanism describes dual-ion batteries in which the Al^{3+} cation directly deposits as Al, whereas the ClO_4^- anion reversibly intercalates into the graphene structure, owing to a soft and polarizable electron cloud.^[102] Whether or not discrete three-electron-transfer events occur, however, has not been empirically proven yet,^[103] and may explain the low operating voltages (1–1.5 V) exhibited by battery prototypes.

The $AlCl_3$ /ionic-liquid electrolytes are sensitive to water, exhibiting H_2 evolution at a more positive voltage onset for as low a H_2O concentration as 7500–10000 ppm, which implies that their manipulation in battery assembly lines should be restricted to controlled dry environments.^[104] Nonetheless, water has been shown to inhibit dendrite formation in Ni electrodeposition by using choline chloride/urea mixtures, which display a compact and corrosion-resistant electrodeposited film by using an electrolyte containing 6 wt % water.^[105]

Non-chloride electrolytes have also been reported for Al-ion batteries, including aluminum bis(trifluoromethanesulfonyl)i-

Figure 13. Cyclic voltammograms of $\text{AlCl}_3/\text{[BMIM]Cl}$ on a) stainless steel, b) aluminum, and c) expanded graphite electrodes, and corresponding SEM images before (d,f,h) and after (e,g,i) prolonged electrodeposition of Al on stainless steel (d,e), aluminum (f,g), and expanded graphite electrodes (h,i). Reproduced with permission from ref. [97] Elsevier, copyright 2018.

amide, which exhibits a voltage window of 3.6 V (in acetonitrile solvent)^[106] and aluminum trifluoromethanesulfonate, which exhibits a voltage window of 3.5 V (in *N*-methylacetamide/urea).^[107] The use of sulfate-based electrolytes creates pitting corrosion on Al metal, whereas the use of nitrate-based electrolytes protects Al metal, albeit at the expense of ion-selective transport.^[108] Fluoride ions are reported to induce uniform corrosion of aluminum in sulfuric acid,^[109] whereas the electrochemical stability windows of $\text{AlCl}_3/\text{[BMIM]X}$ (X is a halide) narrow according to the progression $\text{X} = \text{Cl}^-$ (5.5 V) > Br^- (5.1 V) > I^- (4.7 V).^[110]

4. Summary and Outlook

Water is a notorious catalyst for both formation and degradation reactions, and functions as both an active and spectator species in electrolyte formulations. However, its physicochemical behavior can be strongly influenced by solute species dissolved within. This Review has outlined mechanisms by which dissolved gases, pH, salt concentration, ion identities, and additives critically direct the electrochemistry of aqueous electrolytes in multivalent-ion batteries.

Notably, we have mentioned a strategy for preventing the propagation of short-circuiting dendrites: the use of multiple cations for forming electrostatic ion shields to negate focused metal-ion electrodeposition (as induced by a higher aspect ratio of dendrite nucleation) is a simple, yet elegant, and efficient strategy demonstrated elsewhere.^[111] The supporting cation must also have an electrodeposition potential much lower than that of the main cation in aqueous solvent, for example, Li^+ ions ($E^\circ_{\text{Li}^+/\text{Li}} = -3.04$ V vs. SHE) as supporting ions for Zn^{2+} ions ($E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76$ vs. SHE).

However, the presence of foreign-element ions that electrodeposit at more positive potentials (e.g., Fe^{2+} in the presence of Mg^{2+} : $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.45$ V vs. SHE, $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37$ V vs. SHE) create conductive islands, which do not strip uniformly with the bulk metal anode.^[112] The plated mass of this foreign element focuses a stripping current around its vicinity, leading to a form of localized microgalvanic corrosion and loss of active mass. The incorporation of this foreign element into the electrolyte should therefore be avoided, even at ppm levels, or neutralized. This is a major challenge, given that many anions (chlorides, nitrates, sulfates, fluorides, and bulky moieties of high-performance ionic liquids) inevitably facilitate corrosion of stainless-steel components of battery casings, to some extent. Furthermore, self-corrosion side reactions of metallic anodes arising from foreign-element metal impurities are expected to intensify with progressively lower anodic voltage, namely, $\text{Zn} < \text{Al} < \text{Mg} < \text{Ca} < \text{Li}$.

For the crystallographic engineering of layered-host battery materials for multivalent-ion intercalation, the interplanar lattice spacing requirement can be surmised from the radii of hydrated cations (Figure 14). Table 3 provides a summary of the average ionic radii of H_2O -hydrated cations. For low atomic numbers within a chemical group, water molecules can cause the radius of the hydrated ion to be as high as 14 times that of the unhydrated ion. Among alkali-metal ions, only the hydration shell of Li extends to two layers; the rest have weak interactions with a monolayer of solvating water, as determined by means of large-angle X-ray scattering and double-difference IR spectroscopy.^[113]

Enveloping H_2O can help to shield hard di- or trivalent cations from strongly polarizing Janus-type dangling bonds at the

Figure 14. Trends in the average radii of cations in unhydrated and hydrated states. Adapted from ref. [114] with permission from Prof. B. Railsback.

Table 3. Effective ionic radii in aqueous media, considering one ion unit and its hydration shell.

	Hydrated radius ^[a] [Å]	Hydrated radius ^[b] [Å]	Hydrated radius ^[c] [Å]
Li ⁺	3.82	1.95	1.95–2.28
Mg ²⁺	4.28	2.10	2.00–2.15
Ca ²⁺	4.12	2.46	2.33–2.70
Zn ²⁺	4.30	2.08	2.08–2.17
Al ³⁺	4.75	1.89	1.87–1.90

[a] M–O covalent radius + oxygen ion (O²⁻) radius of 1.4 Å (data compiled from ref. [114b]). [b] M–O covalent radius (data compiled from ref. [115]). [c] M–O covalent radius (data from extended X-ray absorption fine structure experiments reported in ref. [116]).

edge terminations of crystal lattice planes.^[117] However, a higher valence of the multivalent ion results in a larger hydration shell. The effect of this on ionic migration can be estimated from the Einstein–Smoluchowski relationship [Eq. (16)]:

$$D = \frac{\mu_q k_B T}{q} = \frac{k_B T}{6\pi\eta r} \quad (16)$$

in which, for a charged particle, D is the diffusion constant, μ_q is its electrical mobility, q is its charge, k_B is the Boltzmann constant, T is the absolute temperature in Kelvin, η is the dynamic viscosity, and r is the radius of the sphere.

By approximating η and T to be relatively constant for an aqueous environment, the quantitative diffusion values have an inverse relationship with the effective hydrated radii of the cations. Nevertheless, the variations scale within an order of magnitude (30% at most between Li⁺, Mg²⁺, Ca²⁺, Zn²⁺ and Al³⁺); therefore, the kinetics of these hydrated ions in liquid water should not vary much. However, a higher valency of the metal ion results in a more intimate H₂O–metal ion solvation interaction, and more dramatic differences between multivalent-ion desolvation behavior in aqueous and nonaqueous electrolytes can be expected. Indeed, recent reports suggest that aqueous-electrolyte batteries can perform on a par with, if not even better than, nonaqueous-electrolyte batteries, precisely due to better performance against rate-limiting desolvation penalties at the electrode–electrolyte interface. Nonetheless, partial desolvation may still occur, whereas complete desolvation is quite unlikely for lattice-intercalation mechanisms involving multivalent ions.

This Review further consolidates several strategies for extending the electrolyte voltage window. We find that the use of superconcentration/saturation strategies does not appreciably alter the half-cell potentials of the active materials, but facilitates a wider operating voltage window of the electrolyte in certain cases. Furthermore, aqueous-electrolyte batteries based on Mg, Ca, and Al metal anodes are feasible only with the use of interfacial kinetic controls, due to their inherent thermodynamic instability in contact with water. Interface-modifying treatments, in particular, that is, in situ or ex situ formation of an artificial SEI, are emerging as a challenging and exciting field of strategic electrolyte development to enable high energy density in multivalent-ion batteries.

With the transition of multivalent-ion aqueous electrochemistry from traditional primary battery applications to rechargeable battery applications, various opportunities for powering smart grids, rugged portable electronics, low-cost energy-storage solutions are on the horizon; the main advantages are superior volumetric capacity and better manufacturing cost prospects compared with traditional LIBs.

Acknowledgements

This work was financially supported by the National Research Foundation of Singapore (NRF) Investigatorship award number: NRFI2017-08/NRF2016NRF-NRFI001-22. W.M. thanks A. Nagasubramanian (TUM-CREATE, Singapore) and P. Fischer (Technical University of Munich, Germany) for fruitful discussions.

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkali metals · electrochemistry · multivalent ions · solvent effects · water chemistry

- [1] a) Z. P. Cano, D. Banham, S. Ye, A. Hintennach, J. Lu, M. Fowler, Z. Chen, *Nat. Energy* **2018**, *3*, 279–289; b) X. Chen, H. Zhang, Z. Xu, C. P. Nielsen, M. B. McElroy, J. Lv, *Nat. Energy* **2018**, *3*, 413–421.
- [2] a) “Chinese battery maker will soon surpass Tesla capacity”, can be found under <http://www.scmp.com/tech/science-research/article/2131563/chinese-battery-maker-will-soon-surpass-tesla-capacity>, accessed ■■■ please provide date■■■; b) J. Speirs, M. Contestabile, Y. Houari, R. Gross, *Renewable Sustainable Energy Rev.* **2014**, *35*, 183–193; c) C. Xu, W. Zhang, W. He, G. Li, J. Huang, H. Zhu, *Environ. Sci. Pollut. Res.* **2017**, *24*, 20825–20830; d) E. A. Olivetti, G. Ceder, G. G. Gaustad, X. Fu, *Joule* **2017**, *1*, 229–243; e) H. Hao, Z. Liu, F. Zhao, Y. Geng, J. Sarkis, *Resour. Policy* **2017**, *51*, 100–106.
- [3] a) F. Larsson, P. Andersson, B. E. Mellander, *Batteries* **2016**, *2*, 9; b) F. Larsson, P. Andersson, P. Blomqvist, B. E. Mellander, *Sci. Rep.* **2017**, *7*, 10018; c) M. Chen, D. Zhou, X. Chen, W. Zhang, J. Liu, R. Yuen, J. Wang, *J. Therm. Anal. Calorim.* **2015**, *122*, 755–763.
- [4] J. Janek, W. G. Zeier, *Nat. Energy* **2016**, *1*, 16141.
- [5] a) J. M. Tarascon, *Nat. Chem.* **2010**, *2*, 510–510; b) O. Egbue, S. Long, *EMJ-Eng. Manage. J.* **2012**, *24*, 52–62; c) D. Ciekemans in *The Geopolitics of Renewables* (Ed.: D. Scholten), Springer International Publishing, Cham, **2018**, pp. 37–73.
- [6] a) Y. Yamada, A. Yamada, *Chem. Lett.* **2017**, *46*, 1056–1064; b) Y. Yamada, K. Usui, K. Sodeyama, S. Ko, Y. Tateyama, A. Yamada, *Nat. Energy* **2016**, *1*, 16129; c) C. Y. Yang, J. Chen, T. T. Qing, X. L. Fan, W. Sun, A. von Cresce, M. S. Ding, O. Borodin, J. Vatamanu, M. A. Schroeder, N. Eidson, C. S. Wang, K. Xu, *Joule* **2017**, *1*, 122–132; d) F. Beck, P. Ruetschi, *Electrochim. Acta* **2000**, *45*, 2467–2482.
- [7] M. Armand, J. M. Tarascon, *Nature* **2008**, *451*, 652–657.
- [8] a) R. S. Kühnel, D. Reber, C. Battaglia, *ACS Energy Lett.* **2017**, *2*, 2005–2006; b) L. M. Suo, O. Borodin, Y. S. Wang, X. H. Rong, W. Sun, X. L. Fan, S. Y. Xu, M. A. Schroeder, A. V. Cresce, F. Wang, C. Y. Yang, Y. S. Hu, K. Xu, C. S. Wang, *Adv. Energy Mater.* **2017**, *7*, 1701189; c) K. Nakamoto, R. Sakamoto, M. Ito, A. Kitajou, S. Okada, *Electrochemistry* **2017**, *85*, 179–185.
- [9] a) F. Wang, X. L. Fan, T. Gao, W. Sun, Z. H. Ma, C. Y. Yang, F. Han, K. Xu, C. S. Wang, *ACS Cent. Sci.* **2017**, *3*, 1121–1128; b) S. B. Son, T. Gao, S. P. Harvey, K. X. Steirer, A. Stokes, A. Norman, C. S. Wang, A. Cresce, K. Xu, C. M. Ban, *Nat. Chem.* **2018**, *10*, 532–539.
- [10] A. Holland, R. D. McKerracher, A. Cruden, R. G. A. Wills, *J. Appl. Electrochem.* **2018**, *48*, 243–250.

- [11] D. W. Su, A. McDonagh, S. Z. Qiao, G. X. Wang, *Adv. Mater.* **2017**, *29*, 1604007.
- [12] S. Gheyhani, Y. L. Liang, F. L. Wu, Y. Jing, H. Dong, K. K. Rao, X. W. Chi, F. Fang, Y. Yao, *Adv. Sci.* **2017**, *4*, 1700465.
- [13] L. Sanz, D. Lloyd, E. Magdalena, J. Palma, K. Kontturi, *J. Power Sources* **2014**, *268*, 121–128.
- [14] L. Y. Zhang, C. K. Zhang, Y. Ding, K. Ramirez-Meyers, G. H. Yu, *Joule* **2017**, *1*, 623–633.
- [15] a) C. J. Xu, B. H. Li, H. D. Du, F. Y. Kang, *Angew. Chem. Int. Ed.* **2012**, *51*, 933–935; *Angew. Chem.* **2012**, *124*, 957–959; b) N. Zhang, F. Y. Cheng, Y. C. Liu, Q. Zhao, K. X. Lei, C. C. Chen, X. S. Liu, J. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 12894–12901; c) H. L. Pan, Y. Y. Shao, P. F. Yan, Y. W. Cheng, K. S. Han, Z. M. Nie, C. M. Wang, J. H. Yang, X. L. Li, P. Bhattacharya, K. T. Mueller, J. Liu, *Nat. Energy* **2016**, *1*, 16039; d) C. Xia, J. Guo, P. Li, X. X. Zhang, H. N. Alshareef, *Angew. Chem. Int. Ed.* **2018**, *57*, 3943–3948; *Angew. Chem.* **2018**, *130*, 4007–4012.
- [16] W. Chen, G. Li, A. Pei, Y. Li, L. Liao, H. Wang, J. Wan, Z. Liang, G. Chen, H. Zhang, J. Wang, Y. Cui, *Nat. Energy* **2018**, *3*, 428–435.
- [17] a) M. Asnani, S. Sharma, S. E. Lofland, K. V. Ramanujachary, P. A. Buffat, A. Ramanan, *Eur. J. Inorg. Chem.* **2005**, 401–409; b) V. Zima, L. Benes, K. Melanova, M. Vlcek, *J. Solid State Chem.* **2002**, *163*, 281–285.
- [18] A. Shibata, K. Sato, *Power Eng. J.* **1999**, *13*, 130–135.
- [19] a) Q. F. Li, N. J. Bjerrum, *J. Power Sources* **2002**, *110*, 1–10; b) R. M. Dell, *Philos. Trans. R. Soc. London Ser. A* **1996**, *354*, 1515–1527; c) H. Kim, J. Hong, K. Y. Park, H. Kim, S. W. Kim, K. Kang, *Chem. Rev.* **2014**, *114*, 11788–11827; d) S. Boyd, V. Augustyn, *Inorg. Chem. Front.* **2018**, *5*, 999–1015; e) J. Liu, C. Xu, Z. Chen, S. Ni, Z. X. Shen, *Green Energy Environ.* **2018**, *3*, 20–41; f) V. Verma, S. Kumar, W. Manalastas, Jr., R. Satish, M. Srinivasan, *Adv. Sustainable Syst.* **2018**, 1800111.
- [20] L. Ma, S. Chen, H. Li, Z. Ruan, Z. Tang, Z. Liu, Z. Wang, Y. Huang, Z. Pei, J. A. Zapien, C. Zhi, *Energy Environ. Sci.* **2018**, *11*, 2521–2530.
- [21] X. Dong, Y. Wang, Y. Xia, *Sci. Rep.* **2014**, *4*, 6916.
- [22] P. Vanysek in *CRC Handbook of Chemistry and Physics* (Ed.: W. M. Haynes), CRC Press, London, **2014**, pp. 8–20.
- [23] C. Lee, S. K. Jeong, *Chem. Lett.* **2016**, *45*, 1447–1449.
- [24] a) H. H. Hao, K. L. Chen, H. Liu, H. Wang, J. B. Liu, K. Yang, H. Yan, *Int. J. Electrochem. Sci.* **2018**, *13*, 2329–2340; b) J. Yang, C. Hu, H. Wang, K. Yang, J. B. Liu, H. Yan, *Int. J. Energy Res.* **2017**, *41*, 336–352; c) E. Meissner, *J. Power Sources* **1997**, *67*, 135–150.
- [25] D. Pavlov, V. Naidenov, S. Ruevski, *J. Power Sources* **2006**, *161*, 658–665.
- [26] J. K. Gregory, D. C. Clary, K. Liu, M. G. Brown, R. J. Saykally, *Science* **1997**, *275*, 814–817.
- [27] C. Malmberg, A. Maryott, *J. Res. Natl. Bur. Stand.* **1956**, *56*, 1–8.
- [28] G. Markovich, L. Perera, M. L. Berkowitz, O. Cheshnovsky, *J. Chem. Phys.* **1996**, *105*, 2675–2685.
- [29] a) J. Timmermans, A. M. Piette, R. Philippe, *Bull. Soc. Chim. Belg.* **1955**, *64*, 5–23; b) P. Alston Steiner, W. Gordy, *J. Mol. Spectrosc.* **1966**, *21*, 291–301.
- [30] a) R. P. Seward, E. C. Vieira, *J. Phys. Chem.* **1958**, *62*, 127–128; b) R. Payne, I. E. Theodorou, *J. Phys. Chem.* **1972**, *76*, 2892–2900.
- [31] a) W. S. MacGregor, *Ann. N. Y. Acad. Sci.* **1967**, *141*, 3–12; b) H. Dreizler, G. Dendl, *Z. Naturforsch.* **1964**, *19*, 512–514.
- [32] W. M. Haynes in *CRC Handbook of Chemistry and Physics* (Ed.: W. M. Haynes), CRC Press, London, **2014**, pp. 8–118.
- [33] B.-S. Lee, S.-T. Lin, *J. Phys. Chem. B* **2017**, *121*, 5818–5823.
- [34] L. Niedzicki, M. Kasprzyk, K. Kuziak, G. Z. Żukowska, M. Marcinek, W. Wiczeorek, M. Armand, *J. Power Sources* **2011**, *196*, 1386–1391.
- [35] a) D. Baril, C. Michot, M. Armand, *Solid State Ionics* **1997**, *94*, 35–47; b) K. L. Gering, *Electrochim. Acta* **2017**, *225*, 175–189.
- [36] a) D. A. MacInnes, L. G. Longworth, *Chem. Rev.* **1932**, *11*, 171–230; b) L. G. Longworth, *J. Am. Chem. Soc.* **1932**, *54*, 2741–2758; c) L. G. Longworth, *J. Am. Chem. Soc.* **1935**, *57*, 1185–1191; d) J. L. Dye, M. P. Faber, D. J. Karl, *J. Am. Chem. Soc.* **1960**, *82*, 314–318; e) S. Phang, R. H. Stokes, *J. Solution Chem.* **1980**, *9*, 497–505; f) A. G. Keenan, H. G. McLeod, A. R. Gordon, *J. Chem. Phys.* **1945**, *13*, 466–469.
- [37] a) M. Gouverneur, F. Schmidt, M. Schonhoff, *Phys. Chem. Chem. Phys.* **2018**, *20*, 7470–7478; b) T. Frömling, M. Kunze, M. Schönhoff, J. Sundermeyer, B. Roling, *J. Phys. Chem. B* **2008**, *112*, 12985–12990; c) F. Wohde, M. Balabajew, B. Roling, *J. Electrochem. Soc.* **2016**, *163*, A714–A721; d) E. Zygadło-Monikowska, Z. Florjańczyk, P. Kubisa, T. Biedroń, W. Sadurski, A. Puczyłowska, N. Langwald, J. Ostrowska, *Int. J. Hydrogen Energy* **2014**, *39*, 2943–2952; e) V. Lesch, S. Jeremias, A. Moretti, S. Passerini, A. Heuer, O. Borodin, *J. Phys. Chem. B* **2014**, *118*, 7367–7375; f) M. Galiński, A. Lewandowski, I. Stępnik, *Electrochim. Acta* **2006**, *51*, 5567–5580; g) A. Lewandowski, A. Świdorska-Mocek, *J. Power Sources* **2009**, *194*, 601–609.
- [38] a) E. C. Baughan, *J. Phys. Chem.* **1960**, *64*, 1951; b) R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* **1933**, *55*, 2387–2399; c) P. G. Bruce, C. A. Vincent, *J. Electroanal. Chem.* **1987**, *225*, 1–17.
- [39] a) W. Wu, S. Shabagh, J. Chang, A. Rutt, J. F. Whitacre, *J. Electrochem. Soc.* **2015**, *162*, A803–A808; b) A. Bhide, J. Hofmann, A. K. Durr, J. Janek, P. Adelhelm, *Phys. Chem. Chem. Phys.* **2014**, *16*, 1987–1998.
- [40] a) E. S. Beh, D. De Porcellinis, R. L. Gracia, K. T. Xia, R. G. Gordon, M. J. Aziz, *ACS Energy Lett.* **2017**, *2*, 639–644; b) J. Y. Luo, W. J. Cui, P. He, Y. Y. Xia, *Nat. Chem.* **2010**, *2*, 760–765.
- [41] T. Brousse, P.-L. Taberna, O. Crosnier, R. Dugas, P. Guillemet, Y. Scudeller, Y. Zhou, F. Favier, D. Bélanger, P. Simon, *J. Power Sources* **2007**, *173*, 633–641.
- [42] I. B. Butler, M. A. A. Schoonen, D. T. Rickard, *Talanta* **1994**, *41*, 211–215.
- [43] a) A. V. Joshi, J. H. Gordon, S. Bhavaraju (Ceramtec Inc), WO2009097445A3, **2009**; b) S. G. Kim, C. H. Lee, S. T. Woo (LG Chem), KR101423812B1, **2011**.
- [44] D. Shanmukaraj, S. Grugeon, S. Laruelle, G. Douglade, J.-M. Tarascon, M. Armand, *Electrochem. Commun.* **2010**, *12*, 1344–1347.
- [45] W. Li, W. R. Mckinnon, J. R. Dahn, *J. Electrochem. Soc.* **1994**, *141*, 2310–2316.
- [46] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Vol. 1, Pergamon, Houston, TX, **1966**.
- [47] a) S. Drieschner, M. von Seckendorff, E. del Corro, J. Wohlfetzter, B. M. Blaschke, M. Stutzmann, J. A. Garrido, *Nanotechnology* **2018**, *29*, 225402; b) J. Lee, J.-M. Lee, S. Yoon, S.-O. Kim, J.-S. Sohn, K.-I. Rhee, H.-J. Sohn, *J. Power Sources* **2008**, *183*, 325–329; c) A. R. Han, T. W. Kim, D. H. Park, S.-J. Hwang, J.-H. Choy, *J. Phys. Chem. C* **2007**, *111*, 11347–11352; d) L. Jaber-Ansari, K. Puntambekar, S. Kim, M. Aykol, L. Luo, J. Wu, B. D. Myers, H. Iddir, J. T. Russell, S. J. Saldaña, R. Kumar, M. M. Thackeray, L. A. Curtiss, V. P. Dravid, C. Wolverton, M. C. Hersam, *Adv. Energy Mater.* **2015**, *5*, 1500646; e) J. Zeng, M. Li, X. Li, C. Chen, D. Xiong, L. Dong, D. Li, A. Lushington, X. Sun, *Appl. Surf. Sci.* **2014**, *317*, 884–891.
- [48] a) F. Wang, Y. Wu, T. van Ree in *Lithium-Ion Batteries: Fundamentals and Applications*, Vol. 4 (Ed.: Y. Wu), CRC Press, London, **2015**, p. 154; b) D. Chao, C. Zhu, X. Xia, J. Liu, X. Zhang, J. Wang, P. Liang, J. Lin, H. Zhang, Z. X. Shen, H. J. Fan, *Nano Lett.* **2015**, *15*, 565–573.
- [49] a) B. Beverskog, I. Puigdomenech, *Corros. Sci.* **1997**, *39*, 107–114; b) A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. A. Persson, *APL Mater.* **2013**, *1*, 011002; c) K. A. Persson, B. Walldwick, P. Lazic, G. Ceder, *Phys. Rev. B* **2012**, *85*, 235438.
- [50] R. Bedworth, N. Pilling, *J. Inst. Met.* **1923**, *29*, 529–582.
- [51] D. R. Askeland, P. Phulé in *The Science and Engineering of Materials* (Eds.: D. R. Askeland, P. Phulé), Cengage Learning, Boston, MA, **2006**, p. 876.
- [52] ASM in *ASM International, USA* (Ed.: A. International), United States of America, **1987**, pp. 130–133, ISBN: 0-08170-019-0. ■ incomplete information and incorrect ISBN, please provide title, authors/editors and publisher location ■ ■
- [53] M. D. McCluskey, S. J. Jokela, *J. Appl. Phys.* **2009**, *106*, 071101.
- [54] a) D. C. Look, *Mater. Sci. Eng. B* **2001**, *80*, 383–387; b) Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, H. Morkoç, *J. Appl. Phys.* **2005**, *98*, 041301.
- [55] a) D. Linden in *Linden's Handbook of Batteries*, 4th ed. (Ed.: T. B. Reddy), McGraw-Hill, New York, **2010**, pp. 12–13; b) "Duracell Technical Bulletin: Alkaline-Manganese Dioxide", can be found under <https://d2ei442zrkqy2u.cloudfront.net/wp-content/uploads/2016/03/Alkaline-Technical-Bulletin.pdf>, **2018**.
- [56] G. A. Olah, G. K. S. Prakash, J. Sommer, *Science* **1979**, *206*, 13–20.
- [57] V. B. Kazansky, *Top. Catal.* **2000**, *11*, 55–60.
- [58] a) A. Corma, H. García, *Chem. Rev.* **2003**, *103*, 4307–4366; b) K. Tanabe, W. F. Hölderich, *Appl. Catal. A* **1999**, *181*, 399–434; c) K. Arata in *Advances in Catalysis*, Vol. 37 (Eds.: D. D. Eley, H. Pines, P. B. Weisz), Academic Press, San Diego, **1990**, pp. 165–211.

- [59] a) K. Huang, H. Zhou, A. He, Y. Sun, Y. Liu, X. Gao, Y. Zhao, S. Liu, Z. Li, T. Hu, X. Li, C. Liu, Y. Wei, L. Yang, J. Feng, Y. Cai, Z. Yang, Y. Xu, I. Noda, J. Wu, *J. Phys. Chem. B* **2011**, *115*, 7823–7829; b) T. Okuhara, *Chem. Rev.* **2002**, *102*, 3641–3666.
- [60] H. D. Lutz, M. Jung, K. Beckenkamp, *J. Mol. Struct.* **1988**, *175*, 257–261.
- [61] E. Clerici in *Atti della Reale Accademia dei Lincei. Rendiconti, classe di scienze fisiche, matematiche e naturali* (Ed.: A. d. Lincei), Reale accademia dei Lincei, Rome, **1907**, pp. 187–195.
- [62] R. H. Jahns, *Am. Mineral.* **1939**, *24*, 116–122.
- [63] K. H. Büchel, H.-H. Moretto, D. Werner in *Industrial Inorganic Chemistry*, 2nd ed., Wiley-VCH, Weinheim, **2008**, p. 115.
- [64] R. H. Perry in *Perry's Chemical Engineers' Handbook*, 7th ed. (Ed.: D. W. Green), McGraw-Hill, New York, **1997**, pp. 2–123.
- [65] a) H. L. Clever, M. E. Derrick, S. A. Johnson, *J. Phys. Chem. Ref. Data* **1992**, *21*, 941–1004; b) W. M. Haynes in *CRC Handbook of Chemistry and Physics* (Ed.: W. M. Haynes), CRC Press, London, **2014**, pp. 5–92.
- [66] a) R. Parsons, *Rev. Pure Appl. Chem.* **1968**, *18*, 1–5; b) C. D. Fernández-Solis, A. Vimalanandan, A. Altin, J. S. Mondragón-Ochoa, K. Kreth, P. Keil, A. Erbe in *Soft Matter at Aqueous Interfaces* (Eds.: P. Lang, Y. Liu), Springer International Publishing, Cham, **2016**, pp. 29–70; c) O. M. Magnussen, M. R. Vogt, J. Scherer, R. J. Behm, *Appl. Phys. A* **1998**, *66*, S447–S451; d) S. Trasatti, *J. Electroanal. Chem.* **1972**, *39*, 163–184; e) L. Zhang, L. Chen, X. Zhou, Z. Liu, *Adv. Energy Mater.* **2015**, *5*, 1400930.
- [67] a) W. J. Xie, Z. Zhang, Y. Q. Gao, *J. Phys. Chem. B* **2016**, *120*, 2343–2351; b) M. Xu, J. P. Larentzos, M. Roshdy, L. J. Criscenti, H. C. Allen, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4793–4801; c) D. E. Irish, A. R. Davis, R. A. Plane, *J. Chem. Phys.* **1969**, *50*, 2262–2263; d) D. E. Irish, A. R. Davis, *Can. J. Chemistry* **1968**, *46*, 943–951; e) J. Zheng, G. Tan, P. Shan, T. Liu, J. Hu, Y. Feng, L. Yang, M. Zhang, Z. Chen, Y. Lin, J. Lu, J. Neuefeind, Y. Ren, K. Amine, L.-W. Wang, K. Xu, F. Pan, *Chem* **2018**, *4*, 2872–2882.
- [68] P. M. Vollmar, *J. Chem. Phys.* **1963**, *39*, 2236–2248.
- [69] a) Z. G. Hou, X. Q. Zhang, X. N. Li, Y. C. Zhu, J. W. Liang, Y. T. Qian, *J. Mater. Chem. A* **2017**, *5*, 730–738; b) K. E. K. Sun, T. K. A. Hoang, T. N. L. Doan, Y. Y. X. Zhu, Y. Tian, P. Chen, *ACS Appl. Mater. Interfaces* **2017**, *9*, 9681–9687.
- [70] R. M. Jelić, L. G. Joksović, P. T. Djurdjević, *J. Solution Chem.* **2005**, *34*, 1235–1261.
- [71] a) S. B. Lai, M. I. James, X. C. Wu, Y. L. Dong, J. H. Wang, M. Gao, J. F. Liu, X. M. Sun, *Rare Met.* **2017**, *36*, 381–396; b) K. E. K. Sun, T. K. A. Hoang, T. N. L. Doan, Y. Yu, P. Chen, *Chem. Eur. J.* **2018**, *24*, 1667.
- [72] Q. Li, J. Chen, L. Fan, X. Kong, Y. Lu, *Green Energy Environ.* **2016**, *1*, 18–42.
- [73] a) X. Ji, J. Chen, F. Wang, W. Sun, Y. Ruan, L. Miao, J. Liang, C. Wang, *Nano Lett.* **2018**, *18*, 6441–6448; b) D. Hoche, S. V. Lamaka, B. Vaghefinazari, T. Braun, R. P. Petruskas, M. Fichtner, M. L. Zheludkevich, *Sci. Rep.* **2018**, *8*, 7578.
- [74] P. Canepa, G. Sai Gautam, D. C. Hannah, R. Malik, M. Liu, K. G. Gallagher, K. A. Persson, G. Ceder, *Chem. Rev.* **2017**, *117*, 4287–4341.
- [75] E. N. Keyzer, H. F. J. Glass, Z. Liu, P. M. Bayley, S. E. Dutton, C. P. Grey, D. S. Wright, *J. Am. Chem. Soc.* **2016**, *138*, 8682–8685.
- [76] a) D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* **2000**, *407*, 724–727; b) A. Doron, W. Idit, G. Yosef, L. Elena, *Chem. Rec.* **2003**, *3*, 61–73.
- [77] R. Mohtadi, M. Matsui, T. Arthur, S. J. Hwang, *Angew. Chem. Int. Ed.* **2012**, *51*, 9780–9783; *Angew. Chem.* **2012**, *124*, 9918–9921.
- [78] A. Ponrouch, M. R. Palacin, *Curr. Opin. Electrochem.* **2018**, *9*, 1–7.
- [79] A. Ponrouch, C. Frontera, F. Barde, M. R. Palacin, *Nat. Mater.* **2016**, *15*, 169–172.
- [80] a) H. Tomiyasu, H. Shikata, K. Takao, N. Asanuma, S. Taruta, Y.-Y. Park, *Sci. Rep.* **2017**, *7*, 45048; b) P. Padigi, G. Goncher, D. Evans, R. Solanki, *J. Power Sources* **2015**, *273*, 460–464; c) P. Reinsberg, C. J. Bondue, H. Baltruschat, *J. Phys. Chem. C* **2016**, *120*, 22179–22185.
- [81] a) T. Tojo, Y. Sugiura, R. Inada, Y. Sakurai, *Electrochim. Acta* **2016**, *207*, 22–27; b) C. H. Lee, C. S. Kim, S. K. Jeong, *Key Eng. Mater.* **2017**, *724*, 97–101.
- [82] T. Shiga, H. Kondo, Y. Kato, M. Inoue, *J. Phys. Chem. C* **2015**, *119*, 27946–27953.
- [83] R. Y. Wang, C. D. Wessells, R. A. Huggins, Y. Cui, *Nano Lett.* **2013**, *13*, 5748–5752.
- [84] J. Muldoon, C. B. Bucur, T. Gregory, *Chem. Rev.* **2014**, *114*, 11683–11720.
- [85] S. D. Han, N. N. Rajput, X. H. Qu, B. F. Pan, M. N. He, M. S. Ferrandon, C. Liao, K. A. Persson, A. K. Burrell, *ACS Appl. Mater. Interfaces* **2016**, *8*, 3021–3031.
- [86] D. Kundu, S. H. Vajargah, L. W. Wan, B. Adams, D. Prendergast, L. F. Nazar, *Energy Environ. Sci.* **2018**, *11*, 881–892.
- [87] A. R. Mainar, E. Iruin, L. C. Colmenares, A. Kvasha, I. de Meatza, M. Bengoechea, O. Leonet, I. Boyano, Z. Zhang, J. A. Blazquez, *J. Energy Storage* **2018**, *15*, 304–328.
- [88] a) N. Zhang, F. Y. Cheng, J. X. Liu, L. B. Wang, X. H. Long, X. S. Liu, F. J. Li, J. Chen, *Nat. Commun.* **2017**, *8*, 405; b) F. Wan, L. Zhang, X. Dai, X. Wang, Z. Niu, J. Chen, *Nat. Commun.* **2018**, *9*, 1656; c) F. Wang, O. Borodin, T. Gao, X. Fan, W. Sun, F. Han, A. Faraone, J. A. Dura, K. Xu, C. Wang, *Nat. Mater.* **2018**, *17*, 543–549.
- [89] W. Hong, Z. Jia, B. Wang, *J. Appl. Electrochem.* **2016**, *46*, 1085–1090.
- [90] G. Garcia, E. Ventosa, W. Schuhmann, *ACS Appl. Mater. Interfaces* **2017**, *9*, 18691–18698.
- [91] D. Kundu, B. D. Adams, V. D. Ort, S. H. Vajargah, L. F. Nazar, *Nat. Energy* **2016**, *1*, 16119.
- [92] a) B. Lee, H. R. Seo, H. R. Lee, C. S. Yoon, J. H. Kim, K. Y. Chung, B. W. Cho, S. H. Oh, *ChemSusChem* **2016**, *9*, 2948–2956; b) V. Soundharajan, B. Sambandam, S. Kim, M. H. Alfaruqi, D. Y. Putro, J. Jo, S. Kim, V. Mathew, Y.-K. Sun, J. Kim, *Nano Lett.* **2018**, *18*, 2402–2410.
- [93] a) B. J. Hertzberg, A. Huang, A. Hsieh, M. Chamoun, G. Davies, J. K. Seo, Z. Zhong, M. Croft, C. Erdonmez, Y. S. Meng, D. Steingart, *Chem. Mater.* **2016**, *28*, 4536–4545; b) W. Sun, F. Wang, S. Hou, C. Yang, X. Fan, Z. Ma, T. Gao, F. Han, R. Hu, M. Zhu, C. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 9775–9778.
- [94] a) Y.-H. Chen, H.-W. Yeh, N.-C. Lo, C.-W. Chiu, I. W. Sun, P.-Y. Chen, *Electrochim. Acta* **2017**, *227*, 185–193; b) ref. [93b].
- [95] L. D. Reed, E. Menke, *J. Electrochem. Soc.* **2013**, *160*, A915–A917.
- [96] H. Lahan, S. K. Das, *Ionics* **2018**, *24*, 1855–1860.
- [97] D. Muñoz-Torrero, P. Leung, E. Garcia-Quismondo, E. Ventosa, M. Anderson, J. Palma, R. Marcilla, *J. Power Sources* **2018**, *374*, 77–83.
- [98] K. V. Kravchyk, S. Wang, L. Piveteau, M. V. Kovalenko, *Chem. Mater.* **2017**, *29*, 4484–4492.
- [99] H. Chen, H. Y. Xu, S. Y. Wang, T. Q. Huang, J. B. Xi, S. Y. Cai, F. Guo, Z. Xu, W. W. Gao, C. Gao, *Sci. Adv.* **2017**, *3*, ea07233.
- [100] a) H. D. Jiao, C. Wang, J. G. Tu, D. H. Tian, S. Q. Jiao, *Chem. Commun.* **2017**, *53*, 2331–2334; b) M. Angell, C. J. Pan, Y. M. Rong, C. Z. Yuan, M. C. Lin, B. J. Hwang, H. J. Dai, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 834–839; c) G. A. Elia, I. Hasa, G. Greco, T. Diemant, K. Marquardt, K. Hoeppe, R. J. Behm, A. Hoell, S. Passerini, R. Hahn, *J. Mater. Chem. A* **2017**, *5*, 9682–9690.
- [101] Y. Song, S. Q. Jiao, J. G. Tu, J. X. Wang, Y. J. Liu, H. D. Jiao, X. H. Mao, Z. C. Guo, D. J. Fray, *J. Mater. Chem. A* **2017**, *5*, 1282–1291.
- [102] E. J. Zhang, W. Cao, B. Wang, X. Z. Yu, L. L. Wang, Z. Xu, B. G. Lu, *Energy Storage Mater.* **2018**, *11*, 91–99.
- [103] M. S. Whittingham, C. Siu, J. Ding, *Acc. Chem. Res.* **2018**, *51*, 258–264.
- [104] M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, H. Dai, *Nature* **2015**, *520*, 324.
- [105] C. Du, B. Zhao, X.-B. Chen, N. Birbilis, H. Yang, *Sci. Rep.* **2016**, *6*, 29225.
- [106] M. Chiku, S. Matsumura, H. Takeda, E. Higuchi, H. Inoue, *J. Electrochem. Soc.* **2017**, *164*, A1841–A1844.
- [107] T. Mandai, P. Johansson, *J. Mater. Chem. A* **2015**, *3*, 12230–12239.
- [108] S. Y. Li, B. C. Church, *Appl. Surf. Sci.* **2018**, *440*, 861–872.
- [109] T. Xue, W. C. Cooper, R. Pascual, S. Saimoto, *J. Appl. Electrochem.* **1991**, *21*, 238–246.
- [110] H. L. Wang, S. C. Gu, Y. Bai, S. Chen, N. Zhu, C. Wu, F. Wu, *J. Mater. Chem. A* **2015**, *3*, 22677–22686.
- [111] F. Ding, W. Xu, G. L. Graff, J. Zhang, M. L. Sushko, X. Chen, Y. Shao, M. H. Engelhard, Z. Nie, J. Xiao, X. Liu, P. V. Sushko, J. Liu, J.-G. Zhang, *J. Am. Chem. Soc.* **2013**, *135*, 4450–4456.
- [112] D. Höche, S. V. Lamaka, B. Vaghefinazari, T. Braun, R. P. Petruskas, M. Fichtner, M. L. Zheludkevich, *Sci. Rep.* **2018**, *8*, 7578.
- [113] J. Mähler, I. Persson, *Inorg. Chem.* **2012**, *51*, 425–438.
- [114] a) L. B. Railsback, *Variation in hydrated radius of ions (in Some Fundamentals of Mineralogy and Geochemistry)*, can be found under <http://www.gly.uga.edu/railsback/FundamentalsIndex.html>, **2006**; b) E. R. Nightingale, *J. Phys. Chem.-US* **1959**, *63*, 1381–1387.

- [115] I. Persson, *Pure Appl. Chem.* **2010**, *82*, 1901.
[116] H. Ohtaki, T. Radnai, *Chem. Rev.* **1993**, *93*, 1157–1204.
[117] J. Zheng, Y. Hou, Y. Duan, X. Song, Y. Wei, T. Liu, J. Hu, H. Guo, Z. Zhuo, L. Liu, Z. Chang, X. Wang, D. Zherebetsky, Y. Fang, Y. Lin, K. Xu, L.-W. Wang, Y. Wu, F. Pan, *Nano Lett.* **2015**, *15*, 6102–6109.
[118] a) C. Wessells, R. Ruffo, R. A. Huggins, Y. Cui, *Electrochem. Solid-State Lett.* **2010**, *13*, A59–A61; b) A. Dushina, J. Stojadinović, F. La Mantia, *Electrochim. Acta* **2015**, *167*, 262–267; c) J. Stojadinović, A. Dushina, R. Trócoli, F. La Mantia, *ChemPlusChem* **2014**, *79*, 1507–1511.

- [119] R. Trócoli, F. La Mantia, *ChemSusChem* **2015**, *8*, 481–485.

Manuscript received: July 5, 2018

Revised manuscript received: November 22, 2018

Accepted manuscript online: ■■■■, 0000

Version of record online: ■■■■, 0000

REVIEWS

W. Manalastas, Jr.,* S. Kumar, V. Verma,
L. Zhang, D. Yuan, M. Srinivasan*

■■■ – ■■■

Water in Rechargeable Multivalent-Ion Batteries: An Electrochemical Pandora's Box

Revisiting water world: The structure of H₂O seems simple, but its presence commonly dictates what reaction routes and products proceed through matter–matter interactions. Molecular H₂O is reviewed from an electrochemical perspective and its various influences on the feasibility of multivalent-ion batteries are evaluated.

Revisiting water world: Review of molecular water from an #electrochemistry perspective by William Manalastas, Madhavi Srinivasan et al. @NTUsg [SPACE RESERVED FOR IMAGE AND LINK](#)

Share your work on social media! *ChemSusChem* has added Twitter as a means to promote your article. Twitter is an online microblogging service that enables its users to send and read short messages and media, known as tweets. Please check the pre-written tweet in the galley proofs for accuracy. If you, your team, or institution have a Twitter account, please include its handle @username. Please use hashtags only for the most important keywords, such as #catalysis, #nanoparticles, or #proteindesign. The ToC picture and a link to your article will be added automatically, so the **tweet text must not exceed 250 characters**. This tweet will be posted on the journal's Twitter account (follow us @ChemSusChem) upon publication of your article in its final (possibly unpaginated) form. We recommend you to re-tweet it to alert more researchers about your publication, or to point it out to your institution's social media team.

Please check that the ORCID identifiers listed below are correct. We encourage all authors to provide an ORCID identifier for each coauthor. ORCID is a registry that provides researchers with a unique digital identifier. Some funding agencies recommend or even require the inclusion of ORCID IDs in all published articles, and authors should consult their funding agency guidelines for details. Registration is easy and free; for further information, see <http://orcid.org/>.

Dr. William Manalastas, Jr. <http://orcid.org/0000-0002-2364-0604>

Sonal Kumar <http://orcid.org/0000-0001-9917-8922>

Vivek Verma <http://orcid.org/0000-0002-4890-2826>

Dr. Liping Zhang

Dr. Du Yuan

Prof. Madhavi Srinivasan <http://orcid.org/0000-0002-5497-3428>

Author Contributions

W.M. *Conceptualization: Lead; Data curation: Lead; Formal analysis: Lead; Investigation: Lead; Methodology: Lead; Visualization: Equal; Writing – original draft: Lead; Writing – review & editing: Lead*. S.K. *Formal analysis: Supporting; Investigation: Supporting; Methodology: Supporting; Visualization: Equal; Writing – review & editing: Supporting*. V.V. *Investigation: Supporting; Methodology: Supporting; Software: Supporting; Visualization: Equal; Writing – review & editing: Supporting*. L.Z. *Software: Supporting; Visualization: Supporting; Writing – review & editing: Supporting*. D.Y. *Investigation: Supporting; Software: Lead; Writing – review & editing: Supporting*. M.S. *Conceptualization: Supporting; Formal analysis: Supporting; Funding acquisition: Lead; Project administration: Lead; Resources: Lead; Supervision: Lead; Validation: Lead; Writing – review & editing: Supporting*.