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# Application-Based Prospects for Dual-Ion Batteries

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Dual-ion batteries (DIBs) exhibit a distinct set of performance advantages and disadvantages due to their unique storage mechanism. However, the current cyclability/energy density tradeoffs of anion storage paired with the intrinsic required electrolyte loadings of conventional DIBs preclude their widespread adoption as an alternative to lithium-ion batteries (LIBs). Despite this, their reduced desolvation penalty and low-cost electrode materials may warrant their employment for low-temperature and/or grid storage applications. To expand beyond these applications, this Perspective reviews the prospects of solid salt storage and halogen intercalation-conversion as viable methods to increase DIB energy densities to a level on-par with LIBs. Fundamental limitations of conventional DIBs are examined, technology spaces are proposed where they can make meaningful impact over LIBs, and potential strategies are outlined to improve cell-level energy densities necessary for the widespread adoption of DIBs.

## Introduction

Further integration of renewable energy and portable electronics into modern society depends heavily on the advent of improved energy storage technologies. Electrochemical energy storage technologies such as batteries present a complex, but promising opportunity for providing superior performance metrics at a low cost and have thus garnered significant research attention. The lithium-ion battery (LIB) has so far been extremely successful in enabling electric vehicles (EVs) and modern portable electronics such as smart phones; however, the diverse performance needs of various other applications have prompted the investigation of alternative battery chemistries.[1] Among these chemistries, the dual-ion battery (DIB) has been a subject of interest due to its unique performance advantages resulting from its charge-storage mechanism and potential library of cathode materials.[2]

Unlike the "rocking chair" mechanism found in LIBs, DIBs operate via a "salt splitting" storage mechanism in which cations are inserted into the anode while anions are inserted into the cathode during charge, and the ions are released back into the electrolyte during discharge.[2] In this regard, DIB anodes operate identically to LIB anodes and have access to the same materials library. DIB cathodes, on the other hand, require materials capable of reversibly intercalating anions, which significantly diverge from cation-hosting cathode materials. Perhaps the most widely studied DIB cathode is graphite, which was first demonstrated to reversibly host anions as early as 1938, and operates via a similar staging intercalation mechanism to that of the cation-hosting graphite anode.[3,4] Also reliant on an ordered $sp^2$ carbon structure, aromatic crystals (e.g., coronene) have been successfully demonstrated as an anion host, which operate primarily via edge adsorption, similar to hard carbon anodes.[5] Metal-organic-frameworks (MOFs) have also been demonstrated to display reversible electrochemical anion storage, which host charged species in their ordered molecular pore structure.[6] Lastly, there is a relatively large library of polymer hosts with redox-active centers that support anion storage via a chemisorption mechanism.[2a,7] Though there is a diverse set of anion-hosting cathode materials, each present a distinct set of advantages and disadvantages for future employment and scalability.

The foremost advantage of DIBs is the materials cost of the cathodes, which, excluding MOFs, contain no transition metals. Given the established market volatility, mining practices, and scarcity of Co, in addition to the growing cost of Ni, DIBs based on organic materials promise to circumvent the future economic and ethical concerns associated with LIB cathodes.[8] Additionally, the nature of anion storage allows DIBs to be developed for a variety of low-cost cations such as $Na^+$, $K^+$, $Zn^{2+}$, $Mg^{2+}$, $Ca^{2+}$, and $Al^{3+}$, where identifying stable, low-cost, cation-storing cathode materials is known to be a challenge.[1c,d,5c,f,9] Additionally, the kinetics of anion storage has been broadly observed to be substantially improved compared to that of cation storage, regardless of whether said storage is measured to be pseudocapacitive or diffusion limited.[4h,7c,g] As an extreme example, Wang et al. demonstrated the reversible operation of the graphite cathode at a 100C at nearly 80% capacity retention.[4h] While a precise description of this kinetic advantage has yet to be reached, one obvious difference is a substantial reduction in desolvation penalty, which is known to

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limit cation storage, due to the negligible interactions between anion and solvent in solution.[10] Furthermore, the reversibility of anion storage is ostensibly remarkable, where DIB cathodes have demonstrated thousands of stable cycles, though the majority of works do so under half-cell conditions, a critical distinction.[4h,5b,7e,f,9g] These advantages are illustrated in Figure 1.

Despite these advantages, the larger size of anions relative to cations results in significantly reduced specific capacity for DIB cathodes relative to LIB.[2a] Moreover, the tap density of anion-hosting carbon materials is typically inferior to that of transition metal oxide LIB cathodes, which further reduces cell-level energy density at scale.[2b,11] In addition to these inherent disadvantages for DIBs, the "salt splitting" mechanism stores charge from the ions present in the electrolyte, which requires a minimum electrolyte loading in the cell, further reducing cell-level energy density.[2b,11] In principle, the elevated voltage of the graphite cathode ($>5$ V vs. Li/Li$^+$) partially recoups some of the aforementioned energy density losses and has thus garnered substantial attention from the DIB research community. However, the inherent challenges associated with stabilizing a high-volume-change material at such extreme conditions have so far proved to be too large to achieve sufficient cycle life under practical full-cell conditions (e.g., $1<\mathrm{N/P}<1.5$).[2b,4a,c–g,12] To minimize electrolyte volume, increasing salt concentration is necessary, and in principle acts to further reduce electrolyte cost while slightly improving electrolyte cost per cell due to a reduction in solvent requirements.[2b,3b,11] However, this strategy is fundamentally incompatible with solvent fluorination, which have been shown to improve oxidative stability $>5$ V, but typically show reduced salt solubility and are expensive to manufacture at scale.[4a,13] The interdependence of these factors introduces a negative interdependence between cell-level energy density, cyclability, and materials cost for DIBs, which greatly limit their application (Figure 2).

## Areas of Impact for Current Dual-Ion Batteries

While the disadvantages of current DIBs render their degree of future adoption unclear, their performance advantages over LIBs warrant consideration for a number of energy storage applications. Though technologies that require high energy density, such as portable smart devices and electric vehicles, are out of reach for current DIBs, the aforementioned advantages of anion-storing cathode materials make them uniquely equipped to handle specific design requirements and operating conditions.

### *Low-temperature operation*

Though LIBs are ideally suited for operation under ambient conditions, their operating temperature versatility is relatively narrow. In particular, their low-temperature operation is severely limited kinetically, where their energy densities have been observed to suffer dramatically beneath 0 °C.[14] While the ionic conductivity of the electrolyte, migration of ions through the solid electrolyte interphase (SEI), and diffusion of ions

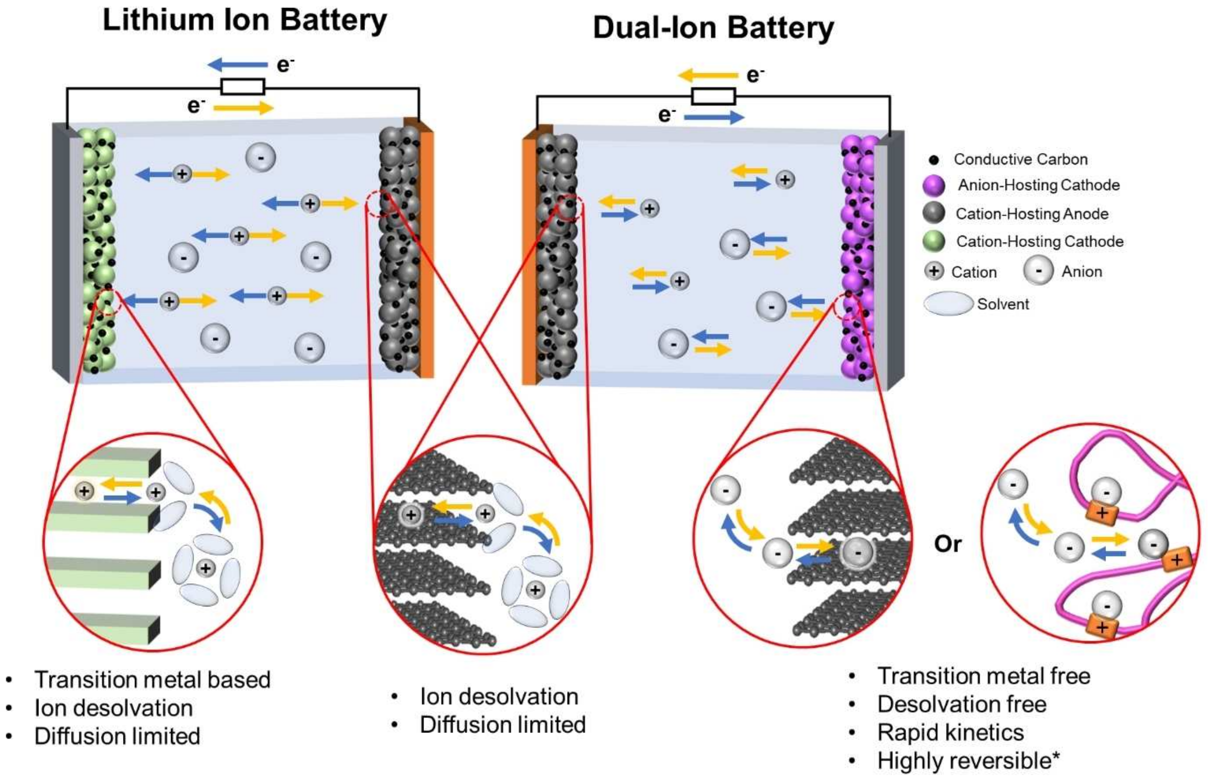

**Figure 1.** Mechanistic schematic of LIBs and DIBs and summary of DIB cathode advantages. * = primarily demonstrated under half-cell conditions.

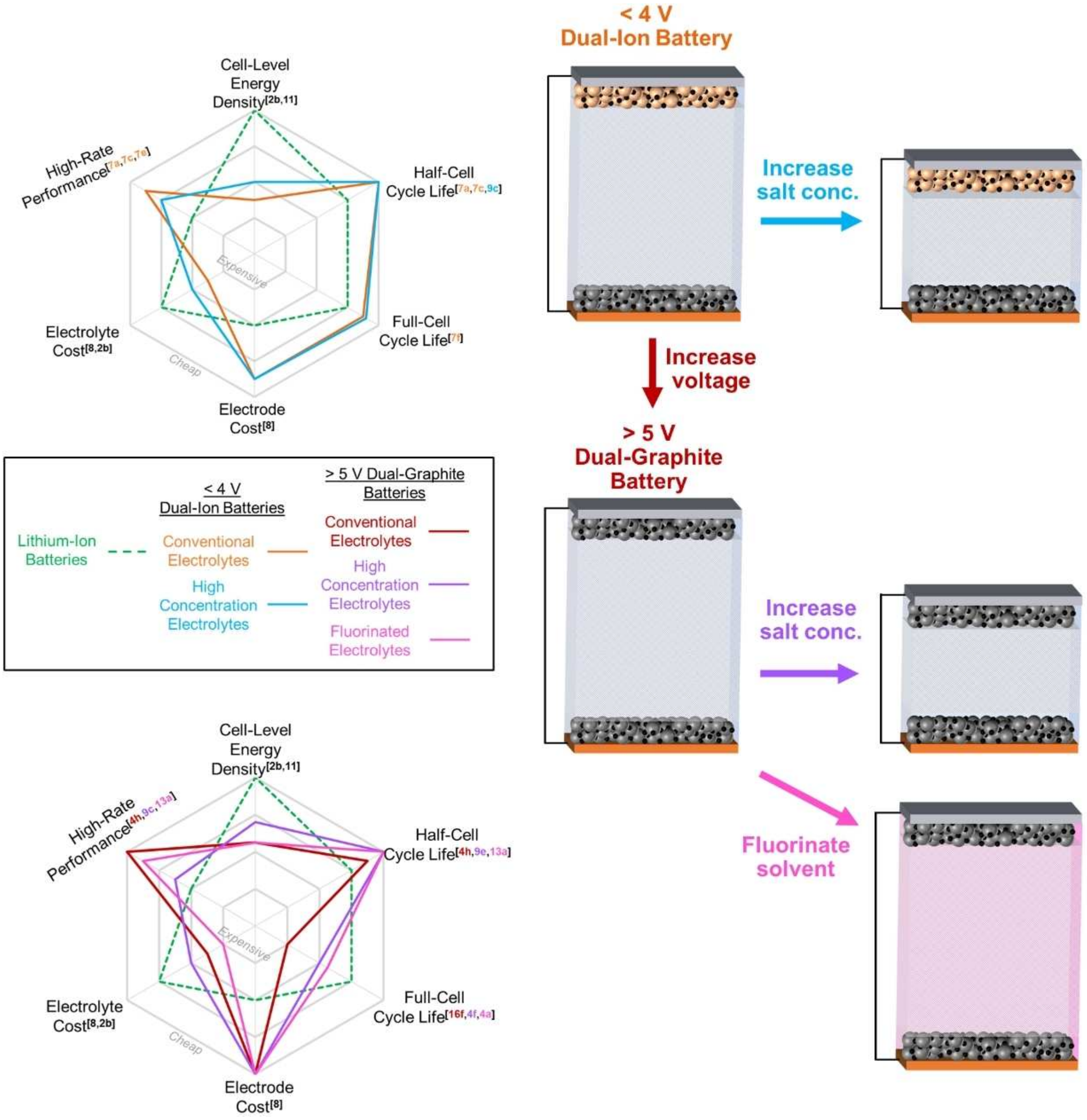

**Figure 2.** Summary of disadvantages and technological realities of improvement strategies applied to DIBs employing aprotic electrolytes. Note that the spider chart designations are largely qualitative and determined from the references provided next to each metric.

through the solid electrode materials all degrade at low temperatures, the charge-transfer process at the interphase has been concluded to dominate the low-temperature performance.[9,14d,15a,b] The energy barrier attributed to ion de-solvation largely defines this charge-transfer behavior, which is highly related to the outer-sphere reorganization energy discussed in Marcus Theory.[15c] In this regard, the $Li^+$ ion (considered a hard acid) is sub-optimal due to the strong binding interactions with the negative dipole found in common solvents, which increases the energy barrier for such reorganization.[15d] However, unlike cations, anions weakly interact with or even repel solvent molecules, giving them an inherent advantage for scaling towards low temperatures due to a reduced barrier for solvation and de-solvation at the interphase (Figure 3).

Though addressing the low-temperature limitations of secondary batteries has gained traction in the literature as of late, relatively few studies focus on DIBs for such applications.[14d,15e] Despite this, the studies available indicate that a variety of anion-hosting cathodes provide superior low-temperature performance retentions compared to conventional LIBs. In 2017, Dong et al. demonstrated all-organic batteries utilizing anion-storing polymer cathodes capable of delivering 70% of room-temperature capacity at −70 °C, when a chemistry utilizing cation storage retained only 22%.[16a] Since then, a number of works have demonstrated similar improvements at reduced temperatures with a variety of anode materials and charge carriers.[16b–d] Due to the previously discussed remarkable kinetic advantages of the graphite cathode, our group has also demonstrated a substantial improvement in low-temperature

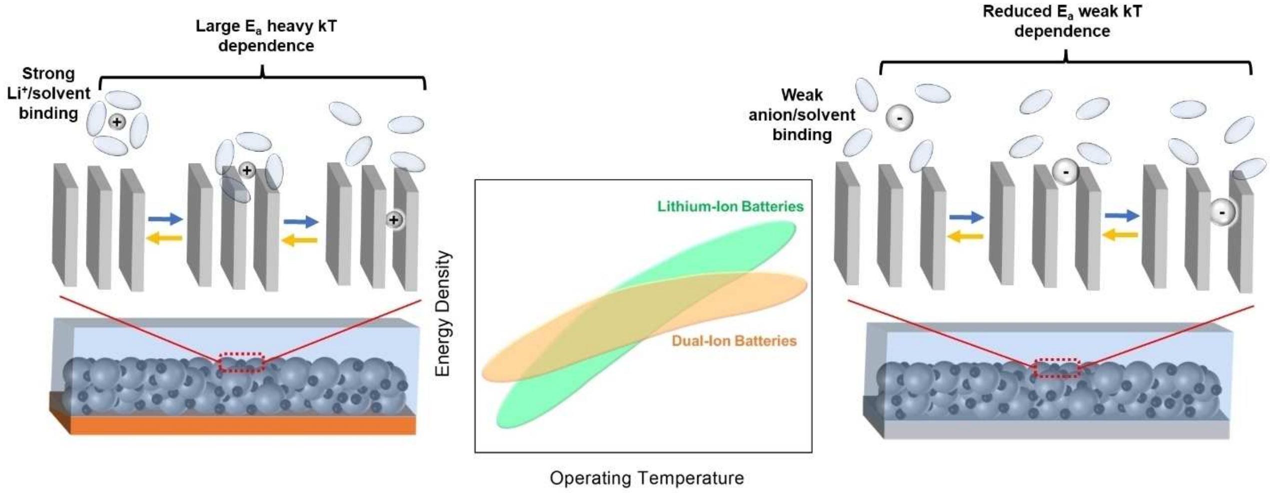

**Figure 3.** Rationale for the low-temperature application of DIBs over LIBs. The pictured energy density vs. temperature relationship is theoretical, qualitative, and highly dependent on the applied electrode and electrolyte chemistry of each system.

performance for dual-graphite cells over conventional LIBs.[16f] Despite this promise, the baseline cyclability of the graphite cathode under full-cell conditions still prohibits their application at scale.

To make a meaningful difference in low-temperature energy storage applications, significant effort must be made towards the operation of DIBs under practical conditions. In principle, the intrinsically superior low-temperature scaling of DIBs should yield a conditional cross-over regime for the energy density of DIBs and LIBs (Figure 3); however, understanding the practical limits of DIB energy density is necessary before isolating such a temperature threshold. In particular, the impact of reduced electrolyte volume may pose immense challenges at scale, given that the consumption of ions in solution would progressively reduce the ionic conductivity during charge. Moreover, the aforementioned studies largely focus on electrodes with areal loadings insufficient for commercial applications. The influence of these factors on the temperature scaling of DIBs must be determined before a conclusion regarding the superior low-temperature battery chemistry is reached.

### *Stationary grid storage*

Unlike EVs and the majority of portable electronic applications, stationary energy storage applications require a distinct set of primary baseline metrics. which LIBs were not necessarily designed to provide. Given the nature of stationary storage, energy density does not take precedence over other considerations, as the size of the battery will likely be dwarfed by the energy harvesting apparatus itself (e.g., most estimates suggest a typical solar farm requires 5–10 acres per MW generated).[17a] Instead, batteries used for grid storage prioritize cost, taking into account materials, frequency of replacement, and operation. These costs are generally represented by levelized cost, measured in $\$\,kWh^{-1}\,cycle^{-1}$, and take into account not only battery capital costs but the lifetime of its use before replacement.[17] Additionally, the energy efficiency and self-discharge performance of prospective grid storage batteries is of high interest to minimize energy loss over the storage period following initial conversion. Traditionally, these metrics have motivated the investigation of flow batteries and reduced-cost chemistries such as Zn-based systems; however, the aforementioned intrinsic advantages of DIBs also warrant attention in this regard.[1c,18a]

While the inherently low cost of DIB electrode materials presents an advantage in levelized cost over LIBs, the necessary high electrolyte volume presents substantial concern at scale. In this regard, flow batteries, which store energy in said electrolyte, and aqueous Zn chemistries, which do not rely on the electrolyte to provide charge carriers, may be preferable. However, these technologies also have significant downsides, where flow cells have well-established issues regarding poor energy efficiency, self-discharge, and cycle life, and reversible operation of the Zn metal anode and multivalent-ion-storing cathodes in low-cost electrolytes remains a challenge.[18] It is therefore paramount that DIB in operation be successfully demonstrated in low-cost, ideally aqueous electrolytes.[2d,17e] To this end, a variety of chemistries have been recently developed with a wide range of aqueous electrolytes utilizing low-cost salts based on $Zn^{2+}$,[5f,7e,19] $Na^{+}$,[20] $Mg^{2+}$,[21] and $NH_4^{+}$[22] with cathodes ranging from $Mn_3O_4$ to graphite (Figure 4). Moreover, a select number of these low-cost systems have demonstrated half-cell cycle lives on the scale of $10^4$, with operating voltages far more attractive for scaling to reduced N/P ratios. Moreover, the development of water-in-salt electrolytes (WiSE) utilizing low-cost salts such as $ZnCl_2$,[19,23a,b] $NaClO_4$,[23c] $KCH_3COO$,[23d] $NH_4CH_3COO$,[23e] and so on present an opportunity for further performance and energy density optimization without adverse economic impacts.

The integration of these low-cost DIB chemistries paired with the demonstrated cycle lives in literature shows great

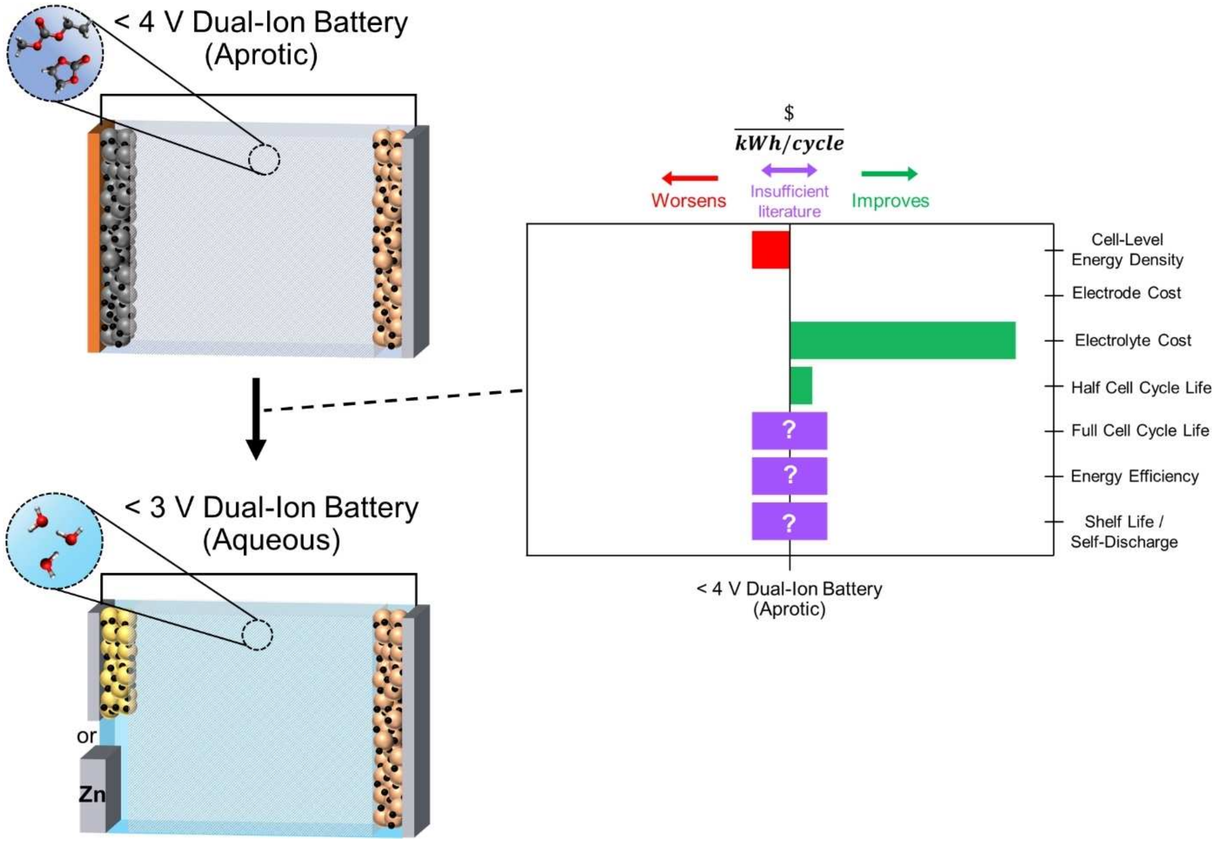

**Figure 4.** Prospects of DIBs employing aqueous electrolytes for reducing the levelized cost necessary for stationary energy storage. The electrode cost of each system is considered comparable, yet likely dependent on the viability of the Zn anode.

promise for reducing levelized cost beneath the long-term goal of 0.1 $\$\,kWh^{-1}\,cycle^{-1}$;[17b] however, a number of aspects must be further investigated before conclusions are made. First, the poor reductive stability of aqueous electrolytes renders typical cation-intercalating anode materials unavailable for use, which necessitates either the advent of novel anodes, or the stabilization of Zn metal in the aforementioned low-cost electrolytes.[17e,18c,d] Additionally, as with any commercial battery system, the impact of practical operating conditions required for optimal energy density on various performance attributes must be elucidated before application at scale. In particular, clear and decisive efforts towards reducing N/P ratio (full-cell balancing), increasing electrode loading, and reducing the electrolyte volume should be made to identify any adverse effects towards the ostensibly advantageous cycle life of DIBs. Such considerations may play a critical role in the participation of DIBs in the technological landscape of grid storage.

## Strategies to Overcome Dual-Ion Battery Limitations

Though current DIBs show promise for fulfilling a limited number of energy storage applications, their primary practical limitation is the lack of cell-level energy density and required electrolyte loading. The improvement of these metrics would not only improve the competitiveness of DIBs for low-temperature and grid storage technologies but may also expand their feasibility into other technologies. Though the energy density of LIBs is likely unreachable for DIBs, a slight reduction may also be tenable to drive down the price of a variety of portable electronics (this rationale is similar to that behind sodium-ion batteries). The following conceptual analysis outlines two strategies that show promise to drive up the energy density of DIBs through solid salt storage to drive down the required electrolyte volume at scale, and the pursuit of redox-active charge carriers to further increase the specific capacities of anion-hosting cathodes.

### *Solid salt storage*

The primary limitation of both gravimetric and volumetric energy density in DIBs is the required electrolyte volume necessary to supply ions to the electrodes.[11] Assuming the cathode capacity is limiting in the full-cell, the minimum required electrolyte amount is defined by the point where the total electrolyte charge is equal to the total cathode capacity [Eq. (1)]:

$$\frac{F \times z \times C_{\text{electrolyte}} \times V_{\text{electrolyte}}}{3.6} = q_{\text{cathode}} \times m_{\text{cathode}} \tag{1}$$

where $F$ is the faraday constant, $q_{\text{cathode}}$ is the specific capacity of the cathode [$\text{mAh}\,\text{g}^{-1}$], $m_{\text{cathode}}$ is the total active mass of the cathode, $z$ is the valence state of the ions, $V_{\text{electrolyte}}$ is the total electrolyte volume, and $C_{\text{electrolyte}}$ is the concentration of the electrolyte [$\text{mol}\,\text{L}^{-1}$]. The minimum required electrolyte loading ($V_{\text{req}}$) can be calculated according to Equations (2) or (3):

$$V_{\text{req}} = 10^3 \times \frac{3.6 \times q_{\text{cathode}}}{F \times z \times C_{\text{electrolyte}}} \left[\frac{\text{mL}_{\text{electrolyte}}}{\text{g}_{\text{cathode}}}\right] \tag{2}$$

$$V_{\text{req}} = 10^6 \times \frac{3.6 \times \rho_{\text{electrolyte}}}{F \times z \times C_{\text{electrolyte}}} \left[\frac{\text{g}_{\text{electrolyte}}}{\text{Ah}}\right] \tag{3}$$

where $\rho_{\text{electrolyte}}$ is the density of the electrolyte [$\text{g}\,\text{mL}^{-1}$]. From this relationship it can be calculated that for a monovalent 4 M electrolyte with an assumed density of 1.4 $\text{g}\,\text{mL}^{-1}$ (used in previous models),[11] the required electrolyte loading for a DIB is around 13.1 $\text{g}\,\text{Ah}^{-1}$. LIBs, on the other hand, only require enough electrolyte to fully wet the pores of the electrodes and separator, and therefore typically employ commercial electrolyte loadings in the range of 2–3 $\text{g}\,\text{Ah}^{-1}$. While this minimum electrolyte loading has been historically managed through the increase of salt concentration, this approach is inherently limited by the salt solubility in the electrolyte (note that reported concentrations are typically with respect to solvent volume instead of total volume, and thereby overestimate the achievable concentration of common electrolytes).[2b,4g] A design solution to reduce the required electrolyte loading of the cell while providing a sufficient ion source to ensure full utilization of both electrodes is therefore highly desirable.

We propose to achieve this required electrolyte reduction through the addition of solid salt stores within the battery pictured in Figure 5a as part of the cathode composite, though the optimal location for such storage within the stack is up for debate. Doing so would provide additional ions to the system to continually replenish the electrolyte concentration during charging (Figure 5b). Though this salt indeed contributes additional passive mass and volume to the overall stack, the ion supply provided by a solid is far denser than that supplied by an electrolyte, which is in large part solvent. While a clear drawback of this strategy is that the employed liquid electrolyte must be fully saturated with salt, the advent of localized-high-concentration electrolytes allows this to be achieved without untenable reductions in ion transport and wetting properties.[24a,b] To demonstrate the feasibility of this solid salt storage, we employ a pouch cell model, which integrates the previously discussed minimum required electrolyte loading with the conventional metrics of previous models.[24c] We assume a 4.5 V, 5 Ah graphite||graphite cell with solid salt storage in the cathode composite (fixed conductive carbon and binder contents of 5% each) and enforce an electrolyte loading that must exceed 110% of both the total cathode capacity and maximum total pore volume of the cathode (accounting for salt dissolution), anode, and separator. Full details are provided in the Supporting Information. As shown in Figure 5c, the inclusion of solid salt storage has the potential to significantly improve both gravimetric and volumetric energy density through the reduction of required electrolyte volume. The degree of improvement is largely dependent on the molecular weight and density of the salt, where $\text{LiBF}_4$ shows a baseline energy density increase from 148 to 174 $\text{Wh}\,\text{kg}^{-1}$ at 14 wt% salt in the cathode compared to an increase of only 4 $\text{Wh}\,\text{kg}^{-1}$ in the lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) case. It is also noteworthy that the optimum salt content also shifts as a function of $M_w$, where the added salt capacity is offset by added passive pore volume at high mass % (Figure 5c).

Though solid salt storage offers a substantial increase in energy density as well as a reduction in electrolyte cost, a number of practical considerations must be addressed. Though the aforementioned projection model assumes salt integration into the cathode composite and a baseline porosity of 30% which then goes onto increase during salt dissolution, the optimal cell location and method for solid salt storage still requires additional thought and effort. Additionally, due to the relationship between molecular weight and energy density improvement identification of a low weight anion with reversible storage performance is also highly desirable. It is also necessary to determine the impact of repetitive internal salt dissolution and precipitation on cycle life. Proper cell design to reduce impact on mass transport during re-precipitation may involve the need to increase separator porosity/thickness, or further electrode structure design. Additionally, ensuring the electrochemical stability of the solid salt in contact with either electrode is crucial to ensuring cycle life. Though the anion stability in solid salt form is likely improved to that in its liquid form due to intimate ion-pairing interactions, the impacts of the precipitation of potentially reactive materials on passivating interphases is relatively unknown.[24a] Despite these lingering questions, solid salt storage may present a solution to the long-standing energy density limitations of DIBs.

### *Halogen intercalation-conversion*

Though solid salt storage promises to significantly improve the required electrolyte loading of DIBs, these requirements still vastly exceed LIBs. Additionally, achieving desirable energy densities would still require the of employment of $>5$ V graphite cathodes, which as previously discussed have not been reversibly demonstrated in limited N/P ratio full-cells due to parasitic reactivity.[2b,4a,c–g,9] Improving the capacity of moderate-voltage anion storage paired with solid salt storage is therefore necessary to achieve DIBs with energy densities rivaling LIBs. As the primary limitation of anion storage capacity is the size/mass of anions found in common battery electrolyte salts, DIBs employing halogen anions ($\text{I}^-$, $\text{Br}^-$, $\text{Cl}^-$, $\text{F}^-$, etc.) have been a subject of investigation for improved capacity. However, the majority of halogen storage cathodes tend to rely on electrode chemistries that undergo substantial phase change, such as $\text{BiF}_3$, and face kinetic and cycling limitations.[25] Halogen

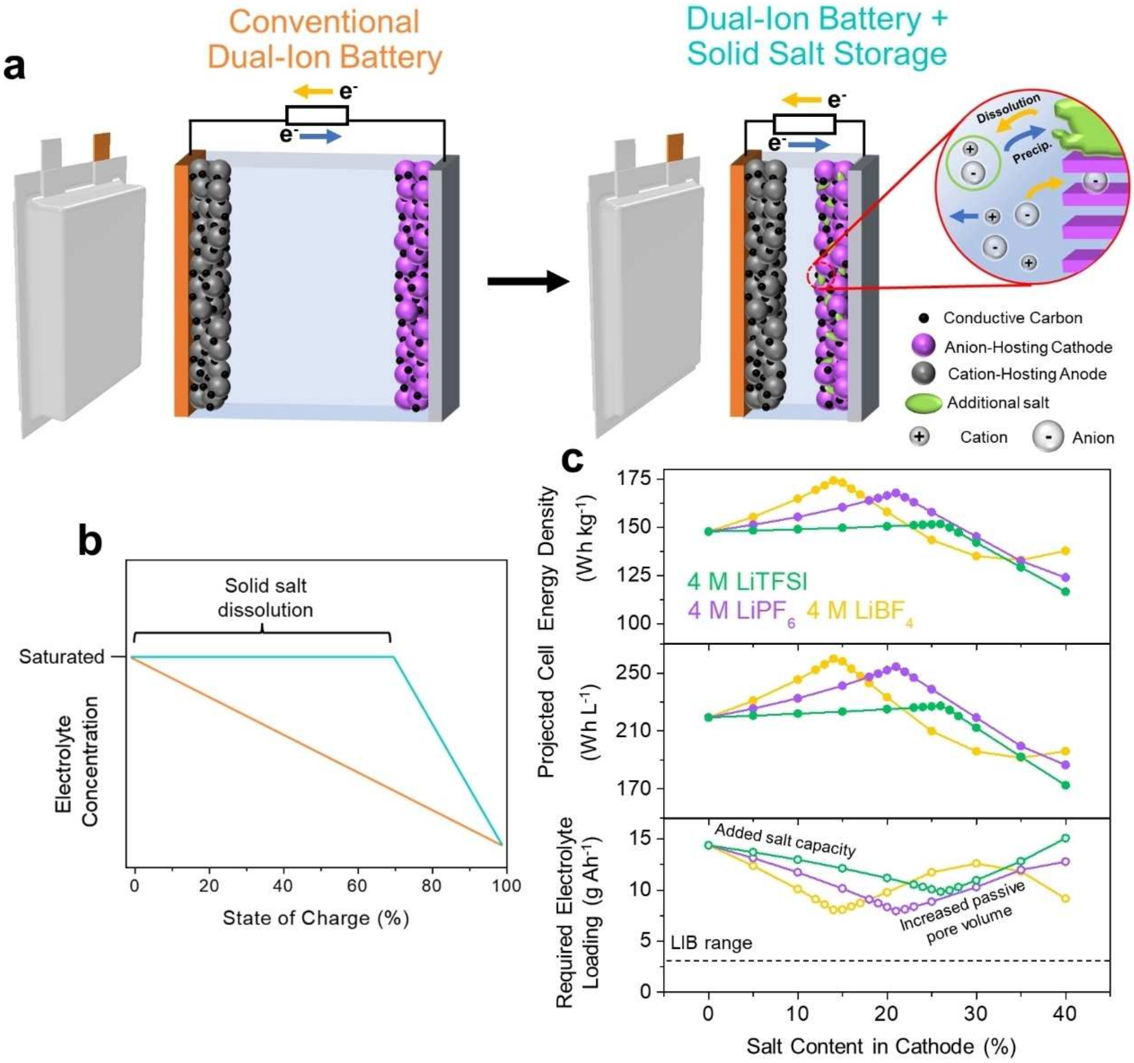

**Figure 5.** Conceptual appeal of solid salt storage for the reduction of required electrolyte loading in next-generation DIBs. (a) Schematic of working mechanism of solid salt storage in the battery's cathode. In principle the salt can be stored anywhere in the cell. (b) Relationship between state-of-charge and salt concentration in the electrolyte, where solid salt storage would facilitate lean-electrolyte conditions. (c) Projected gravimetric energy density and required electrolyte loading as a function of stored salt content in the cathode slurry based on a pouch cell model (Supporting Information). Projection is for 4.5 V, 5 Ah graphite||graphite pouch cells at N/P = 1.2 and 3 mAh cm$^{-2}$ cathode loading. The required electrolyte loading is calculated as the amount of 4 M (1.4 g mL$^{-1}$) electrolyte required to match 110% of the cathode capacity. Full calculation details and assumptions are provided in the Supporting Information, and the model is included as a Supplemental file.

conversion has also been investigated, primarily in iodine chemistries ($I_2$, $I_3^-$, $I^-$), where dissolved anions in the electrolyte undergo redox reactions. However, these cell chemistries encounter many cross-talk-related challenges associated with liquid-phase charge storage and rely on either mesoporous hosts or single-ion conducting membranes to reversibly cycle without substantial shuttling.[19c,26] Hence, the long-term cyclability of DIBs based on high energy halogen chemistries have yet to be realized in limited N/P ratio full-cells.

While these intrinsic tradeoffs between anion-storing cathode capacity and cyclability have historically limited development, a solution may have been realized with the advent of anion intercalation-conversion chemistries (Figure 6a). As demonstrated by Yang et al., $Cl^-$ and $Br^-$ can be co-intercalated within graphite, and if oxidative current is maintained the $Cl^-$ $Br^-$ can be further oxidized to $[BrCl]^-$ within the graphene sheets, with a practical reversible capacity of around 220 mAh g$^{-1}$.[27a] In addition to this remarkable increase in capacity, halogen intercalation-conversion occurs at $\leq$4.5 V vs. $Li/Li^+$, which indicates that long cycle lives may be more achievable that in conventional $>$5 V graphite cathode systems. Works from Guo et al. and Sonnenberg et al. demonstrate the reversible intercalation-conversion of $[ICl_2]^-$ within graphite at a reversible capacity of around 300 mAh g$^{-1}$, which indicates that the entire library of interhalogens may be employed in DIBs.[27b,c] Li et al. have also recently demonstrated the conversion of $I^-$ to $I_3^-$ within a redox-active organic electrode, which may also indicate that the host library for interhalogen storage extends

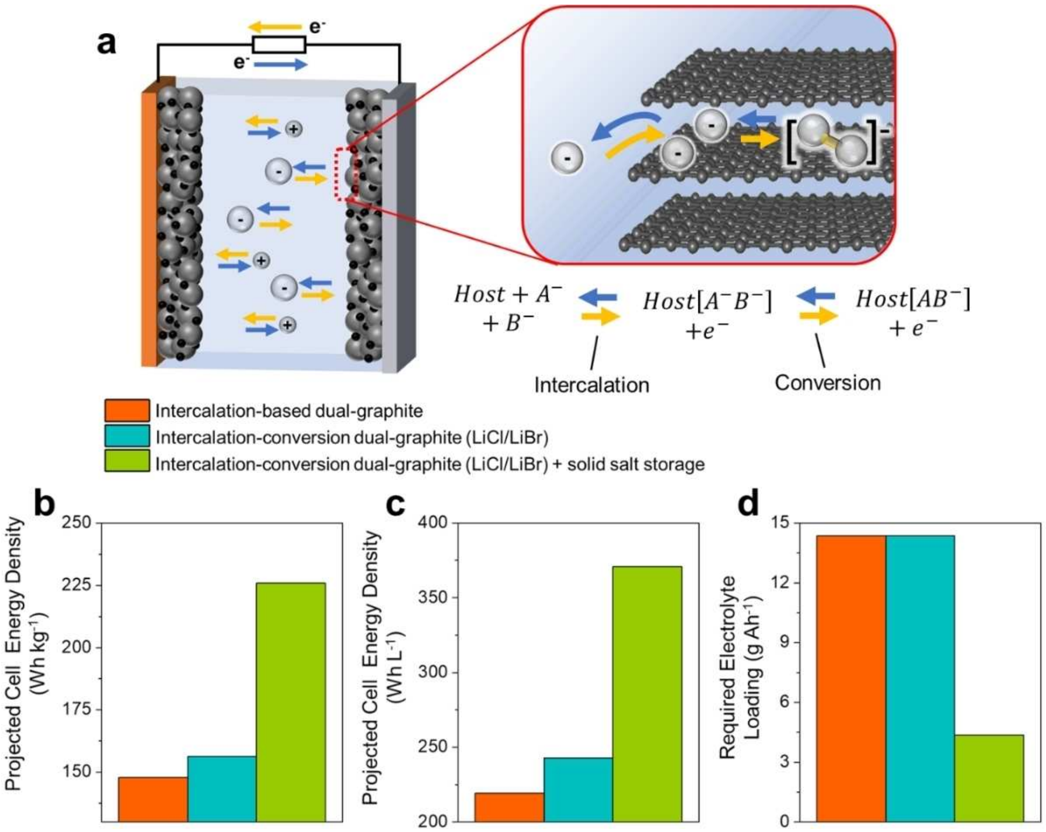

**Figure 6.** Advantages of halogen-based anion intercalation-conversion storage for next-generation DIBs. (a) Schematic depicting the halogen conversion-intercalation charge storage mechanism. Projected pouch cell metrics for conventional dual-graphite and dual-graphite halogen intercalation-conversion chemistries based on the previously discussed model (Supporting Information). (b) Projected gravimetric energy density, (c) projected volumetric energy density, and (d) projected required electrolyte loading. The applied (optimal) solid salt composition for the intercalation-conversion dual-graphite + solid salt storage system was 25% by mass.

beyond graphite.[28] As a demonstration of the promise of such chemistries, we apply the previously discussed cell-level energy density model (Figure 6b–d). These projections indicate that though intercalation-conversion dual-graphite batteries based on $[BrCl]^-$ interhalogens represent a relatively small improvement over conventional dual-graphite systems, their increased capacity in tandem with solid salt storage could in principle reach energy densities of 225 Wh kg$^{-1}$ and 371 Wh L$^{-1}$ at scale (see the Supporting Information for details).

Despite the clear promise of halogen intercalation-conversion DIBs, significant effort must be investigated to further develop and understand the principles dictating their reversibility and scaling feasibility. First, the limited reports of halogen intercalation-conversion in graphite cathodes have so far required WiSE systems such as 21 м LiTFSI + 7 м lithium trifluoromethanesulfonate (LiOTF) or 120 м choline chloride + 30 м $ZnCl_2$ + 5 м KI. To ensure long-term compatibility with the graphite and alkali metal anodes, it is crucial that the barriers to achieving intercalation-conversion in aprotic electrolytes be elucidated. Furthermore, the relatively low half-cell coulombic efficiencies of currently demonstrated systems (≈99%[27a] and ≈90%[27b]) indicate that additional stabilization methods of the intercalation-conversion host must be developed for their integration to low N/P ratio, lean electrolyte full-cells. Along these lines, methods to further catalyze the formation of interhalogens within anion-storing hosts while suppressing their conversion in the electrolyte should be investigated to improve cycling efficiency, stability, and to expand the library of possible interhalogens/interhalogen hosts. Despite these clear barriers, DIBs based on intercalation-conversion may legitimately represent an opportunity for achieving similar energy densities to LIBs at a fraction of the materials cost.

## Conclusions

The dual-ion battery (DIB) is a unique energy storage system with a set of intrinsic advantages and disadvantages that present both exciting performance prospects and daunting design challenges. Though the inherent rapid interphasial kinetics associated with anion storage and the wide library of naturally abundant electrode and electrolyte materials are ostensibly desirable over lithium-ion batteries (LIBs), their projected energy densities lag far behind lithium-ion cells. These reduced energy densities fundamentally stem from the high required electrolyte loadings associated with the dual-ion storage mechanism, and the relatively reduced capacity of anion storage. Though anion-storing graphite cathodes may mitigate this energy loss, their extreme voltages preclude their reversible operation in full-cells and therefore limit practical feasibility. Despite this, their rapid kinetics have been demonstrated to significantly improve cell performance scaling towards low temperatures, which may indicate there are sub-zero conditions at which DIBs exceed the power density of LIBs. Additionally, their low-energy densities do not preclude them from competition in stationary energy storage, where the emphasis is equally placed on materials cost and cycle life. There may be next-generation strategies for DIBs to approach LIB energy densities at the cell level. Through cell-level projection models, we predict that the inclusion of solid salt stores within the battery stack may significantly reduce the required electrolyte loading, thereby improving both gravimetric and volumetric energy density. Furthermore, the recent advent of halogen intercalation-conversion storage may present a lasting solution to the energy density, cycle life, and materials cost tradeoff that currently limits feasibility at scale. Though difficult, there are legitimate paths for widespread adoption of DIBs at scale.

## *Conflict of Interest*

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** dual ion batteries · energy density · energy storage · grid storage · halogen conversion

[1] a) M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652–657; b) J. B. Goodenough, K.-S. Park, *J. Am. Chem. Soc.* **2013**, *135*, 1167–1176; c) M. Song, H. Tan, D. Chao, H. J. Fan, *Adv. Funct. Mater.* **2018**, *28*, 1802564; d) K. Chayambuka, G. Mulder, D. L. Danilov, P. H. L. Notten, *Adv. Energy Mater.* **2020**, *10*, 2001310; e) Y. Tian, G. Zeng, A. Rutt, T. Shi, H. Kim, J. Wang, J. Koettgen, Y. Sun, B. Ouyang, T. Chen, Z. Lun, Z. Rong, K. Persson, G. Ceder, *Chem. Rev.* **2021**, *121*, 1623–1669.

[2] a) I. A. Rodríguez-Pérez, X. Ji, *ACS Energy Lett.* **2017**, *2*, 1762–1770; b) T. Placke, A. Heckmann, R. Schmuch, P. Meister, K. Beltrop, M. Winter, *Joule* **2018**, *2*, 2528–2550; c) M. Wang, Y. Tang, *Adv. Energy Mater.* **2018**, *8*, 1703320; d) X. Zhou, Q. Liu, C. Jiang, B. Ji, X. Ji, Y. Tang, H.-M. Cheng, *Angew. Chem. Int. Ed.* **2020**, *59*, 3802–3832; *Angew. Chem.* **2020**, *132*, 3830–3861.

[3] a) W. Rüdorff, U. Hofmann, *Z. Anorg. Allg. Chem.* **1938**, *238*, 1–50; b) R. Santhanam, M. Noel, *J. Power Sources* **1997**, *66*, 47–54; c) J. A. Seel, J. R. Dahn, *J. Electrochem. Soc.* **2000**, *147*, 892.

[4] a) J. A. Read, A. V. Cresce, M. H. Ervin, K. Xu, *Energy Environ. Sci.* **2014**, *7*, 617–620; b) Z. Huang, Y. Hou, T. Wang, Y. Zhao, G. Liang, X. Li, Y. Guo, Q. Yang, Z. Chen, Q. Li, L. Ma, J. Fan, C. Zhi, *Nat. Commun.* **2021**, *12*, 3106; c) T. Placke, S. Rothermel, O. Fromm, P. Meister, S. F. Lux, J. Huesker, H.-W. Meyer, M. Winter, *J. Electrochem. Soc.* **2013**, *160*, A1979; d) A. Heckmann, J. Thienenkamp, K. Beltrop, M. Winter, G. Brunklaus, T. Placke, *Electrochim. Acta* **2018**, *260*, 514–525; e) T. Placke, O. Fromm, S. F. Lux, P. Bieker, S. Rothermel, H.-W. Meyer, S. Passerini, M. Winter, *J. Electrochem. Soc.* **2012**, *159*, A1755; f) S. Wang, S. Jiao, D. Tian, H.-S. Chen, H. Jiao, J. Tu, Y. Liu, D.-N. Fang, *Adv. Mater.* **2017**, *29*, 1606349; g) J. Tu, W.-L. Song, H. Lei, Z. Yu, L.-L. Chen, M. Wang, S. Jiao, *Chem. Rev.* **2021**, *121*, 4903–4961; h) G. Wang, M. Yu, J. Wang, D. Li, D. Tan, M. Löffler, X. Zhuang, K. Müllen, X. Feng, *Adv. Mater.* **2018**, *30*, 1800533.

[5] a) É. Deunf, P. Moreau, É. Quarez, D. Guyomard, F. Dolhem, P. Poizot, *J. Mater. Chem. A* **2016**, *4*, 6131–6139; b) I. A. Rodríguez-Pérez, Z. Jian, P. K. Waldenmaier, J. W. Palmisano, R. S. Chandrabose, X. Wang, M. M. Lerner, R. G. Carter, X. Ji, *ACS Energy Lett.* **2016**, *1*, 719–723; c) S. Dong, Z. Li, I. A. Rodríguez-Pérez, H. Jiang, J. Lu, X. Zhang, X. Ji, *Nano Energy* **2017**, *40*, 233–239; d) I. A. Rodríguez-Pérez, C. Bommier, D. D. Fuller, D. P. Leonard, A. G. Williams, X. Ji, *ACS Appl. Mater. Interfaces* **2018**, *10*, 43311–43315; e) G. Dai, Y. He, Z. Niu, P. He, C. Zhang, Y. Zhao, X. Zhang, H. Zhou, *Angew. Chem. Int. Ed.* **2019**, *58*, 9902–9906; *Angew. Chem.* **2019**, *131*, 10007–10011; f) H. Glatz, E. Lizundia, F. Pacifico, D. Kundu, *ACS Appl. Energ. Mater.* **2019**, *2*, 1288–1294.

[6] a) M. L. Aubrey, J. R. Long, *J. Am. Chem. Soc.* **2015**, *137*, 13594–13602; b) S. Dühnen, R. Nölle, J. Wrogemann, M. Winter, T. Placke, *J. Electrochem. Soc.* **2019**, *166*, A5474; c) X. Lou, F. Geng, B. Hu, C. Li, M. Shen, B. Hu, *ACS Appl. Energ. Mater.* **2019**, *2*, 413–419; d) C. Li, H. Yang, J. Xie, K. Wang, J. Li, Q. Zhang, *ACS Appl. Mater. Interfaces* **2020**, *12*, 32719–32725.

[7] a) J. K. Feng, Y. L. Cao, X. P. Ai, H. X. Yang, *J. Power Sources* **2008**, *177*, 199–204; b) F. A. Obrezkov, A. F. Shestakov, S. G. Vasilev, K. J. Stevenson, P. A. Troshin, *J. Mater. Chem. A* **2021**, *9*, 2864–2871; c) T. Sun, Q.-Q. Sun, Y. Yu, X.-B. Zhang, *eScience* **2021**, *1*, 186–193; d) S. Xu, H. Dai, S. Zhu, Y. Wu, M. Sun, Y. Chen, K. Fan, C. Zhang, C. Wang, W. Hu, *eScience* **2021**, *1*, 60–68; e) C. Zhang, W. Ma, C. Han, L.-W. Luo, A. Daniyar, S. Xiang, X. Wu, X. Ji, J.-X. Jiang, *Energy Environ. Sci.* **2021**, *14*, 462–472; f) Y. Zhang, Y. An, B. Yin, J. Jiang, S. Dong, H. Dou, X. Zhang, *J. Mater. Chem. A* **2019**, *7*, 11314–11320; g) S. Wang, F. Li, A. D. Easley, J. L. Lutkenhaus, *Nat. Mater.* **2019**, *18*, 69–75.

[8] a) R. Schmuch, R. Wagner, G. Hörpel, T. Placke, M. Winter, *Nat. Energy* **2018**, *3*, 267–278; b) P. Xu, D. H. S. Tan, Z. Chen, *Trends Chem.* **2021**, *3*, 620–630.

[9] a) Y. Liang, H. Dong, D. Aurbach, Y. Yao, *Nat. Energy* **2020**, *5*, 646–656; b) X. Zhang, Y. Tang, F. Zhang, C.-S. Lee, *Adv. Energy Mater.* **2016**, *6*, 1502588; c) K. V. Kravchyk, P. Bhauriyal, L. Piveteau, C. P. Guntlin, B. Pathak, M. V. Kovalenko, *Nat. Commun.* **2018**, *9*, 4469; d) M. Sheng, F. Zhang, B. Ji, X. Tong, Y. Tang, *Adv. Energy Mater.* **2017**, *7*, 1601963; e) 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*, 324–328; f) J. Tu, W.-L. Song, H. Lei, Z. Yu, L.-L. Chen, M. Wang, S. Jiao, *Chem. Rev.* **2021**, *121*, 4903–4961; g) S. Wang, S. Jiao, D. Tian, H.-S. Chen, H. Jiao, J. Tu, Y. Liu, D.-N. Fang, *Adv. Mater.* **2017**, *29*, 1606349.

[10] a) K. Xu, *J. Electrochem. Soc.* **2007**, *154*, A162; b) K. Xu, A. von Cresce, U. Lee, *Langmuir* **2010**, *26*, 11538–11543; c) H. Cheng, Q. Sun, L. Li, Y. Zou, Y. Wang, T. Cai, F. Zhao, G. Liu, Z. Ma, W. Wahyudi, Q. Li, J. Ming, *ACS Energy Lett.* **2022**, *7*, 490–513.

[11] J. Betz, G. Bieker, P. Meister, T. Placke, M. Winter, R. Schmuch, *Adv. Energy Mater.* **2019**, *9*, 1803170.

[12] F. Holtstiege, P. Bärmann, R. Nölle, M. Winter, T. Placke, *Batteries* **2018**, *4*, 4.

[13] a) Y. Wang, Y. Zhang, S. Dong, W. Zhou, P.-K. Lee, Z. Peng, C. Dang, P. H.-L. Sit, J. Guo, D. Y. W. Yu, *Adv. Energy Mater.* **2022**, *12*, 2103360; b) X. Fan, L. Chen, O. Borodin, X. Ji, J. Chen, S. Hou, T. Deng, J. Zheng, C. Yang, S.-C. Liou, K. Amine, K. Xu, C. Wang, *Nat. Nanotechnol.* **2018**, *13*, 715–722.

[14] a) S. S. Zhang, K. Xu, T. R. Jow, *J. Power Sources* **2003**, *115*, 137–140; b) G. Nagasubramanian, *J. Appl. Electrochem.* **2001**, *31*, 99–104; c) M. C. Smart, B. V. Ratnakumar, K. B. Chin, L. D. Whitcanack, *J. Electrochem. Soc.* **2010**, *157*, A1361–A1374; d) N. Zhang, T. Deng, S. Zhang, C. Wang, L. Chen, C. Wang, X. Fan, *Adv. Mater.* **2022**, *34*, 2107899.

[15] a) Q. Li, S. Jiao, L. Luo, M. S. Ding, J. Zheng, S. S. Cartmell, C.-M. Wang, K. Xu, J.-G. Zhang, W. Xu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 18826–18835; b) Q. Li, D. Lu, J. Zheng, S. Jiao, L. Luo, C.-M. Wang, K. Xu, J.-G. Zhang, W. Xu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 42761–42768; c) R. A. Marcus, *J. Chem. Phys.* **1965**, *43*, 679–701; d) M. Okoshi, Y. Yamada, A. Yamada, H. Nakai, *J. Electrochem. Soc.* **2013**, *160*, A2160–A2165; e) A. Gupta, A. Manthiram, *Adv. Energy Mater.* **2020**, *10*, 2001972.

[16] a) X. Dong, Z. Guo, Z. Guo, Y. Wang, Y. Xia, *Joule* **2018**, *2*, 902–913; b) X. Dong, Y. Lin, P. Li, Y. Ma, J. Huang, D. Bin, Y. Wang, Y. Qi, Y. Xia, *Angew. Chem. Int. Ed.* **2019**, *58*, 5623–5627; *Angew. Chem.* **2019**, *131*, 5679–5683; c) J. Chen, Y. Peng, Y. Yin, Z. Fang, Y. Cao, Y. Wang, X. Dong, Y. Xia, *Angew. Chem. Int. Ed.* **2021**, *60*, 23858–23862; d) N. Wang, X. Dong,

B. Wang, Z. Guo, Z. Wang, R. Wang, X. Qiu, Y. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 14577–14583; *Angew. Chem.* **2020**, *132*, 14685–14691; e) B. Jiang, Y. Su, R. Liu, Z. Sun, D. Wu, *Small* **2022**, *18*, 2200049; f) J. Holoubek, Y. Yin, M. Li, M. Yu, Y. S. Meng, P. Liu, Z. Chen, *Angew. Chem. Int. Ed.* **2019**, *58*, 18892–18897; *Angew. Chem.* **2019**, *131*, 19068–19073.

[17] a) S. Ong, C. Campbell, P. Denholm, R. Margolis, G. Heath, *Land-Use Requirements for Solar Power Plants in the United States* **2013**. NREL/TP-6 A20-56290, 1086349; b) U. S. Department of Energy. Grid Energy Storage **2013**, https://www.energy.gov/sites/prod/files/2013/12/f5/Grid%20Energy%20Storage%20December%202013.pdf; c) Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **2011**, *111*, 3577–3613; d) S. Chu, A. Majumdar, *Nature* **2012**, *488*, 294–303; e) X. Ji, *Energy Environ. Sci.* **2019**, *12*, 3203–3224.

[18] a) M. Park, J. Ryu, W. Wang, J. Cho, *Nat. Rev. Mater.* **2016**, *2*, 1–18; b) E. Sánchez-Díez, E. Ventosa, M. Guarnieri, A. Trovò, C. Flox, R. Marcilla, F. Soavi, P. Mazur, E. Aranzabe, R. Ferret, *J. Power Sources* **2021**, *481*, 228804; c) L. E. Blanc, D. Kundu, L. F. Nazar, *Joule* **2020**, *4*, 771–799; d) L. Ma, M. A. Schroeder, O. Borodin, T. P. Pollard, M. S. Ding, C. Wang, K. Xu, *Nat. Energy* **2020**, *5*, 743–749.

[19] a) X. Wu, Y. Xu, C. Zhang, D. P. Leonard, A. Markir, J. Lu, X. Ji, *J. Am. Chem. Soc.* **2019**, *141*, 6338–6344; b) H. Jiang, X. Ji, *Carbon Energy* **2020**, *2*, 437–442; c) J. J. Hong, L. Zhu, C. Chen, L. Tang, H. Jiang, B. Jin, T. C. Gallagher, Q. Guo, C. Fang, X. Ji, *Angew. Chem. Int. Ed.* **2019**, *58*, 15910–15915; *Angew. Chem.* **2019**, *131*, 16057–16062; d) Z. Miao, H. Yu, M. Xia, R. Zheng, Z. Yang, Y. Liu, L. Zhang, J. Shu, *Sustain. Energy Fuels* **2021**, *5*, 3298–3302; e) Q. Guo, K. Kim, H. Jiang, L. Zhang, C. Zhang, D. Yu, Q. Ni, X. Chang, T. Chen, H. Xia, X. Ji, *Adv. Funct. Mater.* **2020**, *30*, 2002825.

[20] a) H. Jiang, Z. Wei, L. Ma, Y. Yuan, J. J. Hong, X. Wu, D. P. Leonard, J. Holoubek, J. J. Razink, W. F. Stickle, F. Du, T. Wu, J. Lu, X. Ji, *Angew. Chem. Int. Ed.* **2019**, *58*, 5286–5291; *Angew. Chem.* **2019**, *131*, 5340–5345; b) H. Yu, C. Deng, H. Yan, M. Xia, X. Zhang, Z.-B. Wang, J. Shu, *Nano-Micro Lett.* **2021**, *13*, 41; c) Q. Nian, S. Liu, J. Liu, Q. Zhang, J. Shi, C. Liu, R. Wang, Z. Tao, J. Chen, *ACS Appl. Energ. Mater.* **2019**, *2*, 4370–4378.

[21] a) K. Kim, Q. Guo, L. Tang, L. Zhu, C. Pan, C. Chang, J. Razink, M. M. Lerner, C. Fang, X. Ji, *Angew. Chem. Int. Ed.* **2020**, *59*, 19924–19928; *Angew. Chem.* **2020**, *132*, 20096–20100; b) Y. Zhu, J. Yin, A.-H. Emwas, O. F. Mohammed, H. N. Alshareef, *Adv. Funct. Mater.* **2021**, *31*, 2107523; c) K. Kim, L. Tang, J. M. Muratli, C. Fang, X. Ji, *ChemSusChem* **2022**, *15*, e202102394.

[22] a) G. Zhou, X. An, C. Zhou, Y. Wu, Y.-E. Miao, T. Liu, *Compos. Commun.* **2020**, *22*, 100519; b) Y. Zhang, Y. An, B. Yin, J. Jiang, S. Dong, H. Dou, X. Zhang, *J. Mater. Chem. A* **2019**, *7*, 11314–11320.

[23] a) C. Zhang, J. Holoubek, X. Wu, A. Daniyar, L. Zhu, C. Chen, D. P. Leonard, I. A. Rodríguez-Pérez, J.-X. Jiang, C. Fang, X. Ji, *Chem. Commun.* **2018**, *54*, 14097–14099; b) C. Zhang, W. Shin, L. Zhu, C. Chen, J. C. Neuefeind, Y. Xu, S. I. Allec, C. Liu, Z. Wei, A. Daniyar, J.-X. Jiang, C. Fang, P. Alex Greaney, X. Ji, *Carbon Energy* **2021**, *3*, 339–348; c) X. Bu, L. Su, Q. Dou, S. Lei, X. Yan, *J. Mater. Chem. A* **2019**, *7*, 7541–7547; d) D. P. Leonard, Z. Wei, G. Chen, F. Du, X. Ji, *ACS Energy Lett.* **2018**, *3*, 373–374; e) J. Holoubek, H. Jiang, D. Leonard, Y. Qi, G. C. Bustamante, X. Ji, *Chem. Commun.* **2018**, *54*, 9805–9808.

[24] a) M. Li, C. Wang, Z. Chen, K. Xu, J. Lu, *Chem. Rev.* **2020**, *120*, 6783–6819; b) S. Chen, J. Zheng, D. Mei, K. S. Han, M. H. Engelhard, W. Zhao, W. Xu, J. Liu, J.-G. Zhang, *Adv. Mater.* **2018**, *30*, 1706102; c) C. Niu, H. Lee, S. Chen, Q. Li, J. Du, W. Xu, J.-G. Zhang, M. S. Whittingham, J. Xiao, J. Liu, *Nat. Energy* **2019**, *4*, 551–559.

[25] a) V. K. Davis, C. M. Bates, K. Omichi, B. M. Savoie, N. Momčilović, Q. Xu, W. J. Wolf, M. A. Webb, K. J. Billings, N. H. Chou, S. Alayoglu, R. K. McKenney, I. M. Darolles, N. G. Nair, A. Hightower, D. Rosenberg, M. Ahmed, C. J. Brooks, T. F. Miller, R. H. Grubbs, S. C. Jones, *Science* **2018**, *362*, 1144–1148; b) T. Yamanaka, A. C. Kucuk, Z. Ogumi, T. Abe, *ACS Appl. Energ. Mater.* **2020**, *3*, 9390–9400; c) Q. Yin, J. Luo, J. Zhang, L. Zheng, G. Cui, J. Han, D. O'Hare, *J. Mater. Chem. A* **2020**, *8*, 12548–12555.

[26] a) M. Wang, T. Li, Y. Yin, J. Yan, H. Zhang, X. Li, *Adv. Energy Mater.* **2022**, *2200728*; b) K. Lu, Z. Hu, J. Ma, H. Ma, L. Dai, J. Zhang, *Nat. Commun.* **2017**, *8*, 527; c) Y. L. Wang, Q. L. Sun, Q. Q. Zhao, J. S. Cao, S. H. Ye, *Energy Environ. Sci.* **2011**, *4*, 3947–3950; d) Y. Zhao, L. Wang, H. R. Byon, *Nat. Commun.* **2013**, *4*, 1896.

[27] a) C. Yang, J. Chen, X. Ji, T. P. Pollard, X. Lü, C.-J. Sun, S. Hou, Q. Liu, C. Liu, T. Qing, Y. Wang, O. Borodin, Y. Ren, K. Xu, C. Wang, *Nature* **2019**, *569*, 245–250; b) Q. Guo, K.-I. Kim, S. Li, A. M. Scida, P. Yu, S. K. Sandstrom, L. Zhang, S. Sun, H. Jiang, Q. Ni, D. Yu, M. M. Lerner, H. Xia, X. Ji, *ACS Energy Lett.* **2021**, *6*, 459–467; c) K. Sonnenberg, L. Mann, F. A. Redeker, B. Schmidt, S. Riedel, *Angew. Chem. Int. Ed.* **2020**, *59*, 5464–5493; *Angew. Chem.* **2020**, *132*, 5506–5535.

[28] a) X. Li, Y. Wang, Z. Chen, P. Li, G. Liang, Z. Huang, Q. Yang, A. Chen, H. Cui, B. Dong, H. He, C. Zhi, *Angew. Chem. Int. Ed.* **2022**, *61*, e202113576.

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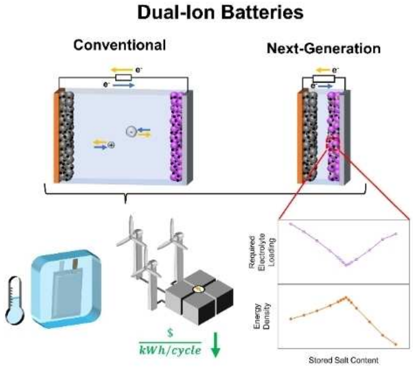
**A critical look**: Dual-ion batteries (DIBs) promise superior kinetics, cycle life, and materials cost, but their achievable energy densities limit their future applications to low-temperature operation and grid-scale energy storage. To overcome this, solid salt storage in the stack and further development of halogen intercalation/conversion cathodes could raise energy density projections to lithium-ion battery levels and are thus vital future research directions.



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**Application-Based Prospects for Dual-Ion Batteries**