

Eutectic Electrolytes in Advanced Metal-Ion Batteries

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ABSTRACT: Metal-ion batteries (MIBs) are promising for large-scale energy storage because they can alleviate the inherent intermittency of renewable energy. As an indispensable part of MIBs, electrolytes influence the electrochemical performance. Recently, the new concept of eutectic electrolytes has aroused extensive research attention in the field of MIBs due to their simple synthesis and eco-friendly features. Nevertheless, the development of eutectic electrolytes is still in its infancy and deserves further attention. This review focuses on the systematic understanding of the relationship between eutectic electrolytes and the corresponding performances of MIBs. First, fundamentals of eutectic electrolytes are described. Then, recent progress in the use of eutectic electrolytes in MIBs is introduced, including the correlations between structure and properties, the chemistry at the electrode interface, and the ion/charge transport mechanism. Finally, the challenges and prospects related to eutectic electrolytes are discussed. This Focus Review will provide better directions to devise advanced eutectic electrolytes for high-performance MIBs.



Renewable energy is essential to promote the contemporary economy and sustainable development. However, its inherent intermittency hinders its further progress in the power grid.^{1,2} Metal-ion batteries (MIBs), as one kind of attractive electrochemical energy storage devices, are the key technology to overcome intermittency issues (Figure 1a).^{3,4} Developing high-performance MIBs systems depends not only on the structural design of stable electrode materials but also on customizing electrolytes to enable the new electrode materials to successfully perform useful functions.^{5–7} An excellent electrolyte should have good compatibility with electrodes, high ionic conductivity, and stable thermal/electrochemical behaviors (Figure 1b).^{8–10}

Recently, various types of electrolytes, such as “water-in-salt”,¹¹ ionic liquids (ILs),¹² organic electrolytes,¹³ solid-state electrolytes,¹⁴ and eutectic electrolytes,¹⁵ have been initiated to improve MIBs. Among them, eutectic electrolytes are essentially a kind of deep eutectic solvents (DESs). Abbott et al. first found that the mixture of urea and a series of quaternary ammonium salts is liquid at room temperature, and they coined the term DESs for this type of mixture whose freezing point is significantly lower than the melting point of each component.¹⁶ As a reaction medium, DESs were originally employed in the synthesis and processing of metals.^{17,18} Then, DESs were explored to build high-performance batteries; as electrolytes they are usually called eutectic

electrolytes.¹⁹ The fundamental physicochemical properties of DESs and their applications in some fields, including redox fluid batteries and nanomaterials synthesis, have been comprehensively reviewed.²⁰ However, the electrochemical mechanism of DESs as eutectic electrolytes for MIBs has not been systematically summarized.

In this review, we focus on the mechanistic understanding between eutectic electrolytes and the corresponding performances of MIBs. We summarize the concept, formation, and properties of eutectic electrolytes, which are of great significance to design excellent-performance eutectic electrolytes for MIBs. Then, we introduce MIBs incorporating eutectic electrolytes, mainly including Li-ion batteries (LIBs), Zn-ion batteries (ZIBs), and Al-ion batteries (AIBs), and further discuss how certain characteristics of eutectic electrolytes can improve the electrochemical performance of MIBs. We also briefly list the DESs, some of which have not yet been applied to MIBs but demonstrate potential as a eutectic electrolyte for MIBs. The summarized information should help

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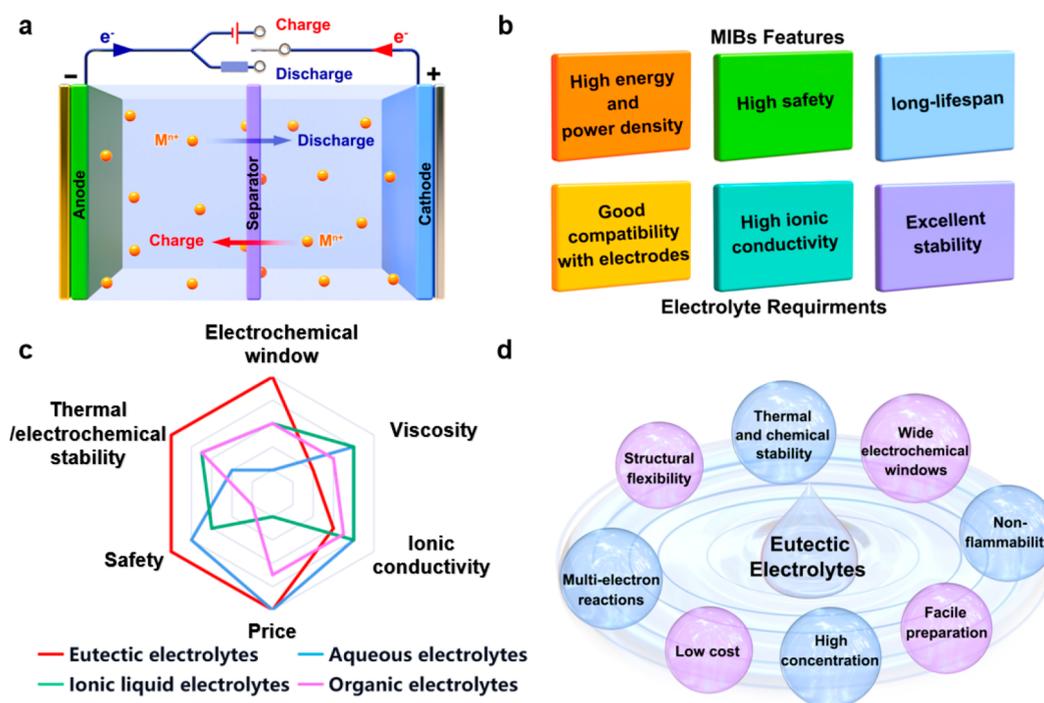


Figure 1. (a) Schematic working principle of typical MIBs. (b) Desired characteristic of MIBs and electrolytes. (c) Radar plots: the properties of different types of electrolytes. The values (distances from the center) range from 0 to 5, where 5 represents the best property and 0 means the property does not suit this type of electrolyte. (d) Advantageous properties of eutectic electrolytes.

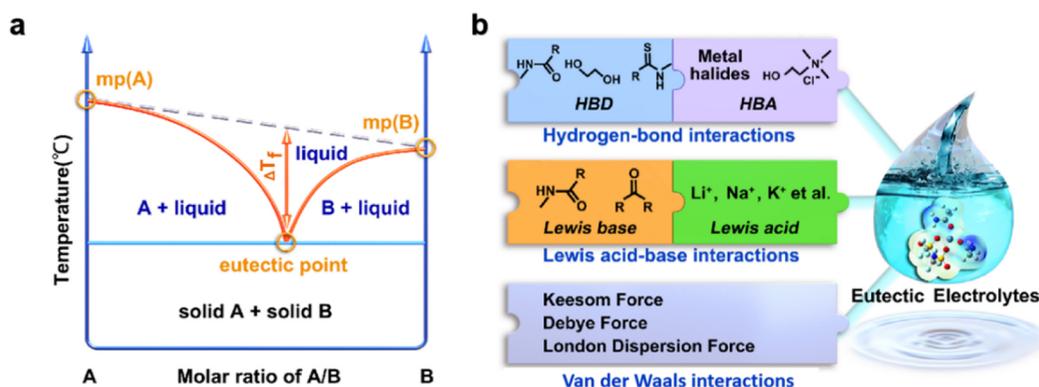


Figure 2. (a) Phase diagram of eutectic electrolytes with two components. (b) Formation mechanisms of eutectic electrolytes.

researchers to conquer the remaining challenges and promote the development of advanced eutectic electrolytes for MIBs.

Fundamentals of Eutectic Electrolytes. Eutectic electrolytes are, in essence, very similar to ILs; for instance, both are composed of charged ion pairs and no independent molecules. But in actuality they are quite different. ILs are mainly systems containing discrete anions and cations.^{21,22} All salts that can be melted without decomposition or vaporization are generally considered to be ILs.²³ In contrast, eutectic electrolytes consist of two or three substances, in which the complex anions and cations are generally generated through the interactions between the different components.^{24,25} For example, the eutectic electrolyte formed by the mixture of zinc chloride (ZnCl_2) and urea contains $[\text{ZnCl}_3]^-$, $[\text{Zn}_2\text{Cl}_5]^-$, and $[\text{Zn}_3\text{Cl}_7]^-$ anions and $[\text{ZnCl}(\text{urea})]^+$, $[\text{ZnCl}(\text{urea})_2]^+$, and $[\text{ZnCl}(\text{urea})_3]^+$ cations resulting from the interactions between ZnCl_2 and urea.²⁶ Thanks to the intermolecular interaction,

eutectic electrolytes usually possess smaller lattice energies than ILs.²⁷

Figure 1c compares the various properties of eutectic electrolytes with those of other electrolytes. It can be seen that IL electrolytes are not economical and friendly,²⁸ aqueous electrolytes have a limited electrochemical window,²⁹ and organic electrolytes are usually toxic and cause environmental damage.^{30,31} In contrast, eutectic electrolytes have a wide electrochemical window and superior thermal/chemical stability as well as being nontoxic and inexpensive. Meanwhile, due to the presence of complex anions and cations, the eutectic electrolytes also possess characteristics that the other electrolytes do not have, including non-flammability, easy synthesis, structural flexibility, and multi-electron reactions (Figure 1d).^{32–35} Notably, during the synthesis of a eutectic electrolyte, no additional solvent is usually required and no traditional reaction occurs between the components.^{36,37} The utilization rate of the synthetic raw materials of the eutectic electrolyte is

nearly 100%, and no further processing and purification are needed, which make eutectic electrolytes feasible for large-scale use.³⁸

Eutectic electrolytes can only be formed under the premise that the intermolecular interactions of the different components are stronger than the original effect of each component individually.²⁰ Adjusting the mixing ratio of the composition can strengthen the intermolecular interactions and reduce the freezing point (T_f) of the system. In the binary phase diagram (Figure 2a), the mixture with the lowest freezing point is regarded as the eutectic point. Moreover, the stronger the intermolecular interactions are, the greater the value of ΔT_f will be.³⁹ Generally, there are three types of interactions dominating the formation of eutectic electrolytes, namely, hydrogen-bond interactions, Lewis acid–base interactions, and van der Waals interactions.

Hydrogen-Bond Interaction. Hydrogen-bond interaction between components represents one of typical interrelations. This type of eutectic mixture consists of at least one hydrogen-bond donor (HBD), such as organic compounds containing hydroxyl groups, and a hydrogen-bond acceptor (HBA), like a negative atom (Cl^-) or matter with a lone pair of electrons.^{40,41} Common HBDs are amide, alcohol, and carboxylic acid molecules, and typical HBAs are metal halides, choline chloride (ChCl), or quaternary ammonium salt analogs (Figure 2b).¹⁹ The hydrogen bond between HBD and HBA moieties is relatively stronger than the individual molecular interactions, which is the decisive factor accounting for lowering the melting point of the mixture. Zhang et al. developed a eutectic electrolyte based on ZnCl_2 and acetamide (Ace) in 2018.⁴² Through the hydrogen bond between ZnCl_2 and Ace, the freezing point of the entire electrolyte system reached -16°C , which is much lower than the melting points of ZnCl_2 (283°C) and Ace (103°C). Besides, the mixing ratio of the composition determines the strength of the hydrogen bond, which greatly affects the physical and chemical properties of the eutectic electrolytes. The freezing point of $\text{Zn}(\text{TFSI})_2$ and Ace at a molar ratio of 1:7 is -52°C , but at 1:5 it is -38°C .⁴³ Notably, substances that meet the conditions for forming hydrogen bonds may not be able to form a uniform eutectic electrolyte. For instance, ammonium chloride (NH_4Cl) is a HBA, and alcohol is a HBD, but due to the insoluble nature of NH_4Cl in alcohol, the mixture of NH_4Cl and alcohol cannot form a uniform liquid.⁴⁴ Therefore, the hydrogen-bond interaction is not the decisive condition for the formation of a eutectic electrolyte.

Lewis Acid–Base Interaction. Lewis acid–base interaction is another mechanism which determines the formation of eutectic electrolytes. The substance donating an electron pair is the Lewis base, and the one accepting an electron pair is the Lewis acid.^{45,46} Amide, carbonate, and ether, as typical Lewis bases, can be mixed with Lewis acids such as alkali cations (Li^+ , Na^+ , and K^+) to viably form a eutectic mixture (Figure 2b).¹⁹ Liang et al. found that the mixture of solid LiTFSI (lithium bis[(trifluoromethyl)sulfonyl]imide) and urea has a melting point down to -37.6°C , resulting from the Lewis acid–base interaction between Li^+ and urea.⁴⁷ Notably, the strength of the Lewis acid–base interaction is affected by the selection of the Lewis acid–base substance and varies greatly. Nevertheless, the Lewis acid–base interactions in eutectic systems are still not strong enough to affect the Lewis chemistry as much as covalent-bond forces. Generally, it is estimated that the Lewis

effect just alters the coordination state, thereby endowing a low melting point.⁴⁸

Van der Waals Interaction. Van der Waals interactions generally include Keesom forces, Debye forces, and London dispersion forces (Figure 2b).¹⁹ Although the van der Waals interaction is relatively weak among all chemical forces, it can exist between any molecules and is essential to the entire mixture system.^{49,50} The van der Waals forces appearing in eutectic mixtures are stronger than the primary molecular interactions of each component, which could regulate the physical and chemical properties. However, the van der Waals force is generally not used as a reference condition for selecting the composition of the eutectic electrolyte, and currently, there are few studies on the van der Waals forces in eutectic electrolytes.

The above three main interactions govern the formation of eutectic electrolytes inseparably. Due to the unique formation mechanisms, in eutectic systems, different molecules interact to form complex anions and cations. Furthermore, adjusting the composition to a specific mixing ratio can make all molecules participate in the interaction, so that only complex ions exist in the entire system. Therefore, in a eutectic electrolyte, where only ions are present, the charge transport depends on ionic mobility instead of the number of charge carriers.²⁰ Besides, during charging/discharging, the eutectic electrolytes can offer ion transport between two interfaces and participate in metal plating/stripping on the electrode.¹⁹ To achieve optimal eutectic electrolytes, the sorts, functions, and quantities of each component based on specific formation mechanisms should be carefully considered. For different MIB systems, choosing a suitable ideal eutectic electrolyte is beneficial to address the remaining challenges of MIBs.

Eutectic Electrolytes for Advanced MIBs. The rapid development of MIBs is restricted by potential safety hazards induced by dendrites, an unstable solid electrolyte interphase (SEI) and high voltage instability, especially when using conventional organic electrolytes.⁴ Owing to the strong intermolecular interactions, the formed eutectic electrolytes have some specific advantages that conventional electrolytes do not offer. Therefore, the appropriate eutectic electrolytes are potential candidates to be used as alternatives to conventional electrolytes to conquer the remaining obstacle of MIBs. The eutectic electrolytes for MIBs are mainly formed via hydrogen-bond and Lewis acid–base interactions, which commonly consist of anhydrous/hydrated metal salts and organic ligands.^{43–51} Nevertheless, even under the same or similar formation mechanisms, the solvent structure and the certain properties of the formed eutectic electrolytes are regulated by the type and mixing scale of the components. Currently, the MIBs with eutectic electrolytes are mainly LIBs, ZIBs, and AIBs. Furthermore, eutectic electrolytes for MIBs can present a wide electrochemical window, stable electrolyte/electrode interphase chemistry, and a particular ions/charge transport.

Eutectic electrolytes for metal-ion batteries present a wide electrochemical window, stable electrolyte/electrode interphase chemistry, and a particular ions/charge transport.

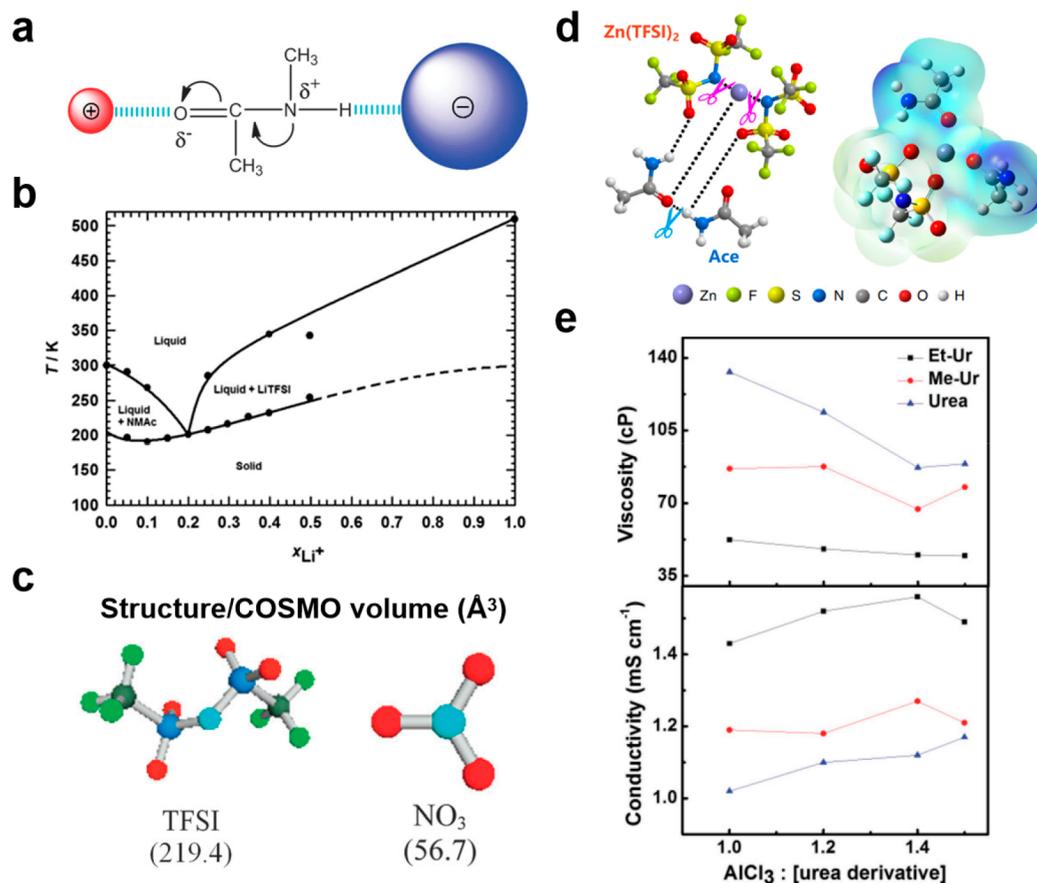


Figure 3. (a) Schematic representation of the cation–MAC–anion system. (b) Solid–liquid equilibrium of the MAC–LiTFSI binary mixture, where x_{Li^+} is the salt mole fraction. (c) Structures and COSMO volumes of studied TFSI[−] and NO₃[−]. Reproduced with permission from ref 53. Copyright 2013 the PCCP Owner Societies. (d) Schematic diagram of the interaction among Zn²⁺, TFSI[−], and Ace to form eutectic solutions, and molecular electrostatic potential energy surface of [ZnTFSI(Ace)₂]⁺. Reproduced with permission from ref 43. Copyright 2019 Nature Publishing Group. (e) Graphical presentation of viscosity and conductivity of AlCl₃:[urea derivative]. Reproduced with permission from ref 56. Copyright 2019 Wiley.

In the following sections, the recent advances in eutectic electrolytes for MIBs, including the composition and structure as well as physical and chemical properties, will be introduced. Then, how the specific properties of the eutectic electrolytes can achieve excellent electrochemical performance of the MIBs will be summarized and discussed. In addition, the specific ions/charge transport mechanism of MIBs using eutectic electrolytes will be presented.

Composition, Structure, and Properties. Theoretically, if the various substances can generate hydrogen bonds and/or Lewis acid–base interactions, and simultaneously meet the mixing proportion range that can form fluids, then at that point these substances can be blended to shape DESs. Nonetheless, the condition that allows the formed DESs to be picked as eutectic electrolytes to advance MIBs is that the DESs possess excellent performance and contain at least one metal salt part. In eutectic electrolytes, the electroactive species usually originate from metal salts. Although ZnCl₂ as HBA and ChCl as HBD can be mixed to form a DES, the large viscosity of 85 000 mPa·s and a eutectic temperature (T_e) of 23 °C make it entirely unsuitable as an electrolyte for advanced ZIBs.²⁶ To accomplish superb eutectic electrolytes for MIBs, the metal salt should have a large ion size and high charge delocalization, which helps to weaken or even break the ionic bonds in the salt, for example, TFSI salt, nitrate, or perchlorate.

Besides, organic solvents containing polar functional groups, for example, *N*-methylacetamide (MAC), Ace, succinonitrile (SN), and urea, are truly reasonable for building high-performance eutectic systems by generating intermolecular interactions with the selected metal salts.⁵²

Boisset et al. reported a multi-functional eutectic electrolyte based on Li salt (LiX, LiTFSI, and LiNO₃) and MAC at a molar ratio of 1:5 for advanced LIBs.⁵³ In the eutectic electrolyte, MAC with C=O and NHR polar groups is able to coordinate with Li⁺ cation and X[−] anion (Figure 3a), which weakens and even breaks the hydrogen bond (N–H···O) of MAC and the ionic bond in LiX. Owing to the intermolecular interactions, LiTFSI–MAC and LiNO₃–MAC have low freezing points of −72 and −75 °C, respectively (Figure 3b). Nevertheless, due to TFSI[−] with larger volume and more delocalized bonds, compared to LiNO₃, LiTFSI is easier to build a eutectic state with MAC (Figure 3c). As a result, LiTFSI–MAC features better ionic conductivity ($\sigma = 1.35\ mS\ cm^{-1}$) and viscosity ($\eta = 78.38\ mPa\cdot s$) than LiNO₃–MAC ($\sigma = 0.76\ mS\ cm^{-1}$, $\eta = 107.19\ mPa\cdot s$).

While constructing a eutectic system, except for the competition between metal salts, the distinction in organic ligand likewise affects the properties. LiTFSI–Ace endows the formed eutectic electrolyte with 1 mS cm^{−1} ionic conductivity.⁵⁴ In contrast, LiTFSI–SN has a higher ionic

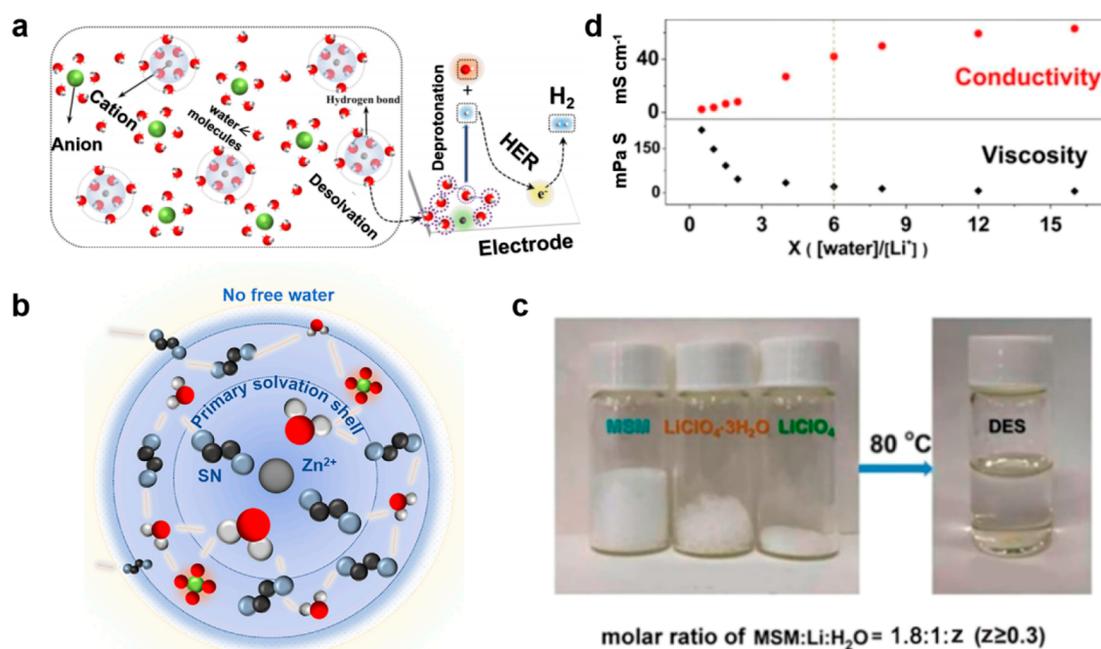


Figure 4. (a) Schematic diagram of the HER process. Reproduced with permission from ref 59. Copyright 2021 American Chemical Society. (b) Schematic diagrams of the Zn²⁺ solvation structure and corresponding interfacial reactions. Reproduced with permission from ref 15. Copyright 2020 Elsevier Inc. (c) Optical images of the electrolyte formation process. (d) The conductivity and viscosity of salt/solvent ratios in the *m*MSM–*n*LiClO₄–*z*H₂O system. Reproduced with permission from ref 60. Copyright 2019 American Chemical Society.

conductivity of 2.85 mS cm⁻¹, which is also better than that of LiTFSI-MAC.⁵⁵ The difference in ionic conductivity values is primarily dictated by the ability of organic ligands to dissociate metal salts. The higher polarity of SN can more adequately weaken the Coulombic interaction between anions and cations in LiTFSI, thereby advancing the dissociation of LiTFSI. Even under an almost identical formation mechanism, the eutectic electrolyte based on Zn(TFSI)₂ and Ace presents a lower ionic conductivity of 0.37 mS cm⁻¹ compared to that of LiTFSI-Ace. This is because of the stronger Coulombic interaction of multivalent cations (Zn²⁺) with anions (TFSI⁻) compared to that of Li⁺ (Figure 3d).⁴³ Angell et al. found that the AlCl₃/Me-Ur (*N*-methyl derivatives of urea) and AlCl₃/Et-Ur (*N*-ethyl derivatives of urea) have better ionic conductivity and viscosity performance than AlCl₃/urea, due to the fact that a single methyl or ethyl group to supplant protons can upset the hydrogen-bonding networks in the urea (Figure 3e).⁵⁶

Albeit the traditional aqueous electrolytes can accomplish high-safety MIBs, their hydrogen evolution reaction (HER) is truly negative for the development of advanced MIBs.^{57,58} As displayed in Figure 4a, during the charging/discharging process, the free and desolvated water molecules will migrate to the electrode surface to undergo a deprotonation process to generate hydrogen, which indicates the HER of water is essentially a process of hydrogen-bond competition in the solution.⁵⁹ Therefore, modifying the aqueous electrolytes into a eutectic system can effectively get rid of the limitation. Yang et al. developed a hydrated eutectic electrolyte by a simple mixing of Zn(ClO₄)₂·6H₂O and SN, in which SN and all water molecules partake in the construction of a Zn²⁺ solvation structure in the form of [Zn(OH₂)_{*x*}(SN)_{*y*}]²⁺ cations (Figure 4b).¹⁵ The intimate effect of SN and Zn²⁺ lessens the affinity between Zn and water and upgrades the dissociation energy of Zn²⁺. Therefore, even if the desolvated water replaced by SN still exists outer the shell of the metal coordination sphere and

is not free state, which effectively suppresses the HER. For the aqueous LIBs with high performance, Jiang et al. reported a eutectic electrolyte based on methylsulfonylmethane (MSM), LiClO₄, and H₂O (Figure 4c).⁶⁰ In the eutectic system, all water molecules are confined surrounding cations, prompting significantly expanded overpotentials of HER. Notably, inside a specific range, expanding the water content can successfully improve the ionic conductivity and viscosity properties of the eutectic electrolyte (Figure 4d). It should be noticed that the excess water will cause the water in the eutectic structure to transform into the ordinary aqueous solution state.

With regard to the composition selection and performance optimization of eutectic electrolyte for MIBs, it is still needed to find more feasible programs. In light of the formation mechanism, some other highly polar molecules, such as dimethyl sulfoxide (DMSO), methanol, and ethylene glycol (EG), are promising to construct high-performance DESs. Besides, introducing some additives such as 1,2-dichloroethane (DCE) and fluoroethylene carbonate (EFC) into the formed eutectic electrolyte is expected to improve the viscosity and conductivity performance.^{61,62}

Electrochemical Window. The electrochemical window (EW) decides the electrolyte's ability to obstruct undesirable electronic transport. A wide EW can viably alleviate self-discharge and short-circuit phenomena.⁶³ Although organic electrolytes have the advantage of a wide EW, their safety hazards outweigh this advantage. Aqueous electrolytes possess high safety characteristic but lose the wide EW.^{64,65} In contrast, eutectic electrolytes, with both wide EW and high safety, are expected to achieve MIBs with high energy density.

Qiu et al. proposed that the Zn(TFSI)₂-Ace eutectic electrolyte (ZES) possesses an expanded EW of 2.4 V (vs Zn/Zn²⁺), outperforming 1 M Zn(TFSI)₂ aqueous electrolytes, which allows the ZES to pair with more high-voltage cathodes (Figure 5a).⁴³ Owing to the strong interaction

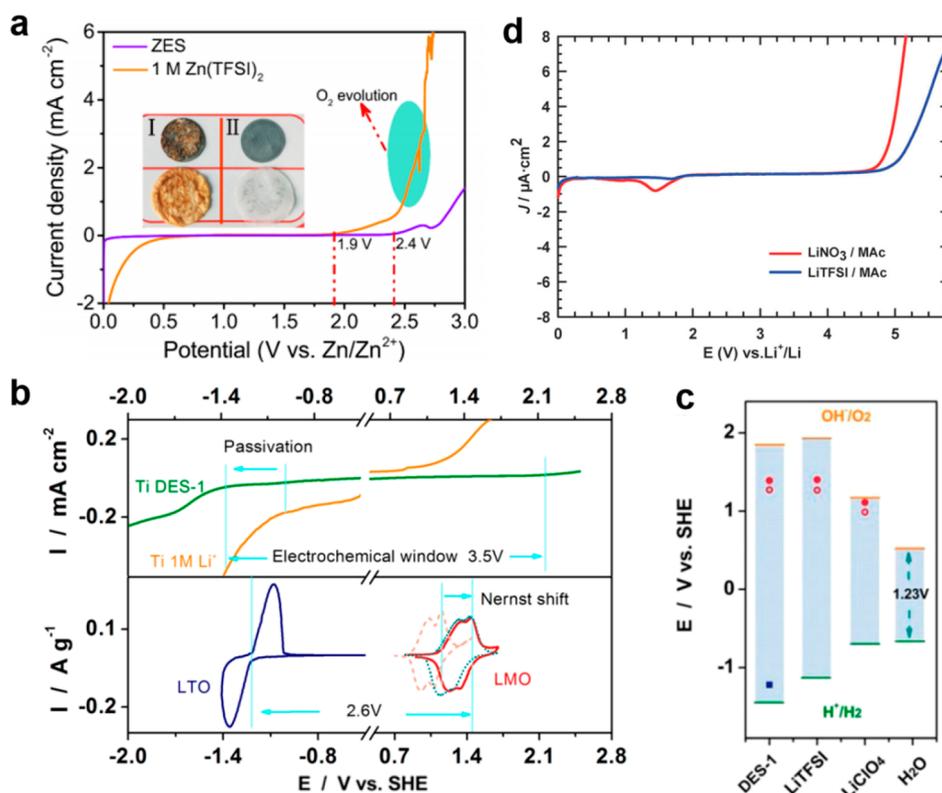


Figure 5. (a) Electrochemical stability of ZES and 1 M Zn(TFSI)₂. Reproduced with permission from ref 43. Copyright 2019 Nature Publishing Group. (b) Linear sweep voltammetry (LSV) of DES-1 (MSM:LiClO₄:H₂O = 1.8:1:1) electrolyte and a typical aqueous solution of 1 mol L⁻¹ LiClO₄/H₂O. Cyclic voltammetry (CV) of LMO and LTO electrodes in DES-1 electrolyte. (c) Illustration of the expanded electrochemical stability window. Reproduced with permission from ref 60. Copyright 2019 American Chemical Society. (d) Electrochemical stability window of LiTFSI-Mac and LiNO₃-Mac electrolytes at $x_{\text{Li}^+} = 0.20$. Reproduced with permission from ref 53. Copyright 2013 the PCCP Owner Societies.

between Zn(TFSI)₂ and Ace (Figure 3d), the ZES has a higher electroactive species concentration than 1 M Zn(TFSI)₂, thereby enjoying a wider EW.

Through linear sweep voltammetry (LSV), Jiang et al. found that the eutectic electrolyte (DES-1) based on the mixing of MSM, LiClO₄, and H₂O at a molar ratio of 1.8:1:1 presents an outstanding wide EW with two electrodes (≥ 3.5 V), which is much wider than those of aqueous LiClO₄ and saturated LiTFSI (Figure 5b,c).⁶⁰ When Li₄Ti₅O₁₂ (LTO) and LiMn₂O₄ (LMO) were selected as the cathode materials, the reversible redox pair presenting the Li⁺ (de)intercalation reaction emerged at -1.45 and 1.2 V, respectively, which further verifies the usability and stability of the wide EW. In DES-1, all water molecules are confined in the eutectic hydrogen-bond structure, greatly reducing the activity of water, which increases the overpotential of the water hydrogen evolution reaction, thereby widening the EW.

Boisset et al. reported that LiTFSI-Mac and LiNO₃-Mac eutectic electrolytes showed wide EWs of 5.3 and 4.7 V, respectively, which indicates the two eutectic electrolytes have a passivation effect on the aluminum collector (Figure 5d).⁵³ It was found that LiTFSI-Mac and LiNO₃-Mac contain 40 and 565 ppm water content, respectively, by Coulometric Karl Fischer titration, which brings about the emergence of an irreversible and small peak at 1.2 V in LiNO₃-Mac. Compared with NO₃⁻, TFSI⁻ has a weaker affinity with water and a stronger interaction with MAC, which prompts LiTFSI-Mac to own a wider EW.

To more adequately and practically exploit the characteristic of the wide electrochemical stability window of the eutectic electrolyte, advanced cathode materials with high voltage can be selected for use in MIBs with the eutectic system to realize high energy density. However, if water is part of the eutectic system, it must be guaranteed that the water will not affect the stability of the chosen anode material. For instance, in the LiNO₃-Mac eutectic electrolyte, the anode material must have an insertion/extraction process above 1.2 V, because of the decomposition of residual water at about 1.2 V.⁵³

Electrolyte/Electrode Interphase Chemistry. The interphase chemistry of electrolyte and electrode is one of the vital factors that dominate the safety concerns and the cycling life of rechargeable batteries.⁶⁶ An unstable cathode electrolyte interphase (CEI) layer on the cathode will result in the continuous decomposition of electrolyte and rapid capacity loss.⁶⁷ Furthermore, an undesirable SEI layer on metal anode is very unfavorable for dendrite suppression, thus achieving low Coulomb efficiency.⁶⁸

The reported Zn(TFSI)₂/Ace eutectic electrolyte becomes dendrite-free by in situ formation of a stable SEI, where TFSI⁻ and Ace can coordinate with Zn²⁺ to form Zn anion complexes ($[\text{ZnTFSI}_m(\text{Ace})_n]^{(2-m)+}$, $m = 1-2$, $n = 1-3$) (Figure 6a).⁴³ Further DFT analysis displayed that TFSI⁻ will be preferentially reductively decomposed before Zn deposition due to the presence of Zn complex anions, which enables TFSI⁻ to participate in the SEI formation. Through XPS spectra of cycled Zn (Figure 6b), it can be confirmed that the

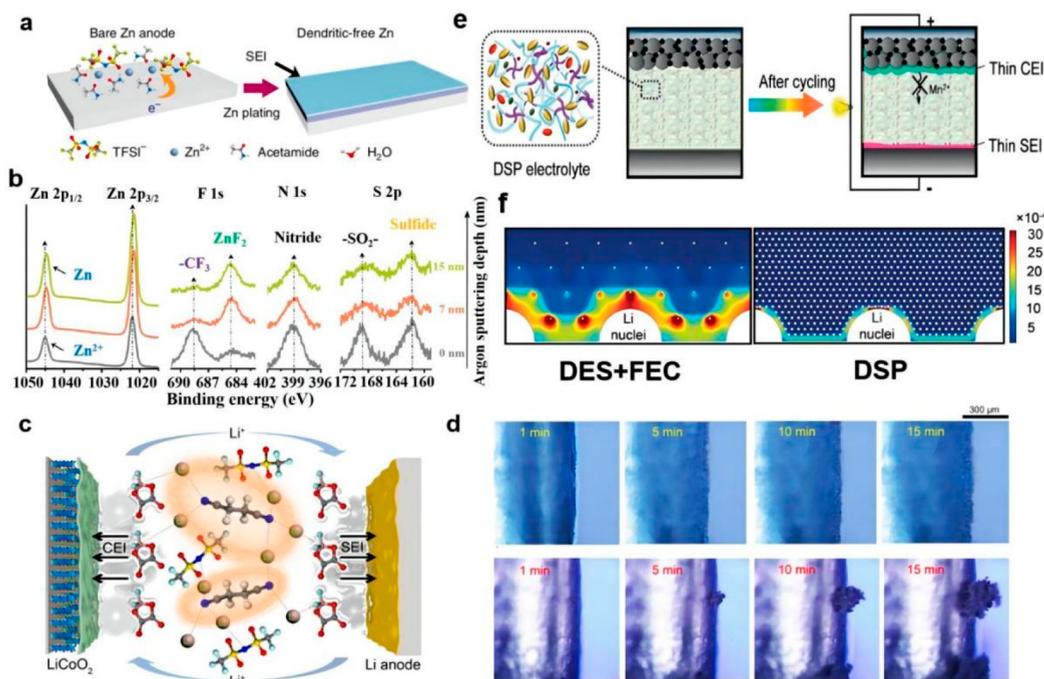


Figure 6. (a) SEI-regulated uniform Zn deposition in ZES. (b) XPS spectral regions for Zn 2p, F 1s, N 1s, and S 2p at various argon (Ar^+) sputtering depths on the SEI. Reproduced with permission from ref 43. Copyright 2019 Nature Publishing Group. (c) Schematic of the SEI and CEI formation and working mechanism in D-DES accumulated on Zn substrate. (d) Deposition morphology of lithium metal foils using an in situ optical microscope D-DES (bottom) and 1 M $\text{LiPF}_6\text{-EC/DMC}$ (top). Reproduced with permission from ref 55. Copyright 2020 American Chemical Society. (e) DES-based self-healing polymer (DSP) electrolytes in Li//LMO cells. (f) Numerical simulations of the Li ion flux distribution on the Li metal anode surfaces. Reproduced with permission from ref 69. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

major components of the formed SEI contain ZnF_2 and S/N-rich organic compounds. Notably, the anion-derived SEI could provide sufficient ion channels to enable Zn^{2+} to transmit and hold good tolerance for the volume changes caused by Zn plating/stripping. Thus, the ZnF_2 -rich SEI can command the metal nucleation and viably repress the growth of dendrites, empowering a dense Zn deposition at a high capacity of 5 mAh cm^{-2} without a surface passivation layer and short-circuit.

Hu et al. introduced two lithium salts (lithium difluoro(oxalate)borate (LiDFOB) and LiTFSI) into SN to form the dual-anion deep eutectic solvent (D-DES) electrolyte, which effectively ameliorates the interphase chemistry of the lithium metal and maintains excellent stability with a high-voltage cathode (Figure 6c).⁵⁵ The hydrogen-bond interaction between the two lithium salts and SN molecules dominated the formation of D-DES. In the eutectic system, the TFSI^- and DFOB^- prior to the SN molecules could produce a chemical reaction with the lithium metal, which promises a stable SEI containing LiF , Li_3N , $\text{Li}_x\text{BF}_y\text{O}_z$, and sulfides on the lithium anode. Meanwhile, the multi-component SEI conveyed incredible electronic insulation, and great mechanical property prompting inhibited side reactions and improved behavior of lithium plating/stripping. The in situ visual test represented that a homogeneous lithium plating/stripping process was achieved in D-DES under a high capacity of 5 mA cm^{-2} , which is different from the behavior of lithium plating/stripping in a carbonate electrolyte with severe dendrite formation and short-circuit (Figure 6d). When LiCoO_2 is used as cathode material, the TFSI^- and DFOB^- anions could take part in the formation reactions of the CEI (Figure 6c). Thereby, the surface of the CEI contains B–F, B–O, and some N- and S-rich components,

possessing uniform and solid coverage, which promotes the excellent high-voltage cycling performance.

Moreover, rational modifications of DESs have advanced their applications in the optimization of interface chemistry. Through in situ thermal polymerization, adding pentaerythritol tetraacrylate (PETEA) monomers, fluoroethylene carbonate (FEC), and 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl methacrylate (UPyMA) into a DES (LiTFSI and MAc) can form a DES-based self-healing polymer (DSP) electrolyte.⁶⁹ LIBs using the DSP not only can realize a robust SEI film but also possess a stable and protective CEI on the LiMn_2O_4 , which impedes the occurrence of side reactions at the interface (Figure 6e). In this electrolyte design scheme, the FEC with high oxidative stability is an exciting additive which can effectively boost the ionic conductivity and electrochemical stability. Meanwhile, the self-healing UPyMA-PETEA can prevent the dissolution of manganese from the cathode, which significantly improves cycle performance. Through simulation (Figure 6f), random and chaotic current-density distribution is observed in the DES + FEC electrolyte, and the current density is stacked on the tops of the Li nuclei, which is conducive to dendrite growth. In contrast, in the DSP electrolyte, the distribution of Li^+ flux is more regular and orderly, which contributes to a homogeneous lithium deposition process.

In the eutectic electrolyte, the metal-containing complex ions are usually associated with metal deposition and determine the interface chemistry between the electrolyte and electrode. The deposition potential and the corresponding sequence of deposition between the anion of the metal salt and

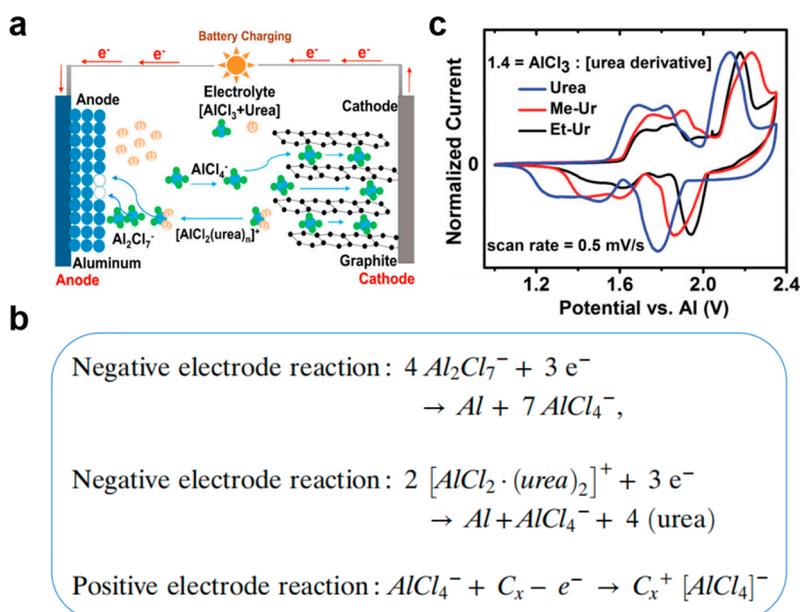


Figure 7. (a) Schematic of battery charging (Al deposition and anion intercalation in graphite). (b) The two pathways of aluminum deposition and the graphite intercalation reaction. Reproduced with permission from ref 27. Copyright 2017 PNAS. (c) Cyclic voltammetry of graphite positive electrode for ratios $AlCl_3/[urea derivative]$. Reproduced with permission from ref 56. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

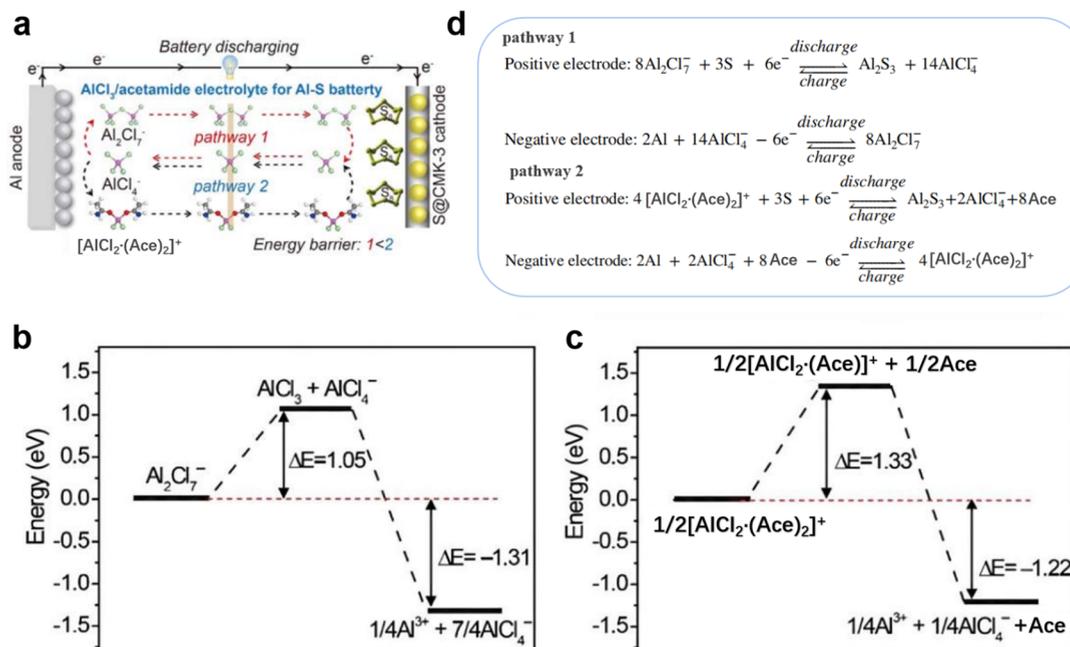


Figure 8. (a) Schematic illustration of the battery discharging process. Energy profiles of dissociation reactions of (b) $Al_2Cl_7^-$ and (c) $[AlCl_2(Ace)_2]^+$. (d) Al^{3+} dissociation reaction routes. Reproduced with permission from ref 70. Copyright 2019 Elsevier B.V.

the organic ligand affect the composition and stability of the SEI and CEI.

Ion and Charge Transport Mechanism. Revealing the working mechanism of rechargeable batteries is essential to promote the further development of batteries. In eutectic electrolytes, due to the presence of complex anions and cations, the multi-electron reactions usually exist in the charging/discharging process, which indicates that the charge transport is dominated by ionic mobility instead of the number of charge carriers.

Angell et al. developed a eutectic electrolyte based on the mixing of $AlCl_3$ and urea at a molar ratio of 1:3 to endow AIBs with a high Coulombic efficiency of 99.7%.²⁷ In the $AlCl_3$ -urea eutectic electrolytes, $AlCl_4^-$ and $Al_2Cl_7^-$ anions and $[AlCl_2(urea)_n]^+$ cations are formed through the heterolytic cleavage of $AlCl_3$. When the AIBs are assembled with graphite as the cathode material, $AlCl_4^-$ ions can intercalate into graphite (Figure 7a). During the charging process, both $Al_2Cl_7^-$ and $[AlCl_2(urea)_n]^+$ will get electrons to achieve aluminum deposition at the negative electrode, and the

positive electrode will produce a process where AlCl_4^- maintains electrical neutrality during carbon oxidation (Figure 7b). When urea derivatives (Me-Ur and Et-Ur) replacing urea are mixed with AlCl_3 to form eutectic electrolytes, it is found that $\text{AlCl}_3/\text{Me-Ur}$ and $\text{AlCl}_3/\text{Et-Ur}$ have a similar graphite embedding process as $\text{AlCl}_3/\text{urea}$.⁵⁶ Further, CV shows that the overall shapes of the three eutectic electrolytes are the same but the potential is shifted in the positive direction, which results from the change of the aluminum deposition potential caused by the change of the organic ligand in the complex cations (Figure 7c). These prove that in the eutectic system the composition of the metal salt dominates the working mechanism of the battery.

The ion and charge transport mechanism of an Al–S battery with eutectic electrolytes is additionally basically the same as that of AIBs. Chu et al. reported $\text{AlCl}_3/\text{acetamide}$ (Ace), as the eutectic electrolyte promises a high capacity of 1500 mA h g^{-1} and excellent rate performance for the Al–S battery.⁷⁰ The Ace is able to coordinate with AlCl_3 to produce $[\text{AlCl}_2(\text{Ace})_2]^+$, AlCl_4^- , and Al_2Cl_7^- ions. Among them, $[\text{AlCl}_2(\text{Ace})_2]^+$ and Al_2Cl_7^- can release the Al^{3+} ion that can be electrochemically dissociated, thereby inducing two reaction mechanism pathways of the Al–S battery with AlCl_3/Ace eutectic electrolyte (Figure 8a). However, since the dissociation energy of $[\text{AlCl}_2(\text{Ace})_2]^+$ (1.33 eV) is higher than that of Al_2Cl_7^- (1.05 eV), the reaction mechanism pathway of $[\text{AlCl}_2(\text{Ace})_2]^+$ is less kinetically favorable during the discharging/charging process of the Al–S battery (Figure 8b,c). Nevertheless, during charging, both $[\text{AlCl}_2(\text{Ace})_2]^+$ and Al_2Cl_7^- are still able to react with S to form Al_2S_3 on the positive electrode (Figure 8d), which indicates the electrochemical reaction is affected by the charge type, ion concentration, and electric layer at the interface. Therefore, the dissociation ability of complex ions does not represent the capacity contribution ability. In the Al–S battery with an AlCl_3/Ace eutectic electrolyte, the above two reaction mechanism pathways both promote some capacity.

In general, for different MIB systems with eutectic electrolytes, such as LIBs and ZIBs, there are similar electrochemical mechanisms including ion and charge transport. Metal salts mainly provide electroactive species that can interact with electrode materials, including intercalation or chemical reactions during charging and discharging. In addition, organic ligands dominate the deposition of metal ions on metal surfaces.

Based on the above, the eutectic electrolytes have a positive effect on safety and economics, as well as interface chemistry and high energy/power density. However, in terms of ionic conductivity and viscosity performance, the eutectic electrolyte needs to be further improved. In addition, side reactions between the eutectic electrolyte and the metal should be avoided as much as possible.⁷¹ Actually, DESs have not been widely used in MIBs. Although potassium, sodium, and magnesium salts can form DESs with some organic ligands with HBD,⁷² their applications in K-ion batteries (KIBs), Na-ion batteries (NIBs), Mg-ion batteries (MgIBs), and Ca-ion batteries (CIBs) have never been reported.

In terms of ionic conductivity and viscosity performance, the eutectic electrolyte needs to be further improved.

The research on DESs has also included their exploration for redox fluid batteries (RFBs) and investigation of the electrodeposition mechanism. Table 1 presents the physicochemical properties of various previously reported DESs containing metal salts. Even under the same or similar formation mechanisms, the physical and chemical properties of the formed DESs with different compositions could differ significantly. Therefore, it is feasible to achieve the desired performance of DESs by adjusting the type, function, and quantity of the components. Notably, different mixing ratios of the same components will also cause changes in properties. For example, the ionic conductivity of the mixture of LiTFSI and MAc when the molar ratio is 1:5 is much lower than that when the molar ratio is 1:4.⁷³ Therefore, when exploring MIBs using eutectic electrolyte, the mixing ratio is a point that must be considered.

Even under the same or similar formation mechanisms, the physical and chemical properties of the formed deep eutectic solvents with different compositions could differ significantly.

Some DESs have been reported but not yet applied to MIBs, such as the DESs for RFBs and the DESs that are only discussed the electrodeposition mechanism (Table 1). Compared with the DESs that have been used as eutectic electrolytes for ZIBs, the DESs based on $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{ChCl}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{DEEA}$ (*N,N*-diethylethanol) show more excellent ionic conductivity, which makes them very suitable as eutectic electrolytes to realize advanced ZIBs.⁷⁴ Excitingly, the $\text{AlCl}_3/4\text{-Pr-Py}$ (4-propylpyridine)-forming DESs possess an amazing conductivity of 50 mS cm^{-1} , which is higher than those of most electrolytes.⁷⁵ Therefore, adopting this DES as a eutectic electrolyte for AIBs is very promising to achieve excellent electrochemical performance.

Although there is no report on the DESs containing sodium salt in metal ion batteries, the DESs containing sodium salt have been well used in capacitors. The mixing of NaNO_3/MAc forming DES is provided with impressive ionic conductivity (3.17 mS cm^{-1}) and viscosity ($12.63 \text{ mPa}\cdot\text{s}$) performance better than many DESs containing other metal salts, which may open the door to the application of DES as eutectic electrolytes to NIBs.⁷⁶ For other types of MIBs such as KIBs, MgIBs, and CIBs, choosing a solvent that does not react with the metal element and a corresponding salt to form the eutectic electrolyte is also very expected to achieve excellent battery performance. EG, DMSO and acetonitrile with HBD and high dielectric constant can dissolve magnesium chloride (MgCl_2) and calcium chloride (CaCl_2), and do not react with Mg and Ca metal elements.^{77,78} Thereby, the mixing of these organic and salt component can form high-performance DESs via adjusting the mixing ratio and introducing some additives, which makes eutectic electrolytes promising to be applied in advanced MgIBs and CIBs. In addition, NaTFSI and KTFSI are excellent salts that constitute high-performance DESs, which could promote F-rich SEI formation on the electrode surface, thereby improving the cycle performance of NIBs and KIBs.⁷⁹

DESs with unique physicochemical properties for use as eutectic electrolytes have triggered substantial research interest

Table 1. Physicochemical Properties of Various DESs

| application | composition | molar ratio | σ (mS cm ⁻¹) | η (mPa·s) | T_c (°C) | ref |
|-------------|---|-------------|---------------------------------|----------------|------------|-----|
| Li Salts | | | | | | |
| LIBs | LiTFSI/MAC | 1:5 | 1.35 | 78.38 | -72 | 53 |
| | LiTFSI/SN | 1:3.3 | 2.85 | 420 | -75 | 55 |
| | LiTFSI/LiDFOB/SN | 1.7:0.3:8 | 1.26 | 753 | -80 | 55 |
| | LiTFSI/Ace | 1:4 | 1 | 99.56 | -67 | 54 |
| | LiNO ₃ /MAC | 1:5 | 0.76 | 107.19 | -75 | 53 |
| | LiClO ₄ /MSM/H ₂ O | 1:1.8:1 | 3.71 | 148 | -48 | 60 |
| capacitors | LiTFSI/Ace | 1:6 | 1.21 | – | -59 | 80 |
| | LiTFSI/MAC | 1:4 | 1.61 | – | -72.1 | 73 |
| | LiCF ₃ SO ₃ /Ace | 1:5 | 0.69 | – | -52 | 80 |
| others | LiTFSI/urea | 1:3.6 | – | – | -33 | 81 |
| Zn Salts | | | | | | |
| ZIBs | Zn(TFSI) ₂ /Ace | 1:7 | – | 789 | -54 | 43 |
| | Zn(ClO ₄) ₂ ·6H ₂ O/SN | 1:8 | – | 25.4 | -95.3 | 15 |
| others | ZnCl ₂ /urea | 1:3.5 | – | 11340 | 9 | 26 |
| | ZnCl ₂ /Ace | 1:4 | – | – | -16 | 26 |
| | ZnCl ₂ /EG | 1:4 | – | – | -30 | 26 |
| | ZnCl ₂ /1,6-hexanediol | 1:3 | – | – | -23 | 26 |
| | ZnCl ₂ /ChCl | 2:1 | – | 85000 | 23 | 26 |
| | Zn(NO ₃) ₂ ·6H ₂ O/ChCl | 1:1 | 9.28 | 106.70 | – | 74 |
| | Zn(NO ₃) ₂ ·6H ₂ O/DEEA | 1:1 | 7.05 | 163.40 | – | 74 |
| | Al Salts | | | | | |
| AIBs | AlCl ₃ /urea | 1.4:1 | 1.12 | 87.1 | – | 27 |
| | AlCl ₃ /Me-Ur | 1.4:1 | 1.27 | 56.8 | – | 56 |
| | AlCl ₃ /Et-Ur | 1.4:1 | 1.56 | 45 | – | 56 |
| RFBs | AlCl ₃ /urea | 1.3:1 | 0.36 | – | – | 61 |
| others | AlCl ₃ /Ace | 1:1 | 0.804 | 60 | -63 | 82 |
| | AlCl ₃ /4-Pr-Py | 1.3:1 | 50 | 42.8 | -56 | 75 |
| Na Salts | | | | | | |
| capacitors | NaNO ₃ /MAC | 1:9 | 3.17 | 12.63 | – | 76 |

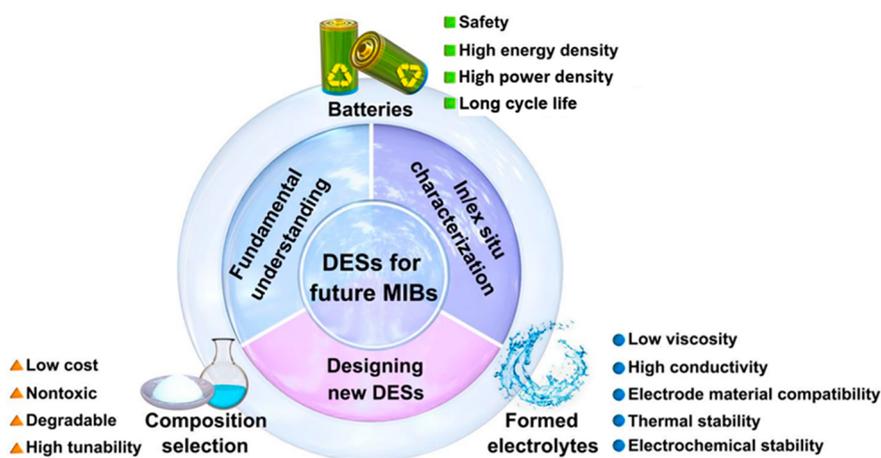


Figure 9. Prospects of DESs for advanced MIBs.

in the field of MIBs. In this Focus Review, the formation mechanisms and characteristics of DESs are discussed. The interaction between the components in DESs is greater than the original force of each component, which greatly reduces the melting point. In general, three intermolecular forces, including hydrogen-bond, Lewis acid–base, and van der Waals forces, dominate the formation of DESs. Recent progress in novel types of eutectic electrolytes for MIBs is systematically

summarized. The discussed DES-based MIBs mainly include Li-based, Zn-based, and Al-based eutectic electrolytes. The main focus is the relationship between structure and properties, electron transfer/ion transport mechanisms, and the resulting electrochemical performance. The eutectic electrolytes system could endow stable SEIs and wide electrochemical windows, curb dendrite formation, and promote low-temperature MIBs. The application and research

on DES in other directions, such as DES-based RFBs and the electrodeposition mechanism of DESs, are briefly listed, which is conducive to broadening the application of DESs in the field of MIBs.

Although DESs are now considered to be one of the classifications of electrolytes and they have been applied to electrochemical energy storage, especially in MIBs, their development is still in the infancy stage. Considerable work is still needed for further research on DESs (Figure 9). Normally, in eutectic systems, ions with large size characteristics and relatively free volume will cause some undesirable viscosity and ionic conductivity compared with common liquid electrolytes at room temperature.⁸³ Due to the high dissolving effect on metal oxides, eutectic electrolytes are currently more biased toward MIBs with organic electrode materials, which is not conducive to the general development of the eutectic electrolyte.^{84,85}

Future work should be devoted to further selecting the appropriate composition of DESs. The suitable composition should be inexpensive, green, environmentally safe, and adjustable at the molecular level. Regarding the determination of the optimal mixing ratio between the components, it is imperative to formulate relevant phase diagrams, which can provide information about the temperature and composition range of the mixture liquid. Notably, the viscosity of DESs formed by liquid components is much lower than that by all solid components, and adding some substances, such as FEC and urea, can effectively reduce the viscosity. These methods of reducing viscosity are essentially the result of hydrogen-bond enhancement.⁸⁶ Further, in order to develop safe MIBs with good electrochemical performance, the formed DESs as eutectic electrolytes are expected to possess high conductivity and high electrochemical stability. In general, temperature is positively correlated with viscosity and conductivity. Therefore, eutectic electrolytes with good thermal stability are very promising to achieve MIBs with good properties at high temperatures due to the enhanced ion transport kinetics. At present, a new way is needed to reduce or avoid the dissolution of metal oxides in eutectic electrolyte so as to realize more electrode materials suitable for eutectic systems. In the theoretical conclusions and the formation mechanisms of DESs that have been applied to some MIBs, replacing its components with or introducing other metal salts can broaden the application of DESs in more types of MIBs, such as KIBs, NIBs, MgIBs, etc. More importantly, a fundamental understanding of the relationship between the components and the exploration of the corresponding coordination geometry by in situ/ex situ characterization becomes even more crucial to further reveal the intrinsic mechanism of DESs subject to various typical MIBs. The DESs studied are expected to nucleate a special area of MIBs, and such investigations are sure to continue in the future.

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