



# **Review Recent Progress of Urea-Based Deep Eutectic Solvents as Electrolytes in Battery Technology: A Critical Review**

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Abstract: Urea, a basic chemical compound, holds diverse applications across numerous domains, ranging from agriculture to energy storage. Of particular interest is its role as a hydrogen bond donor (HBD). This specific characteristic has propelled its utilization as an essential component in crafting deep eutectic solvents (DESs) for battery electrolytes. Incorporating urea into DESs presents a promising avenue to address environmental concerns associated with traditional electrolytes, thereby advancing battery technology. Conventional electrolytes, often composed of hazardous and combustible solvents, pose significant environmental risks upon improper disposal potentially contaminating soil and water and threatening both human health and ecosystems. Consequently, there is a pressing need for eco-friendly alternatives capable of upholding high performance and safety standards. DESs, categorized as organic salts resulting from the blending of two or more compounds, have emerged as promising contenders for the next generation of electrolytes. Urea stands out among DES electrolytes by enhancing ion transport, widening the electrochemical window stability (ESW), and prolonging battery cycle life. Further, its non-toxic nature, limited flammability, and elevated thermal stability play pivotal roles in mitigating environmental concerns and safety issues associated with traditional electrolytes. Laboratory testing of urea-based DES electrolytes across various battery systems, including Al-ion, Na-ion, and Zn-ion batteries, has already been demonstrated. This review examines the evolution of urea-based DES electrolytes by elucidating their structure, molecular interaction mechanisms, performance attributes, and preparation methodologies.

Keywords: urea; battery; ionic liquid; eutectic solvent

# 1. Introduction

In the modern world, battery technology has become an indispensable component of our daily lives [1]. From powering smartphones and laptops to driving electric vehicles and enabling renewable energy storage systems, batteries play a crucial role in shaping our technological landscape [2]. Over the past century, significant strides have been achieved in battery development, notably marked by the commercial inception of lithium-ion batteries by Sony (Tokyo, Japan) in 1991 [3,4]. These batteries have exhibited remarkable characteristics such as high energy and power density, prolonged cycle life, and minimal self-discharge [5–7]. One of the recent advancements in Li battery technologies is the solid-state Li-sulfur battery with high flexibility. This type of battery has high specific and energy densities in addition to being relatively inexpensive [8]. When the battery discharges, the sulfur in the cathode undergoes a series of reductions. First, it forms a long-chain polysulfide through the ring-opening reaction. Then, it breaks down into a short-chain polysulfide and, finally, it becomes Li<sub>2</sub>S. However, usually, the long-chain polysulfide that forms in Li-S batteries can be dissolved and diffused from the sulfur cathode to



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the lithium metal anode in the organic liquid electrolyte. This leads to the depletion of sulfur, rapid capacity fading, and poor Coulombic efficiency when the polysulfide reacts with lithium metal. Therefore, solid-state electrolytes have been studied widely and well discussed previously [8]. Despite their strengths, lithium-ion batteries exhibit limitations of scalability, cost-effectiveness for large-scale applications, and relatively short lifespans of approximately five years [9,10]. Further, concerns regarding the environmental impact and potential health hazards associated with their constituent materials, including plastic casings, lithium, and electrolytes, have stimulated a quest for alternative post-lithiumion battery technologies [10–12]. This pursuit has led to a comprehensive exploration of promising alternatives, such as sodium-ion batteries (SIBs), zinc-ion batteries (ZIBs), and aluminum-ion batteries (AIBs) [13]. For instance, a zinc anode is a promising sustainable energy storage technology due to its advantages such as low cost, its abundance, and large-scale production. Further, it is nontoxic and simple, with high energy storage per unit volume [14]. At the same time, it suffers from dendrites and side reactions [15], resulting in lower operational stability for the anode and decomposition of the electrolyte; therefore, less Coulombic efficiency with poor cycling performance. However, the development of these batteries requires a holistic approach, such as advancements in materials science, fabrication techniques, and anode, cathode and electrolyte formulations.

Electrolytes represent a fundamental component critical to the operational functionality of batteries that enable the flow of electrical energy. These are typically composed of salts dissolved in a solvent that serves as the medium through which ions travel from one electrode to another. Previous focus on electrolyte development primarily centered on two main types: aqueous electrolytes (such as LiNO<sub>3</sub> and KOH) and organic electrolytes (derived from ethylene carbonate and acetonitrile, among others) [16–18]. A recent addition to electrolyte technology involves the emergence of new generations of ionic liquid electrolytes, particularly the introduction of deep eutectic solvents (DES); a novel class sharing attributes with ionic liquids. These advancements mark a significant stride in battery research, offering the potential for improved performance and environmental sustainability in the domain of next-generation batteries [19–22].

Urea is a simple organic compound that has the chemical formula  $CO(NH_2)_2$ . It acts as a hydrogen bond donor (HBD), meaning that it can share its hydrogen atoms with other molecules through electrostatic attraction [23]. Urea is widely available, non-flammable, low-cost, nontoxic, biodegradable, and can be easily obtained from various sources, such as human urine, urea-containing wastewater, and industrial urea. Therefore, it offers environmental and economic benefits for different applications. One of the applications of urea is in the field of electrochemistry, where it can be used to form DESs [24,25]. In this regard, the ionic conductivity of ChCl-urea at room temperature is around 0.0353 mS·cm<sup>-1</sup> [26]. This value is relatively low, but it can be developed in the future by manipulating the DES composition.

In this review, the development of DESs related to urea in battery technology will be discussed and reviewed according to Figure 1.

#### 1.1. Ionic Liquids

Ionic liquids (ILs) are a group of liquid organic salts characterized by certain properties that have motivated researchers to investigate their potential applications in various fields [27,28]. The asymmetrical and bulky structure of constituent ions in ILs differentiates them from conventional salts such as sodium chloride and even molten salts, as depicted in Figure 2 [29–31]. Conventional salts have tightly packed symmetrical ions that exhibit stronger ionic interactions leading to higher melting points compared to ILs. ILs boast a range of significant properties, including non-volatility, low vapor pressure, non-flammability, wide electrochemical stability windows (ESWs), high thermal stability, and good electrical conductivity [27,32,33]. The exceptional properties of ILs, specifically their non-volatility and high ionic conductivity, have been utilized in electrochemical applications. They are good candidates for safe electrolytes in a wide range of energy storage devices, such as batteries and supercapacitors. Moreover, their ability to dissolve a wide range of organic compounds and metals makes them suitable as solvent media [34]. Furthermore, ILs exhibit high ionic conductivity and strong electrostatic interactions making them promising electrolytes in battery technology [34]. Additionally, ILs can be transformed into ionic liquid gels (ionogels) which offer notable advantages, such as high conductivity, and can be considered a method for solidifying ILs without using their lubricant properties [35]. To capitalize on these benefits, Lee et al. utilized a hybrid ionogel in the development of a lithium battery [36]. However, one of the most common problems associated with ionogels and ILs is corrosion, especially when used as solid electrolytes in solar cells, batteries, capacitors, and soft actuators, as well as in their application as lubricants. To address this issue, Yu et al. used urea to obtain a gelator as an ionogel material and showed good anticorrosion properties with copper pieces [35]. This can be ascribed to the ability of the gelator to form bonds with the metal surface which works as a protective film and prevents corrosion. Another problem associated with some ILs is their extreme sensitivity to water. Even a small amount of moisture from the air can cause them to break down and generate hydrochloric acid (HCl), which is a corrosive and undesirable byproduct [37]. This sensitivity to water can be a significant problem in battery systems as ILs can cause damage to typical current collector materials, such as copper, nickel, and even titanium. When these metals are exposed to the ILs, they may corrode or undergo decomposition, which can weaken the overall performance and longevity of the battery [38]. Furthermore, ILs possess weak ionic conductivity at ambient temperatures and insufficient solubility of non-organic salts, which can adversely affect energy performance. To address these challenges and provide alternative electrolytes that are safer, less expensive, offer high ionic conductivity, better chemical compatibility with cell components, and can work well at room temperature, researchers have developed deep eutectic solvents [39,40].



**Figure 1.** The outline of the review, where the introduction covers two subjects and the urea-based deep eutectic solvents section covers six subjects while also discussing performance and mechanism.



**Figure 2.** The difference between ionic solids, molten ionic solids, and ILs. The red color refers to negative charges and the blue color means positive charges.

#### 1.2. Deep Eutectic Solvents

Deep eutectic solvents (DESs) are a class of liquid mixtures composed of two or three compounds [41,42]. These compounds are mixed at a eutectic mixture with a melting point considerably lower than that of each component and even lower than the ideal or traditional eutectic point as illustrated in Figure 3 [43,44]. The synthesis of DESs involves the combination of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) molecule [45], which leads to the formation of a complex between these two molecules and a significant reduction in the freezing point temperature. DESs possess several advantages over conventional ILs, including straightforward synthesis, lower production costs, lower toxicity behavior, high thermal stability, and sustainability from both environmental and economic perspectives [46]. Although ILs and DESs share similarities in their physical properties and practical applications, they differ fundamentally in their precursors and synthesis processes. The preparation of ILs is a complex process involving multiple steps, various reagents, organic solvents, and the generation of waste. Reaction times can be long, up to 48 h, and temperatures range from 25 to 100 °C [46]. The two main steps in IL synthesis are cation formation and anion exchange, which involve the protonation or quaternization of amine and the treatment of halide salt with a Lewis acid or anion metathesis. On the other hand, DESs can be easily prepared through simple heating or grinding. In general, DESs can be classified into four categories with different formulas. Type I DESs consist of a combination of a quaternary ammonium salt and a metal chloride  $(Cat^+ X^- + zMCl_x)$ , for instance, ChCl + ZnCl<sub>2</sub>. Type II DESs are composed of a quaternary ammonium salt and a metal chloride hydrate (Cat<sup>+</sup>  $X^-$  + zMCl<sub>x</sub>·yH<sub>2</sub>O) such as  $ChCl + CoCl_2 \cdot 6H_2O$  [47]. Hydrated metal salts are known for their affordability and resistance to air and moisture, and are suitable for industrial processes. Type III DESs consist of a quaternary ammonium salt and an HBD (Cat<sup>+</sup>  $X^-$  + zRZ), for example, ChCl + urea, where Z is OH, COOH, and CONH<sub>3</sub>. Lastly, Type IV DESs are formed by combining a metal chloride with an HBD ( $zMCl_x + zRZ$ ) such as  $ZnCl_2 + urea$  [47]. One specific DES that has been used recently is composed of urea and aluminum chloride (urea/AlCl<sub>3</sub>) [48]. These DESs are more stable when exposed to water, which means they are less likely to break down when moisture is present. By incorporating such DESs, the sensitivity of AlCl<sub>3</sub>-based electrolytes to water can be significantly reduced. This helps prevent the formation of HCl and corrosion of current collector materials and ultimately contributes to a more robust and durable battery technology [37]. An AlCl<sub>3</sub>-urea DES has advantages such as low-cost and being a non-flammable liquid electrolyte that can support high discharging voltage and high Coulombic efficiency at the same time [49]. In addition, it allows the reversible process of intercalation and de-intercalation into the graphite material cathode of specific anions (AlCl<sub>4</sub><sup>-</sup>), which will be discussed later [50]. Moreover, this combination of AlCl<sub>3</sub> and urea has shown compatibility with various anode materials with good stability [50,51]. Urea can work as a co-solvent due to its remarkable water solubility. Furthermore, it is cost-effective and environmentally friendly, making it a superior choice compared to other organic solvents and additives for battery electrolytes. Ao et al. formulated a multicomponent aqueous electrolyte, referred to as MCAE, which comprises Na, H<sub>2</sub>O, urea, and dimethylformamide (DMF). Their study demonstrated that the voltage window of the Na, H<sub>2</sub>O, urea, and DMF electrolytes extends to 2.8 V, which is higher than the voltage window of water (1.23 V). This expanded voltage range is attributed to the formation of an SEI, which effectively prevents undesirable side reactions [52]. Moreover, according to Hou et al., urea demonstrates a distinctive ability to assimilate into the solvent structure during interactions between ions and solvents [53]. The prepared MCAE showed no electrochemical interaction between 1.4 and -1.4 V which indicates a high stability at this range. The ionic conductivity of the MCAE achieved 8.1 mS·cm<sup>-1</sup> at 20 °C, and it rises to 13.85 mS·cm<sup>-1</sup> at 50 °C [52]. This conductivity is similar to that of "water-insalt" electrolytes, which are employed in high-voltage aqueous Li-ion batteries and have a conductivity of  $10.0 \text{ mS} \cdot \text{cm}^{-1}$  [54]. They also reported that the ionic conductivity of MCAE, when DMF was not included, was approximately 1.259 mS  $\cdot$  cm<sup>-1</sup> at 25 °C. This indicates that the presence of DMF significantly enhances the transport of Na<sup>+</sup> ions in the electrolyte. Moreover, Ao et al. conducted testing on both half and full cells using  $Na_3V_2$  $(PO_4)_3$  (NVP) and NaTi<sub>2</sub> (PO<sub>4</sub>)<sub>3</sub> (NTP) electrodes. In the case of NVP electrodes, the half cells exhibited a charge capacity of 110 mA $\cdot$ h·g<sup>-1</sup> and a discharge capacity of 96 mA $\cdot$ h·g<sup>-1</sup>. Conversely, NTP displayed higher values with a charge capacity of 118 mA $\cdot$ h·g<sup>-1</sup> and a discharge capacity of 138 mA $\cdot$ h $\cdot$ g<sup>-1</sup> [52]. Furthermore, they showed that employing a full-cell configuration with NiHCF as the anode and NTP as the cathode, in the presence of MCAE, delivered outstanding performance and stability. This setup achieved a high cycle number of 2000 with approximately 99% Coulombic efficiency and a capacity of around 50 mA·h·g<sup>-1</sup> [52].



**Figure 3.** The difference between mixing two compounds and mixing them at their eutectic point leads to lower temperatures than the individual compounds. The (deep) eutectic point must be lower than the ideal eutectic point. Higher freezing temperature is visualized by more reddish color, and more dark blue refers to lower freezing temperatures.

#### 2. Urea-Based Deep Eutectic Solvents (DESs)

2.1. XTFSI-Urea (Where X = Li or Zn)

Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and zinc bis(trifluoromethane sulfonyl)imide (ZnTFSI) are inorganic salts with the chemical formulas of  $LiC_2F_6NO_4S_2$  and  $Zn(C_2F_6NO_4S_2)_2$ , respectively [55]. Despite sharing similar physicochemical properties, LiTFSI exhibits several advantages due to its use in Li batteries and its use in combination with urea [56]. Both are white hygroscopic powders [57,58]. LiTFSI has some interesting

properties, such as relatively good ionic conductivity around 2.80 mS·cm<sup>-1</sup> as electrolyte and  $0.0011 \text{ mS} \cdot \text{cm}^{-1}$  for LiTFSI itself without any solvation effect, thermal stability around 200 °C, and electrochemical stability which reaches 4.5 eV [59–61]. An increase in LiTFSI concentration to 21 M resulted in an expansion of the electrochemical stability window to approximately 3.0 V, as reported previously [19,54]. LiTFSI is a soluble and hydrolysisresistant salt that was selected as the electrolyte solute [62]. In dilute electrolytes, Li-ions are effectively solvated in the primary solvation sheath which provides adequate mobility and prevents aggregation [63]. Further, in dilute electrolytes, there is sufficient water to dissolve all the salt; thus, every Li-ion is surrounded by a cluster of water molecules that are bound tightly with Li<sup>+</sup> ions via electrostatic interaction from partial negativity of oxygen, as shown in Figure 4. This leads to sheaths or shells that are crucial for preventing interactions between the ions. The function of the shells is not only to act as a shield but also as ionic carriers. Water molecules can carry Li<sup>+</sup> ions and facilitate the movement in the solution, which leads to an efficient transportation process. The sheath also prevents the aggregation and clustering of ions by hindering their mobility. Therefore, a well-hydrated primary solvation sheath is crucial for the electrochemical properties of the electrolyte. One study revealed that a specific molar ratio of 1:3.6 between LiTFSI and urea resulted in ionic conductivities ranging from  $10^{-4}$  to  $10^{-3}$  S cm<sup>-1</sup> at temperatures between 300 and 330 K [64]. The eutectic melting temperature was determined to be 240 K, while the individual melting temperatures of LiTFSI and urea are 507 and 405 K, respectively [65].



**Figure 4.** Li<sup>+</sup> cation is surrounded by water molecules in the first and second sheath, which are bound by electrostatic force (H-bond) between the oxygen of water and Li+. The last sheath contains free water molecules and anion of [TFSI]<sup>-</sup>.

## 2.1.1. Performance

The performance of LiTFSI/urea was even investigated in non-DES systems or conventional aqueous systems such as a LiTFSI-H<sub>2</sub>O-PEG-urea electrolyte with an anode and cathode of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO) and LiMn<sub>2</sub>O<sub>4</sub> (LMO). In this system, an irreversible plateau was observed in the first cycle. However, this plateau gradually disappeared completely by the 11th cycle. This can be ascribed to the formation of a passivation layer on the electrodes which can resist the decomposition of aqueous electrolytes [66]. Additionally, at charging and discharging voltages of 1 and 3.1 V, respectively, the specific capacity observed was approximately 160 mA·h·g<sup>-1</sup> during the initial cycle. Nevertheless, this capacity decreased to around 150 mA·h·g<sup>-1</sup> by the 11th cycle and declined further to 80 mA·h·g<sup>-1</sup> after approximately 60 cycles, eventually reaching 40 mA·h·g<sup>-1</sup> after 180 cycles. Despite this decrease in capacity, the Coulombic efficiency (C.E) was maintained at around 92% [66].

However, in this conventional aqueous electrolyte system, it is important to understand the effect of urea addition to electrolytes. In this aqueous electrolyte, the electrochemical window is extended despite the existence of water, which can be attributed to the hydrogen bonding between urea and Li<sup>+</sup>, in addition to water with PEG, which restricts the activity of water [66]. When  $Zn(TFSI)_2$  is added to the electrolyte, the resulting component is LZTFSIurea. This component comprises two reactive ions,  $Li^+$  and  $Zn^{2+}$ . The appropriate ratio for obtaining LZ-DES is Li/Zn of around 20, while the molar ratio of Li/urea is between 1:3 and 1:3.8. The conductivity of this system was around 0.084 mS/cm at a ratio of 1:3 and a temperature of 30  $^{\circ}$ C [67]. Zhao et al. added H<sub>2</sub>O to the DES system with a molar ratio of 2 (LZ-DES/2H<sub>2</sub>O). This addition increased conductivity and decreased viscosity to 1.85 mS/cm and 0.139 Pa $\cdot$ s at 30 °C, respectively [67]. The usage of the Zn(TFSI)<sub>2</sub> DES system can aim also to address the side-reaction challenge of Zn aqueous and dendrite formation, as shown in Figure 5. That is clear in the paper, where a dendrite-free layer was obtained after around 40 min at  $0.2 \text{ mA} \cdot \text{cm}^{-2}$ . Moreover, the water in LZ-DES led to a decrease in the corrosion behavior [67]. The electrochemical cell using LZ-DES/2H<sub>2</sub>O initially underwent a 30 h induction period after which it consistently cycled over 2400 h (equivalent to 3.3 months) without notable overpotential. This means that after an initial phase of stabilization, the cell continued to operate smoothly and, without water, exhibited the same stable cycling performance but with less amplified polarization. It has also been reported that regular aqueous electrolytes are highly sensitive to the operating rate, leading to early failures in their cells, sometimes within just 20 h (first cycle). In the case of LZ-DES/2H<sub>2</sub>O, the cycling of Zn plating and stripping remains stable even after 400 h, displaying consistent voltage responses in each cycle [67]. Sim et al. added PAN-DMF to a LiTFSI-urea DES which enhanced conductivity at ambient temperature from  $2.54 \times 10^{-4}$ to  $3.82 \times 10^{-3}$  S·cm<sup>-1</sup> from PAN-DMF-LiTFSI to PAN-DMF-LiTFSI-urea [68].



Figure 5. Important key points were demonstrated in the discussed papers.

#### 2.1.2. Mechanism

The strong electrostatic interactions between Li<sup>+</sup> and the oxygen atoms of urea and TFSI<sup>-</sup> were found to be the primary cause of the observed stability. It has been hypothesized that the presence of highly polar Lewis bases, such as urea, which act as electron donors and effectively counteract the electrostatic interactions between Cat<sup>+</sup> and X<sup>-</sup>, may facilitate the gradual replacement of TFSI<sup>-</sup> ions with urea molecules in the first coordination shell around lithium ions leading to the formation of DESs at a certain molar ratio [69]. An analysis of the radial distribution function (RDF) between Li<sup>+</sup> ions and H<sub>2</sub>O in the non-DES electrolyte of LiTFSI-H<sub>2</sub>O-PEG-urea revealed a distinct peak at 2 Å, signifying close coordination in the first coordination shell [66]. In contrast, the RDF between Li<sup>+</sup> ions and TFSI<sup>-</sup>

exhibits a peak around 4.5 Å, designating a secondary coordination shell. This means that  $H_2O$  is predominant in the primary coordination shell surpassing the involvement of TFSI<sup>-</sup>. Despite the coordination structure of [Li ( $H_2O$ )<sub>3</sub>(TFSI)<sup>-</sup>], indicating a 25% occurrence belonging to TFSI, water molecules constitute 86% of the occurrence in the first shell. Consequently, a higher concentration of TFSI compared to  $H_2O$  may result in the prevalence of TFSI around Li<sup>+</sup>. Furthermore, the introduction of PEG contributed to a reduction in the occurrence of H<sub>2</sub>O in the first shell by 7% and around 3% for TFSI, replaced by PEG. The PEG molecules envelop the central Li<sup>+</sup> with multiple bonds playing a crucial role in impeding  $H_2O$  molecules from entering the primary coordination shell of Li<sup>+</sup>, as depicted in Figure 6. This leads to a configuration where 79% of the water molecules surround the first coordination shell. Moreover, urea exhibits a greater affinity for coordination with Li<sup>+</sup> compared to PEG. In this system, the occurrence of in the first shell is approximately 36%, while PEG is around 7%, indicating that urea displaces PEG around Li<sup>+</sup> ions from the first to the second shell and bulk [66]. That means urea tends to be in the first solvation shell around Li<sup>+</sup> in the aqueous system. Moreover, Nandy et al. investigated a urea-LiTFSI DES and showed that, for the lowest urea mole fraction, there is a comparable binding strength to Li<sup>+</sup>, indicated by the calculated value of the minimum potential of mean forces (PMF) by an MD simulation in the system of  $Li^+[(TFSI^-)_x (urea)_{4-x}]$  [69]. This implied a moderate binding affinity for both components. As urea concentrations increased, there was a decrease in the minimum PMF for TFSI<sup>-</sup>, whereas a slight increase was observed for urea. Consequently, an increase in urea concentration strengthens the Li<sup>+</sup>-TFSI<sup>-</sup> coordination shell, while the binding energy between urea and the Li<sup>+</sup> remains almost unchanged [69]. In addition, the coordination numbers for urea and TFSI- around the Li<sup>+</sup> have been calculated and investigated. Around the Li+, the closest coordination shell includes at least one urea molecule due to shorter nearest-contact distances between urea molecules and Li<sup>+</sup> compared to TFSI<sup>-</sup> ions in the DES as well as in conventional aqueous systems, which has been discussed before. Therefore, urea molecules dominate the local environment around Li<sup>+</sup> ions, signifying the gradual replacement of TFSI<sup>-</sup> for urea from the first coordination shell around the Li<sup>+</sup> [65]. Therefore, a steady rise in the coordination numbers attributed to urea, while the coordination numbers related to TFSI<sup>-</sup> ions exhibit a consistent decrease. This encourages urea to play its role as a donor and Li<sup>+</sup> as an acceptor, leading to DES formation at certain ratios of urea: LiTFSI. Lesch et al. noticed that RDF between urea, LiTFSI, and Li depends on the quantity of urea in the system [65]. The most calculated stable structure belongs to  $Li^+[(TFSI^-)_x (urea)_{4-x}]$  due to the lower HUMO and LUMO energies, which indicates the electrochemical stability window. That means the highest electron affinity structure [69]. This suggests the formation of a LiTFSI-urea DES induces dissociation which results in the separation of Li<sup>+</sup> cations and  $[TFSI]^-$  anions Li<sup>+</sup>[(TFSI<sup>-</sup>)<sub>x</sub> (urea)<sub>y</sub>] [69]. The introduction of urea weakens the ionic bonds between the Li<sup>+</sup> and TFSI<sup>-</sup>, with the formation of hydrogen bonds between urea and the TFSI<sup>-</sup> [65,69]. In addition, the presence of water molecules can further disrupt the Li<sup>+</sup>-TFSI<sup>-</sup> interactions and establish hydrogen bonds with both TFSI<sup>-</sup> and urea [67]. This behavior is similar to the water behavior with PEG in the aqueous electrolyte, which leads to an extension of the electrochemical window. Furthermore, urea is a Lewis base due to the presence of lone pairs on its nitrogen and oxygen atoms that can form bonds with Li<sup>+</sup> [69]. Finally, urea molecules are smaller than TFSI<sup>-</sup> anions, which leads to greater mobility of urea within the DES. This enhanced mobility might lead to lower viscosity, higher diffusion for Li<sup>+</sup> ions, and higher ionic conductivity [67]. However, it is crucial to reach a balance between urea and TFSI<sup>-</sup> ions to optimize the urea concentration and maximize electrolyte performance.



**Figure 6.** The affinity of Li<sup>+</sup> to urea is higher than TFSI- and PEG, and this affinity increases with increasing concentrations of urea, which leads to a higher number of urea molecules around Li<sup>+</sup>. Therefore, urea can take the place of water and even PEG in the first shell in this non-DES system (conventional aqueous electrolyte). This behavior of urea in a non-DES system is extremely similar to the behavior of LiTFSI-urea in a DES. The urea molecules concentrate in the first shell around Li<sup>+</sup> and then hydrogen bonds are formed leading to low lattice energy and deep eutectic behavior at a certain molar ratio [47].

#### 2.2. AlCl<sub>3</sub>-Urea

Aluminum (Al) batteries are a promising option but they face several challenges including a low discharge voltage plateau and limited capacity. Furthermore, Al batteries need suitable electrolytes to deal with the natural layer of aluminum oxide that forms on the surface of the metal [70,71]. One approach to improve Al-ion batteries involves using a cathode made of graphite, an aluminum anode, and an electrolyte comprising AlCl<sub>3</sub> with an organic electrolyte which is IL. These ILs could successfully remove the passive aluminum oxide layer. There is a particular IL, known as [EMIM]Cl, that has the advantage of increasing capacity. However, [EMIM]Cl is relatively expensive. As an alternative, urea was chosen due to its cost-effectiveness and nontoxic nature, making it more environmentally friendly [50,72]. In this regard, Li et al. prepared a ternary DES containing AlCl<sub>3</sub>, urea, and [EMIM]Cl to be used in battery applications. They used this ternary chemical mixture due to the high polarization potential and electrical conductivity of AlCl<sub>3</sub>-[EMIM]Cl and urea for its non-flammability, and low cost [73]. Consequently, Ng et al. prepared AlCl<sub>3</sub>/urea at a molar ratio of 1.3 and showed that, after 25 cycles, the charge-specific capacity was around 75 mA $\cdot$ h·g<sup>-1</sup> at 100 mA $\cdot$ g<sup>-1</sup>, but when current density increased to 1000 mA·g<sup>-1</sup>, the specific capacity deteriorated to around 45 mA·h·g<sup>-1</sup> after 125 cycles [74].

# 2.2.1. Performance

The usage of urea as an electrolyte in Al-ion batteries, particularly in a molten  $AlCl_3/urea$  electrolyte, has shown promising results. Urea, when incorporated into the electrolyte of Al-ion batteries, has demonstrated its potential to enhance the performance of these batteries. Specifically, a molten  $AlCl_3/urea$  electrolyte with a molar ratio of 1.5 at an elevated temperature of 120 °C has been investigated [50]. The choice of using an elevated temperature is not arbitrary, as it addresses a critical issue raised by Jiao et al., where they reported that  $AlCl_3/urea$  at room temperature exhibits poor ionic conductivity, limiting its practical application [50]. The utilization of this innovative electrolyte has yielded impressive results in terms of battery stability and capacity retention. After 10 cycles, the Al-ion battery achieved an outstanding 99.5% capacity retention rate (C.R.), a strong indicator of the battery's resilience and long-term performance. Even after 100 cycles, the battery re-

tained 95.3% of its initial capacity [50]. The specific capacity of the Al-ion battery during the first cycle was approximately 93 mA·h·g<sup>-1</sup>. This value is interesting as it represents a 33% improvement over the traditional AlCl<sub>3</sub>/[EMIM]Cl (ethyl methylimidazolium chloride) electrolyte, which had an initial specific capacity of 70 mA $\cdot$ h·g<sup>-1</sup>. Such a substantial increase in specific capacity suggests that the use of urea in the electrolyte composition offers an advantage in terms of energy storage capabilities. Further, temperature was investigated due to its critical role in the performance of the AlCl<sub>3</sub>/urea electrolyte. Conductivity in the system exhibits an increase with rising temperature, reaching its peak at 120 °C. Beyond this point, further improvements in conductivity become less significant. This observation underscores the importance of the operating temperature in optimizing the performance of Al-ion batteries utilizing AlCl<sub>3</sub>/urea electrolyte [50]. In addition, the Coulombic efficiency of the battery at 120 °C was approximately 98.6%. This high Coulombic efficiency indicates that most of the charge-discharge process is reversible, making the Al-ion battery an efficient energy storage system [1]. Li et al. prepared various molar ratios of AlCl<sub>3</sub>-Urea and investigated its cyclic voltammograms (CV) at 333 K [75]. They reported that there was no oxidation or reduction at a ratio of 1.2 and this is because of the unreduced  $AlCl_4^-$ . After increasing the molar ratio,  $AlCl_4^-$  was reduced to  $Al_2ClO_7$ , and the oxidation/reduction process took place [75].

## 2.2.2. Mechanism of AlCl<sub>3</sub>-Urea Interactions

The combination of urea alongside AlCl<sub>3</sub> resulted in the formation of AlCl<sub>2</sub>-2urea, accompanied by the loss of a Cl ion, thus resulting in an overall positive charge. Conversely, AlCl<sub>3</sub> can accommodate this Cl<sup>-</sup> ion to give rise to AlCl<sub>4</sub><sup>-</sup>, thereby incurring a negative charge. This fundamental interplay is a driving force behind the formation of a DES that incorporates urea. Furthermore, introducing more AlCl<sub>3</sub> in the presence of AlCl<sub>4</sub><sup>-</sup> leads to the combination of Al ions and Cl ions to form Al<sub>2</sub>O<sub>7</sub> species, which also carries a negative charge. The introduction of [EMIM]Cl leads to the separation of the EMIM<sup>+</sup> cation and Cl<sup>-</sup> anion, as depicted in Figure 7. Electrons are predominantly distributed around the imidazole ring, resulting in a weakening of the Coulombic interaction between the cation and the surrounding ions. This weakening effect directly influences the dissociation properties, as reduced Coulombic interactions facilitate the separation of cations and anions, consequently elevating the ionic conductivity [73]. Furthermore, the rise in the molar ratio causes an increase in the electrolyte acidity, resulting in the corrosion of the aluminum foil anode and a rapid decline in the battery's capacity [50].



Figure 7. The molecular interaction in [EMIM]Cl and AlCl<sub>3</sub>, and urea systems.

According to the study conducted by Jiao et al., the reaction between  $AlCl_3$  and urea takes place in three distinct stages [50]. The first stage is between urea and  $AlCl_3$  (Equation (1)).

$$n[urea] + AlCl_3 \rightarrow [AlCl_2.n(urea)]^+ + AlCl_4^-$$
(1)

The second stage is the reaction between AlCl<sub>3</sub> and the AlCl<sub>4</sub> (Equation (2)).

$$AlCl_3 + AlCl_4^- \to Al_2Cl_7^-$$
<sup>(2)</sup>

The third stage is the reaction between the of  $Al_2Cl_7^-$  and  $AlCl_4^-$  (Equation (3)).

$$AlCl_3 + Al_2Cl_7^- \to Al_3Cl_{10}^-$$
(3)

These stages of the reaction are intricately controlled by the molar ratio of AlCl<sub>3</sub>-tourea. At a molar ratio of 1.1, the primary product is  $AlCl_4^-$ . As the molar ratio increases, the excess  $AlCl_3$  can react with the  $AlCl_4^-$  ions, resulting in the formation of  $Al_2Cl_7^-$ . This continues until the molar ratio reaches 1.5. Beyond this point, as the ratio increases further,  $Al_2Cl_7^-$  is consumed in subsequent interaction with  $AlCl_3$ , giving rise to the formation of  $Al_3Cl_{10}^-$  [50].

There was a suggestion that the reduction of  $2AlCl_2 \cdot (urea)_2^+$  species is responsible for the electrodeposition and stripping of aluminum ions, as indicated by the following electrochemical reaction (Equations (4) and (5)) [74].

$$2\text{AlCl}_2 \cdot (\text{urea})_2^+ + 3\text{e}^- \rightleftharpoons \text{Al} + \text{AlCl}_4^- + 4(\text{urea}) \tag{4}$$

$$4\mathrm{Al}_{2}\mathrm{Cl}_{7}^{-} + 3\mathrm{e}^{-} \rightleftharpoons \mathrm{Al} + 7\mathrm{Al}\mathrm{Cl}_{4}^{-} \tag{5}$$

Ng et al. led the development of an aluminum-based battery utilizing a urea-based ionic liquid analog as the electrolyte, an aluminum anode, and a graphite cathode [74]. Their work scrutinized the reaction mechanism of urea in conjunction with AlCl<sub>3</sub>. They revealed that the electrochemical activity only initiates in an acidic environment when the molar ratio follows the condition of AlCl<sub>3</sub> : urea > 1, emphasizing the absence of reactivity at a 1.0 molar ratio. In the acidic environment of AlCl<sub>3</sub>/urea, Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> was formed. Upon this observation, they proved that the primary driver of reactivity and reversible electrodeposition was the Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> species and not 2AlCl<sub>2</sub>·(urea)<sub>2</sub><sup>+</sup> alone [74]. They reported that 2AlCl<sub>2</sub>·(urea)<sub>2</sub><sup>+</sup> + 2Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> + 3e<sup>-</sup>  $\rightleftharpoons$  2Al + 4AlCl<sub>4</sub><sup>-</sup> + 2(urea) can explain why there is insignificant reactivity in a neutral environment (molar ratio = 1). That is because the absence of Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> leads to only AlCl<sub>4</sub><sup>-</sup> not 4AlCl<sub>4</sub><sup>-</sup>. Therefore, all the ionic species that arise from the electrolyte actively participate in the reactions. The electrolyte serves not only as a medium for ion transport but also as an active material in the electrochemical processes. Further, AlCl<sub>4</sub><sup>-</sup> can be reduced to Al and 4Cl<sup>-</sup> as follows (Equation (6)) [74]:

$$AlCl_{4}^{-} + 3e^{-} \rightleftharpoons Al + 4Cl^{-} \tag{6}$$

Finally, the overall reaction is then (Equation (7)).

$$AlCl_2 \cdot (urea)_2^+ + 2Al_2Cl_7^- + 3Cn \rightleftharpoons Al + 3Cn[AlCl_4] + AlCl_4^- + 2(urea)$$
(7)

# 2.3. ChCl-Urea

Choline chloride (ChCl) is a quaternary ammonium salt that has a melting point of 302 °C [76,77]. It can be combined with urea and exhibit good solvent properties such as a freezing point at 12 °C [78]. ChCl is a cost-effective, biodegradable, and nontoxic salt, approved without any time limitations under Council Directive 70/524/EEC8 for nutritional supplementation in all animal species [79]. ChCl-urea also has been known as Reline in many previous investigations [80–82].

#### 2.3.1. Performance

In a study conducted by Kao-ian et al., the performance of a Zn | MnO<sub>2</sub> cell battery was evaluated using an electrolyte of ChCl-urea-ZnCl<sub>2</sub>. The battery exhibited an open-circuit voltage of approximately 1.5 V and was discharged to a lower voltage of 0.4 V, then charged to a higher voltage of 1.9 V. The discharge capacity of the battery was 170 mA $\cdot$ h $\cdot$ g<sup>-1</sup> in the first cycle, decreasing gradually to 133, 114, 99, and 92 mA·h·g<sup>-1</sup> in the second, third, fourth, and fifth cycles, respectively. After ten cycles, the capacity stabilized at around  $90 \text{ mA} \cdot h \cdot g^{-1}$  [83]. In another experiment, ChCl-urea-CuCl was tested and it showed an increase from -0.293 V to 1.23 V (vs. Ag/AgCl) due to the Cu-to-Cu (I) transition. At 1.58 V, Cu (I) transforms to Cu (II), and then the mixture decomposes [84]. Additionally, increasing the temperature leads to an increase in reduction potential (shifting to a higher voltage value) [85]. Cao et al. investigated the electrolyte composition of ChCl-urea-CoCl<sub>2</sub> and reported that increasing the scan rate resulted in a rise in peak current and a shift of the reduction peak potential towards more negative values. They also observed quasireversible behavior for the Co (II) reduction process, which was attributed to the formation of an intermediate species that contributes to the overall electrochemical reaction. This intermediate species forms and decays on a comparable timescale to the electron transfer step, resulting in a larger-than-expected peak potential separation and a deviation from ideal reversible behavior [86]. Wang et al. prepared ChCl-urea-(ethyleneglycol)EG ZnO and chose ZnO to enhance the performance of a ChCl-urea DES. The problem was the high viscosity of the formed DES. However, the incorporation of chloride ions from NaCl into the ChCl-urea-EG-ZnO electrolyte showed high benefits for zinc electrodeposition, which enhances current efficiency by reducing power consumption and yielding smooth and dense zinc deposits [87]. This improvement was attributed to a combination of factors, including the catalytic effect of chloride ions on zinc electrodeposition, the reduction of overpotential, and the modification of the electrodeposition mechanism. While an increase in chloride ion concentration slightly diminishes the diffusion coefficient of Zn (II) ions, the overall benefits are higher than this minor drawback. The current density at a voltage around -0.8 V is around 5 mA·cm<sup>-2</sup> for no Cl<sup>-</sup> ions addition, while exceeding 20 mA·cm<sup>-2</sup> at 0.9 g·L<sup>-1</sup> with Cl<sup>-1</sup> ions [87].

#### 2.3.2. Mechanism

When ions form hydrogen bonds with their surroundings, they impede movement and restrict ionic conductivity [88]. However, water can enhance ionic mobility and conductivity, as the strong hydrogen bond facilitates ionic transportation [89]. For instance, the ionic conductivity of ChCl-Urea was around 1.07 mS·cm<sup>−1</sup> at 30 °C, which increased with the addition of water. Water increases the ionic conductivity from 15.78 mS·cm<sup>-1</sup> at 12.2 wt% of water to 54.80 mS·cm<sup>-1</sup> at 51.0 wt% of water [88]. While water addition initially leads to a decrease in ionic concentration due to dilution, it also exhibits two other effects, these being a reduction in viscosity and improved ionic mobility. The decrease in viscosity usually arises from the breakup of intermolecular interactions. This effect facilitates the movement of ions through the solution. In addition, water molecules act as hydrogen bond breakers that can liberate ions from their solvation shells and enhance their mobility. The optimal water content, corresponding to the point where the combined effects of reduced viscosity and increased ionic mobility outweigh the dilution effect, is reported to be around 58.1 wt% [88]. The interplay between viscosity reduction and ionic concentration dilution can determine the effect of water on the ionic conductivity of ChClurea. Based on the experimental findings reported by Zhu et al., it was observed that the viscosity reduction is the major impact when the water content is below 41.0 wt%. This leads to an improvement in the ionic conductivity of the ChCl-urea DES. This reduction in viscosity leads to an increase in ionic conductivity as it enhances the mobility of ions within the solution by weakening intermolecular interactions. In contrast, when the water content exceeds 51.0 wt%, the dilution effect becomes more dominant causing a decrease in ionic concentration. This decline in ionic concentration is more dominant than the viscosity

reduction, resulting in a decrease in overall ionic conductivity [88]. This observation means it is easy to tune the conductivity of a ChCl-urea DES through the addition of water, without incorporating other compounds. In a study conducted by Du et al., it was found that the combination of ChCl-urea and water led to a decrease in viscosity which, in turn, increased the ionic conductivity of the system. However, the low potential window of water also hurts the potential window [90]. By experimenting with different ratios of ChCl-urea and water, the researchers found that a combination of ChCl-urea at a eutectic point with 6% water resulted in a remarkable 91% reduction in viscosity, which had a direct and positive impact on the overall conductivity of the system, increasing it by around 75% [90]. Two studies conducted by Zhu et al. and Li et al. [88,91]. reported that a ChCl – urea DES has an electrochemical window of 1.8 V which is higher than that of pure water at 1.23 V. Meanwhile, Li et al. synthesized Au-ChCl-urea, where ChCl works as a hydrogen bond acceptor and urea is a hydrogen bond donor. They reported that the electrolyte at the electrodeposition has good corrosion resistance, which increases with the addition of  $Co^{2+}$  [91]. The interaction between urea and ChCl was based on hydrogen bonding as shown in Figure 8, which was confirmed by infrared spectroscopy. This interaction was observed by changes in the vibrational modes of the -NH<sub>2</sub> groups. The bands corresponding to the asymmetric and symmetric stretching modes of -NH<sub>2</sub> shift from 3448 and 3359  $\text{cm}^{-1}$  to 3421 and 3349  $\text{cm}^{-1}$ , respectively [90].



Figure 8. The possible bonding configurations between urea, and ChCl.

When water was introduced into this system, it had a direct effect on the dissociation of ChCl with Ch<sup>+</sup> cations and Cl<sup>-</sup> anions. Water molecules can form hydrogen bonds with urea via NH-OH bonds. This interaction occurs instead of ChCl or by replacing the ChCl position with urea, leading to a higher degree of ionic dissolution for ChCl. Therefore, the presence of water in a ChCl-urea DES means that water forms hydrogen bonds with urea, which enhances the ionic dissociation of ChCl, as shown in Figure 9 [90].

A system comprised of Zn/MnO<sub>2</sub> for the anode/cathode with an electrolyte of ChClurea-ZnCl<sub>2</sub> has been studied. This system shows intercalation and formation of Zn<sub>x</sub>MnO<sub>2</sub> in the fully charged battery. That can occur through various stages, where the first stage is the oxidation of Zn metal. The ions of Zn<sup>2+</sup> can coordinate with Cl<sup>-</sup> from the electrolyte to form [ZnCl<sub>4</sub>]<sup>2-</sup>. This anion works as a charge carrier for carrying Zn<sup>2+</sup> ions to MnO<sub>2</sub> where reduction occurs. That means the formation of Zn<sup>2+</sup> by separating from Cl<sup>-</sup> and then intercalating in MnO<sub>2</sub>. The following equations describe the electrochemical reaction (Equations (8)–(10)) [83].

Anode reaction at discharge:

$$xZn + 4xCl^{-} \rightleftharpoons x[ZnCl_{4}]^{2-} + 2xe^{-}$$
(8)

Cathode reaction at discharge:

$$x[ZnCl_4]^{2-} + MnO_2 + 2xe^- \rightleftharpoons Zn_xMnO_2 + 4xCl^-$$
(9)

Total reaction:

$$xZn + MnO_2 \rightleftharpoons Zn_xMnO_2 \tag{10}$$

Theoretical studies have investigated the local environment of ChCl-urea-LiCl and found that  $\text{Li}^+$  ions in the electrolyte coordinated with  $\text{Cl}^-$  anions, forming  $\text{LiCl}_3^{2-}$  units [92]. Each lithium cation in the electrolyte is closely surrounded by three chloride anions, forming a flat triangular structure which is the  $\text{LiCl}_3^{2-}$  unit. These  $\text{LiCl}_3^{2-}$  units are surrounded by urea which forms an intricate network of hydrogen bonds [92]. The interaction between lithium and urea or choline is indirect and mediated by the chloride due to these species being in the second coordination shell of the lithium, as shown in Figure 10 [92].



**Figure 9.** The effect of water in the formation of hydrogen bonds with urea and increasing dissociation of ChCl ions. The dashed blue and green dot lines represent atomic bonding.



**Figure 10.**  $\text{LiCl}_3^{2-}$  which is formed from Li<sup>+</sup> cations and Cl<sup>-</sup> anions, and Cl<sup>-</sup> are in the first shell, while choline and urea are in the second shell. Urea and choline interact with LiCl<sub>3</sub> anions via hydrogen bonds.

#### 2.4. [C8mim] Br-Urea

In a study conducted by Nada et al., the influence of urea on viscosity was investigated by preparing an ionic liquid (IL) containing aqueous 1-octyl-3-methylimidazolium bromide [C8mim] Br-Urea. The findings revealed that the addition of urea resulted in a rapid decrease in viscosity with an increase in the concentration of urea [93]. This can be attributed to the fact that urea works as a strong structure-breaker, forming urea–water complexes by making hydrogen bonds with the icebergs around the hydrophobic long tail of the [C8mim] cation. As a result, the hydrogen bonds between water and urea weaken the hydrophobic interactions between the [C8mim] cations causing the ionic liquid structure to become less rigid and the mixture to flow more easily [93]. Additionally, the presence of urea increased the relative permittivity, consequently weakening the Coulombic interaction between the [C8mim]<sup>+</sup> cations and Br<sup>-</sup> anions. Therefore, the hydrophobic bonding is weakened leading to a reduction in viscosity [93].

#### 2.5. Al (TfO)<sub>3</sub>-Urea

Aluminum trifluoromethane sulfonate (Al  $(TfO)_3$ ) has been tested as a replacement for AlCl<sub>3</sub>, which has been associated with safety concerns due to its sensitivity to air and moisture [94]. However, the binary composition of urea/N-methyl-acetamide (NMA) has poor conductivity around  $10^{-6}$  mS·cm<sup>-1</sup>. The addition of Al(TfO)<sub>3</sub>, on the other hand, improved conductivity with values reaching as high as  $2.5 \text{ mS} \cdot \text{cm}^{-1}$  [94]. The effect of solvents on the ionic conductivity of the system has been investigated, with a focus on the relationship between the dielectric constant and ionic conductivity. Mandai et al. observed that solvents with high dielectric constants effectively weaken the strong electric field generated by charged species, leading to a reduction in ion-ion interactions and the dissociation of salts into their constituent ions [94]. This is because when a salt is dissolved in a solvent, the ions in the salt become surrounded by solvent molecules, which interact with the ions through electrostatic forces [95]. Solvents with high dielectric constants can weaken the electrostatic forces between ions by polarizing the solvent molecules, leading to the development of partial positive and negative charges on the ends of the molecules [96]. These partial charges on the solvent molecules can interact with ions, therefore leading to a reduction in the electrostatic forces between the ions, as illustrated in Figure 11 [94–96]. Hence, solvents with high dielectric constants are more effective at dissociating salts into their constituent ions.

Mandai et al. synthesized the electrolyte which contains Al[TfO]<sub>3</sub>, alongside urea and NMA. In their work, they observed that the molar fraction of NMA to urea, particularly at a molar fraction of 0.760 and molar ratio of 1:15:4 (5:75:4) for Al: NMA: urea exhibited the highest ionic conductivity [94]. This observation confirms the role of urea in enhancing the dissociation of Al [TfO]<sub>3</sub> in electrolytes when it reaches specific molar fractions. Peters et al. studied the dissociation mechanism, focusing on the 1:4 ratio of Al [TfO]<sub>3</sub> to urea, and attempted to understand why it resulted in the highest ionic conductivity. Their investigation revealed that the bidentate structure formed between urea and Al [TfO]<sub>3</sub> played a significant role. Before adding urea, the dissociation of Al [TfO]<sub>3</sub> leads to the formation of [Al (TfO)-solvent] + species. Urea helps oxygen atoms in the TfO anion to interact with the hydrogen bonds. This interaction helps to dissociate the [Al (TfO)<sub>2</sub>solvent] + species into [AlTfO-urea<sub>2</sub>-solventx]. The [AlTfO-urea<sub>2</sub>-solvent<sub>x</sub>]<sup>2+</sup> complex is more soluble in the solvent than the [Al (TfO)<sub>2</sub>-solvent]<sup>+</sup> species and this leads to an increase in the ionic conductivity of the solution [37]. These results indicate the ability to create a high energy density in electrochemical devices, specifically in batteries. This DES has not been tested in a real battery system; however, a similar system has been tested by Lin et al., this being urea–1-methylimidazolium trifluoromethylsulfonate (urea-MIMTfO). They reported the high electrochemical window of urea-MIMTfO around 3.5 V. Their investigations involved testing a graphite electrode incorporating Bi<sub>2</sub>O<sub>3</sub>, revealing a comparatively low window for this system. These outcomes suggest the potential efficacy of the system in facilitating the reduction of  $Bi_2O_3$  in a simplified, single-step process [97].



**Figure 11.** The effect of a high dielectric solvent on the interaction between ions and the effect of polarization leading to weak ion–ion interaction. On the **left** side, the ions have strong interactions with each other, as shown by their opposite alignment. The positive ions are blue, and the negative ions are white. Then, the high dielectric solvent is used for solvation. On the **right** side, the ions have weak interactions with each other. This is because the high dielectric solvent molecules surround and separate the ions, as shown by the colorful spheres. The solvent molecules have partial charges, as illustrated by the plus ( $\delta$ +) and minus ( $\delta$ -) symbols, due to the polarization effect. The weak interaction and the polarization effect led to improved dissociation and high ionic conductivity. The atoms are arbitrary in this illustration, to demonstrate the idea.

# 2.6. $XClO_4$ -Urea (Where X = Na, and Li)

# 2.6.1. Performance

The electrochemical stability windows of the LiClO<sub>4</sub>-urea-MgCl<sub>2</sub>-water electrolyte reach 2.92 V, as highlighted in Figure 12. In addition, there is a positive correlation between the urea ratio and the ionic conductivity. Further, the increase in  $H_2O$  from 4 to 6 wt.% results in a rise in ionic conductivity from 0.97 to 4.33 mS⋅cm<sup>-1</sup> but a decrease in ESW from 3.29 to 2.72 V [98]. Therefore, the water content is significant for the properties of the electrolyte. Moreover, an electrolyte of LiClO<sub>4</sub>-urea-water was incorporated in a cell containing  $Li_4Ti_5O_{12}$  and  $LiMn_2O_4$  with a mass ratio of 0.7:1 and an Al current collector. This cell exhibited a discharge voltage plateau at 2.2V and approximately 125 mA·h·g<sup>-1</sup> and 104 mA $\cdot$ h $\cdot$ g<sup>-1</sup>, respectively, in the initial charging/discharging cycle [99]. Additionally, the initial Coulombic efficiency was around 83%. The discharging capacity demonstrated a value of about 148 mA $\cdot$ h·g<sup>-1</sup> and excellent cycling stability, displaying a capacity decay rate per cycle of 0.011% at 10 C for 1000 cycles. After resting at an open circuit for 150 h following a full charge, the battery maintains about 86% of its initial capacity, demonstrating a slow rate of self-discharge [99]. Hou et al. used LiClO<sub>4</sub>-H<sub>2</sub>O-urea electrolytes with  $LiMn_2O_4$  and  $Mo_6S_8$  electrodes. They showed that the battery maintains a high capacity of 75% after 500 charging and discharging cycles at 0.1 C, with an average Coulombic efficiency of 99.5% [53]. The system can store a high amount of energy, even when charged and discharged quickly. At a rate of 0.1 C, it can store 45 mA $\cdot$ h $\cdot$ g<sup>-1</sup> and at a rate of 30 C, it can store 28 mA $\cdot$ h·g<sup>-1</sup>. This result implies that the battery is suitable for tasks demanding a combination of high power and high energy. Moreover, the battery can maintain its high performance over a long time. After 2000 cycles at a high rate of 10 C, it can still store 86% of its original energy [53]. This is due to the high ionic conductivity and small interfacial activation energy of the aqueous electrolyte [53]. In addition, capacity was maintained after 100 cycles with an average Coulombic efficiency of 98.9% at 0.5 C. Even at a rate of 20 C charged with LiClO<sub>4</sub>-H<sub>2</sub>O-urea, the cell retains a discharge capacity of 20 mA $\cdot$ h·g<sup>-1</sup> (based

on the combined mass of anode and cathode active materials). Furthermore, after 500 cycles at 10 C, the battery retains 85% of its capacity [53]. They also reported that usage of NaClO<sub>4</sub>-H<sub>2</sub>O-urea allows the utilization of a high-potential symmetrical sodium-ion battery using Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> as both the cathode and anode materials. The usage of a NaClO<sub>4</sub>-urea DES exhibits an energy efficiency of 80%. Further, at a rate of 0.1 C, the cell demonstrates a stable voltage plateau at 1.7 V, delivering a discharge capacity of 37 mA·h·g<sup>-1</sup>. In addition, high cycling stability is observed with around 80% capacity retention over 200 cycles. Furthermore, the battery demonstrated substantial capacities at varying rates: 37, 32, 30, 25, 21, and 18 mA·h·g<sup>-1</sup> at 0.1, 0.5, 1, 5, 10, and 20 C, respectively. Even at 5 C, it retains 72% of its initial capacity after 1000 cycles, maintaining a high CE close to 100% [53]. These results suggest that the formation of a stable SEI layer through urea coordination with Na<sup>+</sup> is significant for achieving consistent and stable cycling performance [53].



Figure 12. Highlighting the promising ability of DESs based on urea in batteries.

# 2.6.2. Mechanism

In dilute aqueous solutions, Li<sup>+</sup> cations interact with water molecules, forming clusters known as  $[Li(H_2O)_4]^+$  [99]. In "water-in-salt" electrolytes, the high concentration limits the formation of primary hydration shells such [Li (H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> due to insufficient water molecules. Consequently, there is a deficiency of accessible water as a solvent, intensifying interactions between ions. This scenario leads to reduced ionic conductivity and heightened viscosity. However, the interaction between Li<sup>+</sup> and water molecules cause a change in the O–H bond within the water molecule due to charge transfer through the Li–OH<sub>2</sub> bond. Therefore, deprotonation might occur because of the weak bond between O and H. Consequently, this leads to the generation of acidic solutions. As the electrolyte concentration rises, the pH levels of the solutions decrease, indicating a higher degree of acidity. At increased concentrations of LiClO<sub>4</sub>, there is a heightened probability of the hydrogen evolution reaction (HER,  $H_2O + e^- = 1/2 H_2 + OH^-$ ) occurring during battery operation, as demonstrated in Figure 13 [53]. Urea can increase the pH values of the electrolyte solutions, making them more neutral. This shift implies that urea molecules displaced some of the water molecules in the primary solvation shell around Li<sup>+</sup> ions. As a result, more neutral solutions can effectively inhibit hydrolysis [53]. Consequently, Zhang et al. prepared an electrolyte based on DES of LiClO<sub>4</sub>-urea and they reported that urea molecules can provide dual traits by exhibiting excellent coordination with Li<sup>+</sup> ions and creating hydrogen bonds with water [99]. The major advantage of lithium salt anions is their ability to coordinate strongly, forming strong interactions with organic compounds. This facilitates the stability of the [Li ( $H_2O$ ) x (organic)y]<sup>+</sup>-anion, in addition to its existence in

the liquid phase even at room temperature. The selection of  $ClO_4^-$  as the anion component was based on its strong interactions with organic materials and its cost-effectiveness [53]. Table 1 provides a summary of various electrolyte types based on urea along with their key parameters relevant to complete battery systems. Table 1 also shows the change in specific capacity with the changes in current rate and number of cycles which reaches 1000 cycles in batteries. Moreover, Table 2 shows different electrolyte systems with reduction and oxidation information. The redox current and oxidation current are collected and listed in the table with the potential window which is estimated from the difference between oxidation and reduction voltage.



**Figure 13.** When the concentration of the electrolyte in water increases, the electrolyte pH values become lower, creating a more acidic environment. This acid environment favors the HER process, which produces  $H_2$  gas. A charge transfer occurs between Li-OH<sub>2</sub> leading to a weakening O-H bond in water. Therefore, protonation occurs and, in the end,  $H_2$  is released. With the addition of urea to the electrolyte, the pH values can be increased, resulting in more neutral solutions that inhibit the HER. This means that urea can reduce water splitting and the release of  $H_2$  gas, which can lower the efficiency and safety of the battery. Therefore, urea can enhance the stability window of the electrolyte, allowing it to operate at higher voltages without damaging the battery.

**Table 1.** Numerous electrolytes based on urea and their related parameters in full battery. The signs of \* and \*\* mean  $mA \cdot g^{-1}$  and C, respectively.

Anode//Cathode	Electrolyte	Specific Capacity (m·A·h·g <sup>-1</sup> )	Cycle Number	Discharge Voltage (V)	Charge Voltage (V)	Current Rate (* mA·g <sup>-1</sup> )/ (** C)	Coulombic Efficiency (%)	Ref.
Al//natural graphite	AlCl <sub>3</sub> /Urea	50	100	1.0	2.1	600 *	99	- - - [74] -
		48	500	1.0	2.1	600 *	98	
		47	1000	1.0	2.1	600 *	95	
		91	10	0.5	2.2	100 *	99	
		89	50	0.5	2.2	100 *	99	
		87	1000	0.5	2.2	100 *	-	
NVP	- Na-H2O-urea-DMF	110	1	0	0.9	0.2 **	-	- - - - -
		138	1	-1.1	-0.2	0.2 **	-	
		98	2	0	0.9	0.2 **	-	
		125	2	-1.1	-0.2	0.2 **	-	
NVP//NTP		80	100	0.6	1.6	0.2 **	-	
		65	1	0.6	1.6	1 **	-	
		55	1	0.6	1.6	5 **	-	
		60	100	0.6	1.6	10 **	99	

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# Table 1. Cont.

Anode//Cathode	Electrolyte	Specific Capacity (m·A·h·g <sup>-1</sup> )	Cycle Number	Discharge Voltage (V)	Charge Voltage (V)	Current Rate (* mA·g <sup>-1</sup> )/ (** C)	Coulombic Efficiency (%)	Ref.	
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> (LTO)// LiMn <sub>2</sub> O <sub>4</sub> (LMO)		160	1	1	3.1	1 **	-	- [66]	
	LiTFSI – H <sub>2</sub> O – PEG – urea	95	50	1	3.1	1 **	92		
		60	100	1	3.1	1 **	92	- [00]	
		40	200	1	3.1	1 **	92	-	
		70	18	1.5	2.2	2 **	-	- - - - [67] -	
	LZ-DES/2H <sub>2</sub> O	80	25	1.5	2.2	1 **	-		
Zn//LMO		90	10	1.5	2.2	0.5 **	-		
		120	30	1.5	2.2	0.06 **	-		
		35	1	1.5	2.2	2 **	-		
		45	1	1.5	2.2	1 **	-		
	LZ-DES	55	1	1.5	2.2	0.5 **	-		
		80	1	1.5	2.2	0.06 **	-		
		125	1	1.1	2.5	0.5 **	-	- - - - - - -	
		100	10	1.1	2.5	0.5 **	-		
		95	50	1.1	2.5	0.5 **	-		
		90	100	1.1	2.5	0.5 **	-		
LTO//LMO	LiClO <sub>4</sub> -urea	95	1	1.5	2.5	1 **	-		
		65	1	1.1	2.5	10 **	99		
		55	1	1.1	2.5	20 **	-		
		62	500	1.1	2.5	10 **	99		
		60	1000	1.1	2.5	10 **	99		
		50	1	0.8	2.2	0.1 **	98	- - - [53] -	
		40	100	0.8	2.2	0.1 **	98		
	LiClO <sub>4</sub> -H <sub>2</sub> O-urea	37	500	0.8	2.2	0.1 **	98		
M0658//LMO		40	30	0.8	2.2	1 **	98		
		35	50	0.8	2.2	10 **	98		
		30	70	0.8	2.2	30 **	98		
		35	200	-	-	0.1 **	99		
		35	100					-	
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> //Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>		20	1000	-	-	5 **	99	- [53] -	
		25	100						
	ChCl-urea-ZnCl <sub>2</sub>	90	1	0.4	1.9	50 *	-	- - - [83]	
		70	1	0.4	1.9	100 *	-		
		55	1	0.4	1.9	200 *	-		
$Zn//MnO_2$		200	1	-	-	50 *	85		
		80	50	-	-	50 *	85	-	
		60	50	-	-	100 *	45	-	
		40	140	-	-	100 *	35		
PCDI-rGO//LMO	LiClO4-urea-MgCl2-water	45		0	2.5	30 *	-	- - - [98] - -	
		44	1			50 *	-		
		43	1			100 *	-		
		32	1			500 *	-		
		25	1			1000 *	-		
		17	50	-	-	200 *	95		
		14	100			200 *	95		
		10	200			200 *	95		

Composition	Scan Rate (mV·s <sup>−1</sup> )	E Oxidation (V)	E Reduction (V)	Jox (mA·cm <sup>-2</sup> )	Jred (mA·cm <sup>−2</sup> )	Eox – Ered	Reference	Refs.
KCL-FeCl <sub>3</sub>	20	0.8	0.3	20	-60	0.5		[88]
ChCl-urea-Zn (OTf)2	20	-0.6	-1.3	-30	8	0.7		. <u> </u>
ChCl-urea-ZnCl <sub>2</sub>	20	-0.7	-1.6	-8	8	0.9		
ChCl-urea-ZnSO <sub>4</sub>	20	-0.7	-1.6	-30	11	0.9	Ag/AgCl	[100]
ChCl-urea-Zn (OTf) <sub>2</sub>	100	-0.4	-1.5	-10	15	1.1		
ChCl-urea-ZnCl <sub>2</sub>	100	-0.4	-1.8	-20	15	1.4		
ChCl-urea-ZnSO <sub>4</sub>	100	-0.6	-1.7	-30	25	1.1		
ChCl-urea-CoCl <sub>2</sub> —	20	-0.1	-0.9	-5	5	0.8	Ag wire	[101]
	100	0	-1.1	-10	8	1.1		
ChCl-urea-H <sub>2</sub> O	20	0.7	0.5	20	-60	0.2		[88]
ChCl-urea-H <sub>2</sub> O-FeCl <sub>3</sub>	100	0.8	0.3	40	-100	0.5		
ChCl-urea	20	1.3	-1	-	-	2.3		[85]
ChCl-urea-EG-ZnO –	10	-0.9	-1.4	10	-5	0.5	Ag/AgCl	[87]
	90	-0.7	-1.6	25	-15	0.9		[]
Urea-MIMTfO	50	2.5	-1.0	-	-	3.5		
Urea-MIMTfO + graphite electrode filled with Bi <sub>2</sub> O <sub>3</sub>	50	0	-0.25	3	-4	0.25	Ag	[97]
LiClO <sub>4</sub> -urea-water	0.5	1.5	-1.5	-	-	3	SHE	[99]

Table 2. Various electrolytes and their oxidation and reduction voltage in addition to their window.

#### 3. Preparation

A study conducted by Zhao et al. involved the mixing of urea, LiTFSI, and ZnTFSI [67]. The temperature was raised to 60 °C to improve wettability, and a specific ratio of LiTFSI/urea of 1.3 and LiTFSI/Zn(TFSI)<sub>2</sub> of 20 was used. The mixture was magnetically stirred overnight at 90 °C. To add H<sub>2</sub>O, LZ-DES was blended with water at a molar ratio (n) for H<sub>2</sub>O/Li, shaken thoroughly, and left to stand for about 24 h. A blend of PAN-DMF-LiTSI-urea was prepared by adding 1g of PAN and 0.667 g of LiTFSI to DMF and stirring vigorously in a 10 mL container for 2 h at 60 °C. Then, 0.4186 g of urea was added at a 1:3 ratio with LiTFSI and continuously stirred at 60 °C for several hours to obtain a homogeneous mixture. The mixture was cast into a Petri dish and desiccated for 2 days [69]. Li et al. produced AlCl<sub>3</sub>-urea by slowly mixing both compounds in a sealed vessel for different molar ratios of 1.2, 1.3, and 1.5 at room temperature and under a high-purity argon atmosphere in a glove box while maintaining the content of oxygen and water below 0.1 ppm [75]. The reaction began spontaneously without raising the temperature, and the solid mixture was allowed to cool gradually to room temperature [75]. ChCl-urea was obtained by mixing in a ratio of 1:2 and heating the mixture at 80 °C until it became a homogeneous liquid. The mixture was sealed with a preservative film and cooled down to room temperature [88]. For ChCl-urea-water, the same process was followed, but the water was added in the final step in the desired amount [88]. Wong et al. prepared a ChCl-urea DES at a ratio of 1:2. The chemicals were accurately weighed and combined in a bottle, which was continuously stirred on a magnetic hot plate set to 120 °C for four hours [102]. The bottle was then purged with inert nitrogen for 15 min to remove any moisture. The mixture was finally sealed with parafilm to maintain an anhydrous environment. To obtain ChCl-urea-CoCl2 DES, ChCl was dried under vacuum at 80 °C for 24 h. Appropriate amounts of ChCl and urea were weighed according to a molar ratio of 1:2 and mixed in a round-bottomed flask. The mixture was stirred at 80 °C until a colorless and transparent liquid was formed. CoCl<sub>2</sub> was added directly to the DES as the cobalt source to achieve the desired concentration of ChCl-urea-CoCl<sub>2</sub> DES. Bucko et al. synthesized ChCl and urea DES by combining and heating them to 60 °C in a sealed beaker [103]. The mixture was continuously stirred using a PTFE-coated magnetic stirrer until a homogeneous, clear liquid phase was formed. To minimize the water content, the initial precursors were dried in a vacuum dryer for 2 h. The prepared DES was then further dried in a vacuum chamber at 80 °C for 3 h under a pressure below 10 bar. The ChCl-urea-EG DES was prepared by combining ChCl, urea,

and EG in a 2:4:1 molar ratio. The mixture was stirred at 80 °C until a uniform, colorless liquid was obtained. Then, 30 g of ZnO was gradually added to 1 L of ChCl-urea-EG DES and stirred continuously at 70 °C until the ZnO was completely dissolved. The resulting solution was a ChCl-urea-EG-ZnO DES. According to the method previously reported by Ru et al., a ChCl-urea DES was prepared. To obtain the ChCl-urea-PbO DES, appropriate amounts of dry ChCl and urea were mixed with PbO in a dry argon atmosphere. The mixture was then heated in an oil bath, and after 4 h at 80 °C, complete dissolution of PbO was achieved [26]. Li et al. prepared a hard gold-ChCl-urea DES by mixing a molar ratio of 1:2 for ChCl/urea in a vacuum at 80 °C and leaving it for 24 h. Then, the mixture was used as a solvent for solving 4 g/L of HAuCl<sub>4</sub>·4H<sub>2</sub>O with a complexing agent of DMH (50 g/L) [91]. Further, Du et al. dried ChCl and urea before they were used in a vacuum oven at 353 K. Then, a 1:2 ChCl/urea ratio was mixed in a beaker with manual stirring by a glass rod for 30 seconds (open air) to minimize the moisture in the mixture. Then, continuous stirring was carried out in a vacuum oven for around 30 min at a temperature of 353 K [90]. Zhu et al. mixed urea and ChCl on a magnetic stirrer at 343.15–353.15 K for 1–2 h and dried the mixture after that in a vacuum box for 24 h at 343.15 K [104]. Peters et al. used formamide, NMA, acetonitrile, and propylene carbonate as solvents, along with urea, and acetamide as hydrogen bond donors (HBDs). Before mixing, all the components were dried to reduce the water content at 0.2 mbar and 80 °C. The solvents were mixed slowly with HBDs and Al(TfO)<sub>3</sub> was added with a ratio of 4:1 for urea/Al(TfO)<sub>3</sub> [37]. Mixing and storage were performed in an argon environment in a glove box. The exact mol% are 75:5:20 for NMA, Al(TfO)<sub>3</sub>, and urea, respectively [37]. The formation of a DES involves the combination of lithium salt  $LiClO_4 \cdot 3H_2O$  and urea in a 1:2 mol ratio. To achieve this, 16.04 g of LiClO<sub>4</sub>·3H<sub>2</sub>O and 12 g of urea are mixed in an agate mortar until a clear solution is obtained [99]. Hou et al. prepared NaClO<sub>4</sub>-H<sub>2</sub>O-urea and LiClO<sub>4</sub>-H<sub>2</sub>O-urea using ratios of 1:3:2 [53]. On the other hand, Tsai et al. used an argon gas-filled glove box to prevent moisture contamination during the preparation of the dual cations DES. Initially, urea, anhydrous magnesium chloride (MgCl<sub>2</sub>), and LiClO<sub>4</sub> were combined in a molar ratio of 100 20: 1 (urea:  $MgCl_2$ : LiClO<sub>4</sub>). A specific amount of water was then carefully added to these precursors, and the resulting mixture was stirred at 80 °C for 2 h to ensure complete mixing and formation of LiClO<sub>4</sub>-urea-MgCl<sub>2</sub>-water [98]. To prepare the urea-based DES, urea was used as the HBD and mixed with the HBA compound. Depending on the desired moisture, the HBD and HBA can be dried or not. The precursors are then mixed and heated to dissolve in water with continuous stirring until the DES compound is formed. Finally, the urea-based DES is dried to minimize the water content or moisture from the air. These synthesis steps are illustrated in Figure 14.



Figure 14. A schematic diagram shows the preparation steps for urea-based DES.

#### 4. Summary and Future Perspective

Urea-based deep eutectic solvents (DESs) are a promising alternative to conventional electrolytes for battery applications, as they offer several advantages such as low cost, high safety, and enhanced electrochemical performance. This article has reviewed the recent advances of urea-based DESs, focusing on their composition, mechanism, and performance. The discussed composition according to the order of reviewing: Li and/or ZnTFSI-Urea, AlCl<sub>3</sub>-Urea, ChCl-Urea, [C8mim] Br-Urea, Al(TfO)<sub>3</sub>-Urea, and Na or LiClO<sub>4</sub>-urea. The main points illustrating that urea-based DESs are promising can be summarized as:

- Urea is a well-known, widely used, and inexpensive compound that has several advantages including non-toxicity, low flammability, and high thermal stability, making it safer and more environmentally friendly than conventional electrolytes;
- Urea-based DESs have a relatively high electrochemical stability window (ESW) and ionic conductivity, which are crucial for the performance and efficiency of batteries. In addition, Urea-based DESs can support relatively high discharging voltage, high Coulombic efficiency, and high specific capacity of various battery types, such as lithium-ion, zinc-ion, or aluminum-ion batteries.

However, despite these remarkable qualities, the ideal composition of DESs optimized for specific battery types and electrodes remains elusive. This challenge arises due to the limited volume of research dedicated to urea-based DESs. Consequently, there exists a pressing need for further comprehensive studies within this domain to explore a wide spectrum of compositions and the addition of hydrogen bond acceptors (HBAs) in conjunction with urea. These additional investigations will significantly contribute to the refinement and understanding of urea-based DESs, facilitating their potential deployment in various battery technologies.

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