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Commentary

High-entropy electrolytes in boosting battery performance

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Abstract

Entropy, once overlooked, is an essential aspect of electrolytes. Recently emerged high-entropy electrolytes with multiple components provide vast compositional space and interfacial chemistry possibilities for electrolyte design. It is noteworthy that high-entropy electrolytes exhibit extraordinarily high ionic conductivity at low temperatures, thereby creating a new direction for batteries to operate at ultra-low temperatures. This commentary discusses the underlying mechanism, challenges encountered, and potential solutions of high-entropy electrolyte design in the hope of sparking future research in this subject.

Keywords: electrolyte design, high-entropy, low temperature, batteries

1. Introduction

The concept of high entropy is well known in the materials and scientific research communities as an effective strategy to discover new materials in the metastable phase. For example, high-entropy alloys with ordered structures but disordered compositions of multiple elements can achieve unprecedented physical and mechanical properties. In the field of materials science, the entropy-controlled design concept has led to countless discoveries and has greatly impacted the development of structural materials, thermoelectrics, and catalysts. In the past decade, the idea of high entropy has had a considerable impact on battery development, both in terms of electrodes and electrolytes [1].

Conventional carbonate-based electrolytes encounter a bottleneck for advanced batteries due to their narrow operating temperature range, and limited electrochemical stability. Electrolyte plays a critical role in batteries as an ion conductor, and as a reactant for electrochemical reactions at the electrode/electrolyte interface, contributing to the formation of solid-electrolyte interphase (SEI) and cathode–electrolyte interphase (CEI). Therefore, advanced electrolytes with better electrochemical compatibility and wide operating temperature range are highly required for the further development of advanced batteries. The idea of high entropy has proved to be a valuable tool for rational electrolyte design. High-entropy electrolytes with multiple components provide vast compositional space with diverse solvation structures and interfacial chemistry possibilities that can achieve more robust SEI/CEI, thus substantially improving lithium battery performances.

In this commentary, we recount the key technological developments of high-entropy electrolytes and discuss how high-entropy electrolytes can impact the battery field. In the first part, we discuss the milestones of high-entropy electrolytes from the solid-state electrolyte to non-aqueous electrolyte and to aqueous electrolyte. In the second section, we highlight the merits of high-entropy electrolytes for

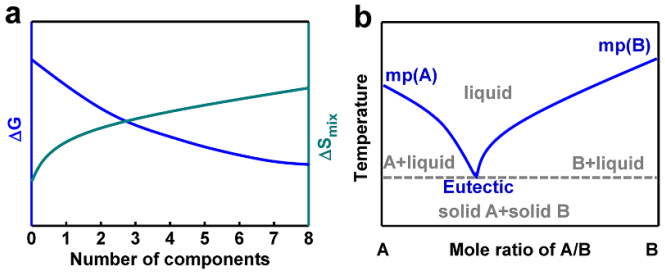

Figure 1. (a) Increasing the number of components is a promising strategy to increase the entropy and lower the Gibbs free energy. (b) Phase diagram of eutectic mixture with two components, showing the eutectic point is lower than the melting point of each component.

low-temperature applications. In the last section, we explore the perspective of the future of high-entropy electrolytes, in which machine learning can be used to accelerate the screening process.

2. High-entropy electrolyte design

An ideal electrolyte requires good chemical and electrochemical stability in combination with good ionic transport capability. Thermodynamically, the Gibbs free energy is a universal rule for all electrolytes, regardless of the various components. Gibbs free energy is defined as the enthalpy of the system minus the temperature multiplied by the entropy of the system (equation (1))

$$\Delta G = \Delta H - T\Delta S. \tag{1}$$

Based on the definition, Gibbs free energy is determined by the competition between ΔH and ΔS. The introduction of multiple components to increase ΔS represents a strategy to outweigh the increased ΔH, in principle, to reduce Gibbs free energy (figure 1(a)). The concept of high-entropy electrolytes was first implemented in all-solid-state batteries and thereafter in non-aqueous electrolytes and aqueous electrolytes.

2.1. High-entropy solid-state electrolytes

Unexpected properties can be achieved by increasing the number of elements, randomly distributed on the same lattice sites. In the quest for all-solid-state batteries, the most challenging task is to discover solid-state electrolytes with ultra-high ionic conductivity. Ceder's group reported three high-entropy electrolytes–$Li(Ti,Zr,Sn,Hf)_2(PO_4)_3$, $Na(Ti,Zr,Sn,Hf)_2(PO_4)_3$ and $Li_3(La,Pr,Nd)_3(Te,W)_2O_{12}$ with orders-of-magnitude higher ionic conductivity in solid-state superionic conductors [2]. High-entropy mixture of metal cations introduces local structural distortions and therefore creates a percolation network of overlapping site-energy distribution to minimize the energy barrier for ion diffusion. In analogue to oxides, high-entropy lithium argyrodites ($Li_{6.5}(P_{0.25}Si_{0.25}Ge_{0.25}Sb_{0.25})S_5I$) with multication substitution is reported to possess a low activation energy of 0.2 eV for Li diffusion along with high ionic conductivity of 13 mS cm^{-1} [3]. In contrast to cationic mixing, the same group demonstrated an unequal distribution of elements over the respective lattice sites of high-entropy lithium argyrodites with polyanionic mixing including $Li_6PS_5(Cl_{0.33}Br_{0.33}I_{0.33})$, $Li_6P(S_{2.5}Se_{2.5})(Cl_{0.33}Br_{0.33}I_{0.33})$, and $Li_6(Ge_{0.5}P_{0.5})(S_{2.5}Se_{2.5})(Cl_{0.33}Br_{0.33}I_{0.33})$ [4]. The ionic conductivity was marginally affected by such an anion mixing but the activation energy is largely lowered to 0.22 eV. All these works pave the way for developing high-entropy solid electrolytes to achieve superior conduction.

2.2. High-entropy non-aqueous electrolytes

As for liquid electrolytes, many efforts are devoted to modulating the enthalpy in the electrolytes, such as the strength of bonding between lithium ions and solvents without considering it from the perspective of entropy [5]. There are two possible reasons as follows. First, unlike specific configurational entropy that can be calculated in solids [3], the 'entropy' of liquid electrolytes is very hard to be measured and compared because of the lack of long-range order in liquids. But it is still possible to consider high-entropy solid and liquid electrolytes based on the same general concept of entropy. Second, the success of commercial carbonate-based electrolytes has led to the binary solvent design concept being considered as a guideline. In addition, great efforts have been devoted to single-salt and single-solvent systems to simplify the electrolyte composition and establish electrolyte-performance relationships. These certainly limit the exploration of multi-component strategies.

While diving deeper into the development of commercial carbonate-based electrolytes, we find that the multi-component strategy is the path toward advanced electrolytes. It is well known that ethylene carbonate (EC) is an essential component in commercial electrolytes to form robust SEI, but EC is a transparent crystalline solid at room temperature with a melting point of 37 °C. Therefore, the commercial electrolytes in most Li-ion batteries contain a binary mixture of EC and low viscous linear carbonate solvents with low melting points. The inclusion of a linear carbonate solvent lowers the viscosity and freezing temperature of the overall electrolyte and promotes faster ionic transport. On a broader extent, the high-entropy effect encompasses the incorporation of additional components in the system, which can lead to enhanced properties and behaviors beyond what individual components alone can provide. Theoretically, introducing a wider variety of miscible solvent components is an effective way to increase the functionality of the electrolyte. The high-entropy concept provides vast compositional space and interfacial chemistry possibilities for liquid electrolyte design. Unfortunately, few studies have investigated electrolytes beyond quaternary solvent mixtures. Recently, a high-entropy liquid electrolyte based on the mixture of 10 solvents (EC- diethyl carbonate-propylene carbonate-ethyl methyl carbonate-ethyl propionate-ethyl acetate-methyl butanoate-butyl acetate-methyl propionate-propyl butyrate) was developed, showing a remarkable high conductivity of 0.6 mS cm^{-1} at −60 °C [6]. It is also nice to see some nice

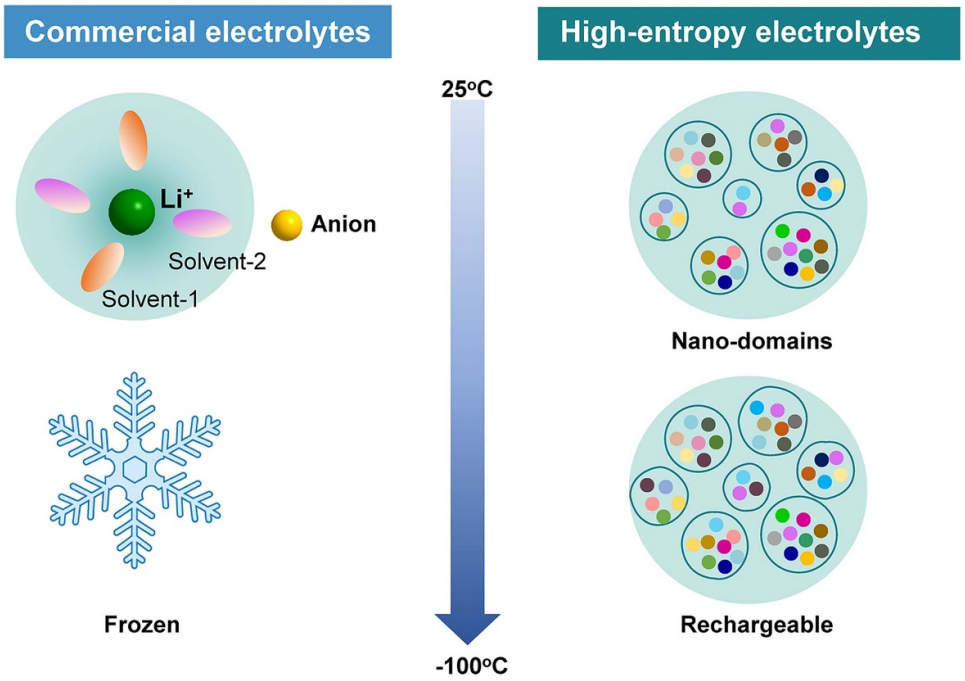

Figure 2. Schematic illustrations of the difference between commercial carbonate-based electrolytes and high-entropy electrolytes upon the decrease of temperature.

attempts of triple-salt and multiple anions, which are capable to support the high-voltage operation of 4.5 V with high safety and long cycling stability [7]. The solubility of lithium salts in high-entropy electrolytes was raised, stabilizing electrode-electrolyte interphases.

2.3. High-entropy aqueous electrolytes

The high entropy design concept can be extended to aqueous electrolytes as well. Most recently, Wang *et al* developed a high-entropy aqueous electrolyte of $Li_2ZnCl_4{\cdot}9H_2O$, characterized by a unique frustrated solvation structure where the cations, anions, and water solvent are well-tuned to deliver a high-entropy state [8]. Benefiting from the high-entropy solvation environment illustrated by simulations, the $Li_2ZnCl_4{\cdot}9H_2O$ electrolyte exhibits a substantial decrease in hydrolysis and enables close to 100% Coulombic efficiency for Zn stripping/platting. In addition, a eutectic point was observed in LiCl-$ZnCl_2$ binary phase diagram. Figure 1(b) schematically illustrates the eutectic effect, in which a mixture of two or more substances possesses a lower freezing point than both. A ternary eutectic aqueous electrolyte was developed for stable 2.5 V $LiMn_2O_4$||$Li_4Ti_5O_{12}$ cells, implying eutectic components are good candidates for high-entropy electrolytes [9]. In other words, the eutectic effect contributes to enhancing the mutual solubility between various components such as solvents in the high-entropy electrolytes.

3. Boosting low-temperature performance

The capacity of lithium-ion batteries at temperatures below −20 °C hitherto experiences a significant drop-down of its room temperature capacity. This is because commercial electrolytes almost exclusively use EC as a major solvent component. However, EC has a rather high melting point (37 °C), which leads to significantly increased viscosity and severely decreased Li^+ conductivity at low temperatures. As shown in figure 2, the high melting point nature of EC limits the liquidus temperature of commercial electrolytes. The EC electrolytes will be frozen at low temperatures (−30 °C), thus resulting in battery failure.

On the contrary, high-entropy electrolytes are highly favorable for battery operation at low temperatures given their intrinsic high entropy characteristic. In principle, the increased system entropy in high-entropy electrolytes would significantly depress the freezing point. As expected, the ten-solvents-based high-entropy electrolyte exhibited an unprecedented low freezing point of −130 °C based on the differential scanning calorimetry results [6]. This high-entropy electrolyte enables $LiMn_2O_4$|| $Li_4Ti_5O_{12}$ cells to be charged and discharged at an ultra-low temperature of −60 °C, far exceeding the performance of commercial electrolytes. Likewise, the Zn-air batteries with a high-entropy $Li_2ZnCl_4{\cdot}9H_2O$ electrolyte can maintain stable cycling at −60 °C, retaining 80% of room-temperature power density [8]. These exceptional performance is due to the frustration of Li^+–$ZnCl_4^{2-}$ ion pairs into shorter aggregates (nano-domains in figure 2) in combination with the disruption of the free solvent hydrogen-bond network. Additionally, high-entropy solid electrolytes are expected to be less sensitive to temperature, endowing the ability to operate under low temperatures. Meanwhile, the performance of high-entropy electrolytes operating at high temperatures (like 60 °C) needs to be carefully evaluated. There is no doubt that the development of batteries with high-entropy electrolytes capable of operating stably at low temperatures is critical to motivating greater adoption in colder areas.

4. Future of high-entropy electrolytes

High-entropy electrolyte represents a new type of electrolyte that goes beyond all current electrolytes including the usual 'solvent-in-salt' and 'soft solvating' electrolytes [10], which will revolutionize the aqueous, non-aqueous, and solid-state rechargeable batteries. Any great change requires a long period of exploration, which inevitably comes with difficulties and hardships, high-entropy electrolytes are no expectation. Despite being very promising, they are still subject to some limitations. For example, there is a lack of practical definition of 'high-entropy' for liquid electrolytes. One way to classify the 'high-entropy liquid electrolyte' can be based on the decreased ion clustering, which favors anion-participated solvation structure and reduces the melting point of the electrolytes. As noted above, both high-entropy non-aqueous and aqueous electrolytes enable a decrease in melting temperature of the electrolytes. From this perspective, high-entropy liquid electrolytes refer to electrolyte solutions with entropically favorable small ion clusters, containing multiple cations and/or anions and/or solvents. For another example, finding an appropriate component to realize high-entropy electrolytes mainly relies on the trial-and-error approach. The aforementioned eutectic compositions can be used as a broad guideline for selection, but it is far from being satisfactory. As such, an alternative strategy to overcome this shortcoming is to combine machine learning with experimental data for fast screening. Finding the optimal composition of high entropy electrolyte is challenging because the number of the possible combinations grows exponentially with the number of constituents. To overcome this challenge, advanced models which can predict and prioritize high-order combinations, even in large screens are highly needed. Several studies have already shown that machine learning provides a shortcut to rapidly screen new electrolyte components including salts, solvents, and additives based on known properties like dielectric constant, dipole moment, donor number, etc. It is evident that the future of high-entropy electrolytes is strongly correlated with the emerging machine-learning technique.

5. Conclusion

High-entropy electrolyte offers a wider choice of solvents, salts, and additives in designing the next generation of high-performance electrolytes. Here, we revisited key technological developments related to high-entropy electrolytes, from solid-state to non-aqueous and then to aqueous, highlighting the application of high-entropy electrolytes in low-temperature operation. Fundamental theoretical studies on basic high-entropy electrolytes are still necessary, such as machine learning-assisted fast screening.

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Author contributions

J X conceived the original idea and drafted the manuscript.

Conflict of interest

The authors declare no competing interests.

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