

Chapter

Investigation of Boron-Based Ionic Liquids for Energy Applications

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Abstract

As a result of its electron-deficient nature, boron is utilized as the building block of ionic liquids (ILs) in energy applications (EAs) by composing a number of anions, cations, and negatively charged clusters chemically, electrochemically, and thermally. Anionic boron clusters, for example, feature distinctive polycentric bonding and are an important component of low-viscosity room temperature ILs (RTILs) utilized in electrochemical devices. In this context, recent breakthroughs in the synthesis of boron-containing ILs and various materials derived from them provide a powerful opportunity for further investigation in the field of energy research to improve and develop the properties of these boron-based ILs (BBILs). This review has provided a brief summary of boron atom or molecule-based ILs with unique features that make them ideal candidates for particular EAs. This perspective can guide further research and development of the unique properties of green and halogen-free BBILs.

Keywords: boron, ionic liquids, energy applications

1. Introduction

With the increasing utilization of solar and wind energy worldwide, the intermittent nature of these resources restricts the sustainability of the energy supply. Due to environmental concerns regarding air quality, reducing the impact of fossil fuel use has required the development of new energy technologies for alternative energy options. In addition, minimizing the effect of fossil fuel consumption owing to environmental concerns regarding air quality issues mandates the development of new technologies for alternative energy solutions. There is great potential for discovering new energetic materials and employing them in applications in all of these energy technology development initiatives. BBILs are a novel class of energetic materials with a wide variety of characteristics that may be tailored to specific applications in the energy area [1].

Paul Walden first discovered ILs in 1914 and determined that the ethylammonium nitrate salt had a low melting point of 13°C [2–4]. In 1992, Wilkes and Zaworotko created air and water-stable ILs, known as the second generation, utilizing 1ethyl-3-methylimidazolium cation ([EMIM]⁺) and tetrafluoroborate ([BF₄]⁻) or hexafluorophosphate anion ([PF₆]⁻). They discovered that whereas these ILs are normally water insensitive, prolonged exposure to moisture produces alterations in their

characteristics [4]. The continuous fascination with ILs arises from their excellent features in future research and potential applications [1, 5, 7].

ILs are a novel family of solvents with melting temperatures less than 100°C, consisting of a combination of a bulky cation and an inorganic or organic anion [1, 2, 4–10]. An advantage of low melting point solvents is that they have negligible vapor pressures.

As a result, unlike liquids, ILs do not evaporate under standard conditions. ILs are salts with high thermal stability (most ILs are stable up to about 300–400°C) [9], chemical stability, nonflammability, a broad electrochemical window (2–6 V) [10, 11], and high electrical conductivity (1.3–8.5 mS cm⁻¹) [12]. ILs are also less hazardous and effective solvents for both organic and inorganic compounds.

ILs are prominent solvents in electrochemistry due to the constituent anions being oxidized at sufficiently large potentials and organic cations being reduced at low potentials. ILs are generally aprotic, so problems with hydrogen ions that occur in protic solvents can be avoided. In recent years, ILs have great attention as an environmentally friendly (“greenness”) liquid that is a candidate to replace commonly used, solvent-based, volatile, and flammable electrolytes that tend to be corrosive [6]. When creating ILs for applications, commonly at least one ion is weakly coordinated; either the cation or the anion is weakly coordinated; and in some ILs, both the ions are weakly coordinated. Solvent properties of ILs vary depending on the nature of the ions in their structure; anions with high charge density and organic cations with short alkyl chains stabilize more polar molecules [13, 14]. ILs have advantages as well as disadvantages. **Table 1** shows the summary of the physicochemical properties of ILs. The main disadvantages are high density, high viscosity, and low conductivity.

ILs are liquids showing high ion density. The density of ILs typically ranges between 1.2 and 1.5 g cm⁻³, while certain ILs, such as those based on the dicyanamide anion, has a density of less than 1 g cm⁻³. Because viscosity is important in conductivity and diffusion, conductivity decreases as viscosity increases. ILs have a significantly higher viscosity (30–50 cP) than water (H₂O = 0.89 cP at 25°C) [15].

(30–50 cP) than water (H₂O = 0.89 cP at 25°C) [15]. The conductivities at room temperature for ILs are in the wide range of from 0.1 to 18 mS cm⁻¹, but even at the highest conductivity, they are much lower compared to conventional aqueous

| Properties | Values | Advantages | Disadvantages |
|-------------------|--|---|---|
| Low melting point | < 100°C | Liquid at ambient temperature Wide temperature interval for applications | High viscosity |
| Nonflammability | | Non-volatility Thermal stability Flame retardancy | Less toxic |
| Composed by ions | Cation and an inorganic or organic anion | Unlimited combinations possible A wide electrochemical window High ion conductivity Designable/Tunable | High ion density Low conductivity (compared to conventional aqueous electrolyte solutions) |

Table 1. Summary of the physicochemical properties of ILs (adapted from Refs [13–16]).

electrolyte solutions. Dilution of pure ILs with molecular fluids provides an increase in the conductivity of the medium. For example, pure [EMIM][BF₄⁻] has a specific conductivity of 14 mS cm⁻¹, while 2 moles of dm⁻³ solution in acetonitrile shows a conductivity of 47 mS cm⁻¹. In this context, it can be said that diluting pure ILs with a molecular diluent also reduces the viscosity of the mixture [16].

At room temperature or below, RTILs are typically composed of organic or inorganic anions with weak basic properties and organic cations with low molecular symmetry [11, 13, 16]. It is a liquid group that offers more advantages over organic electrolyte solutions, including low vapor pressure, nonflammability, electrochemical and chemical stability, and high ionic conductivity. RTILs are currently of great interest in both academia and industry. To date, thousands of RTILs with unique physical features and functionalities have been created for use in energy applications. Some special boron-based RTILs have been investigated in EAs such as electrolyte materials in lithium batteries, fuel cells, and solar cells, as they exhibit ionic conductivity values of more than 10–2 S cm⁻¹ at room temperature [11, 13, 16–22].

This review emphasizes on the highlights of boron's ability to facilitate the development of BBILs in EAs such as an atom and small molecule activation toward hyperbolic fuel additive, dye synthesized solar cells (DSSCs), advanced secondary batteries, hydrogen production and storage, electrolyte materials for electroreduction, and CO₂ capture.

The first chapter emphasizes the role of boron cations and anions in the production of BBILs designed for usage in various EAs. Following that, examples of boron cations and anions found in the literature are given. Then, BBILs utilized in EA were thoroughly explored. Before detailing the selected examples of each area, a brief introduction was made and then closed with a brief perspective. Ultimately, this review highlights BBILs with less toxic and less expensive starting materials for future energy demands, as well as the possibility for ILs to play an essential part in meeting some of the future difficulties.

1.1 Boron's role in ILs

With the increasing demand for renewable energy and green chemistry, boron has been playing a key role in energy-related research, from synthesizing energy-rich molecules to energy storage to converting electrical energy to light. In this regard, specifically constructed ILs have attracted the attention of researchers by including a variety of tribologically active elements such as sulfur, nitrogen, phosphorus, nitrogen, zinc, molybdenum, halogens, boron, and so on. Among these elements, boron's versatile chemistry makes it prominent in its use in EAs. Given the growing interest in boron chemistry, it is critical to understand why and how boron may become a favored element in IL functionalization [22–31].

Boron is one of the few elements known to show excellent harmony with ILs energy applications [22, 31]. **Table 2** lists the physical, atomic, and other characteristics of boron. Boron, symbol B, atomic number 5, and group 3A of the periodic table, is not found in elemental form in nature but may be produced in pure form by several processes [24, 25]. This position of boron between metals and nonmetals allows it to be employed in a wide range of research areas. Boron has an empty p orbital, so it has an electron deficiency. It has a sensitivity to undergo chemical reactions to saturate the coordination sphere and valence shell. Owing to the chemical properties and orbital nature of boron allow the formation of many useful ILs, including neutral, anionic, and cationic species.

| Boron (${}_5\text{B}$) | |
|--------------------------|--|
| Phase | Solid |
| Atomic number | 5 |
| Electron configuration | $1s^2 2s^2 2p^1$ |
| Allotropes | α -rhombohedral, α -tetragonal boron, β -rhombohedral boron, β -tetragonal boron, γ -orthorhombic |
| Isotope | ^{10}B , ^{11}B |
| Density (liquid) | 2.08 g/cm ³ |
| Melting point | 2076°C |
| Molar heat capacity | 11.087 J/(mol·K) |
| Atomic weight | 10.81 |
| Electronegativity | 2.04 |
| Thermal conductivity | 27.4 W/(m·K) |

Table 2.
Physical, atomic and other properties of boron.

While forming a compound, the empty p-orbital of the boron can lead to significant delocalization and is attacked readily by nucleophiles such as water or halides [22–38]. As a result, by bond cleavage of the neutral tri-coordinated borate, boron readily forms trivalent compounds with electrophile molecules such as oxides, sulfides, nitrides, and halides. Moreover, fluoride (F^-) and boron trifluoride $[\text{BF}_3]^-$ may combine to create $[\text{BF}_4]^-$ the anionic tetracoordinated borate species [31].

Because boron has an intrinsic electron deficiency, it is primarily defined by its Lewis acidity since it easily forms adducts by seizing electron pairs from Lewis bases [22, 28–30]. However, when certain conditions are met, the boron atom can become negatively charged or polarized and therefore, act as a nucleophile or Lewis base [27–30]. For example, boron and hydrogen combine to form many borane anions. The high hydrogen capacity of these borane anions makes them a suitable material for hydrogen storage. They are also possible candidates for ILs employed in electrochemical devices due to their unsymmetrical borate anions and bulky and anionic boron aggregates.

Many boron-atom/molecule-based ILs can be developed by tailoring cation-anion ion couples for specific purposes. Hitherto, elemental boron, carboranes, and organoboron compounds (cationic borinium (R2B1L2), borenium (R2B1L1), and boronium ions (R2B1), tetrahedral boron anions ($[\text{BH}_4]^-$, $[\text{B}_{12}\text{H}_{12}]^-$), orthoborate anion ($[\text{BO}_3]^-$) were often employed in the synthesis of BBILs [22, 23, 28, 31]. Because of its electron-deficient nature, boron forms a series of highly chemically, electrochemically, and thermally stable anions and negatively charged boron clusters. For instance, organoboron anion compounds from the boron ion family have been frequently used in the formation of stable ILs in recent years, as they can dissolve in solvents with a low dielectric constant with reasonable solubility [31]. It has been indicated that carborane-based ILs with relatively high boron content, such as 1-carba-closododecaborate $[\text{CB}_{11}\text{H}_{12}]^{-1}$, are exceptionally stable toward oxidation and coordination reactions due to their unique molecular structures [31, 32, 39–46].

As shown in **Figure 1**, designing BBILs for different EAs is often done by tailoring component ions with functional groups. The ion structure (like a positive-negative charge, small-large) greatly affects the physicochemical properties of ILs and, ergo, also affects the application to be used. For example, adding hydrophobic alkyl chains to its component ions causes changes in the chemical properties of ILs, increasing the viscosity and melting temperature that are undesirable in electrochemical devices. Therefore, it is necessary to achieve functionalization without destroying the basic properties of BBILs.

1.2 The choice of boron cations and anions in the formation of ionic liquids

The physicochemical characteristics of all ILs, not just boron-related ILs, depend on the nature of cations and anions and their combination. Generally, when designing ILs, properties such as melting point, conductivity, viscosity, air and moisture stability, hydrophobicity, miscibility with water, and density must be adjusted and optimized for the application to be utilized. According to Plechkova and Seddon et al. [5], the cation is responsible for the physical properties of an IL, for example, density, viscosity, and melting point, while the anion is accountable for the chemical properties and reactivity. For example, halides as anions with hydrogen in position 2 (CH ... X⁻) lead to higher melting points. For this reason, it can be said anions play a critical role in higher melting and lower melting points, as well as cations [34]. The anion type has a significant effect on the hydrophobicity and hydrophilic tuning tunable of IL. Fluoridation of the anion leads to promoted hydrophobicity and weaker hydrogen

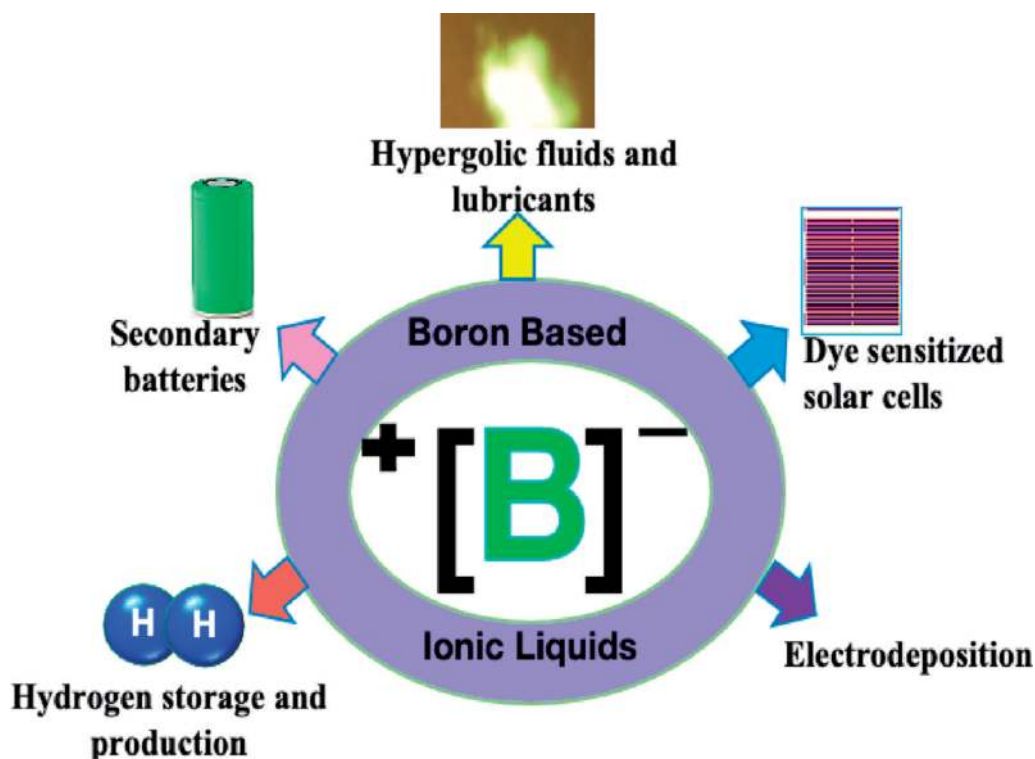


Figure 1.
Modification of BBILs for energy-related applications.

bonding, and hence lower melting temperatures; it also increases thermal and electrochemical stability. Besides halides, the inorganic anions $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ are often utilized in designing ILs. The modification of the cation by N-alkylation is critical in adjusting ILs. Increasing cation size and chain length lowers IL melting values while increasing viscosity. Also, the cation's branched alkyl chains induce a greater melting temperature in IL. In this context, melting points appear to be more connected to cation asymmetry [13] because this asymmetry causes packing inefficiency and hence prevents crystallization. Asymmetric cation salts with just C1 symmetry, for example, have lower melting temperatures than identical salts containing C2v symmetry cations [36]. It has been noted that the absence of strong hydrogen bonding correlates to lower IL melting temperatures [36].

The most commonly used cations in the formation of ILs are N,N'-dialkylated imidazolium ions, due to their ease of synthesis and favorable physical and chemical properties. Cations of imidazolium impart low melting points, high conductivity, and low viscosity properties to ILs [34]. Quaternary ammonium is also used as the cation for some EAs. The use of ILs using 1,3-dialkyl imidazolium cations in high-energy electrochemical devices such as lithium-ion batteries is not possible due to the electrochemical instability of the cation. Therefore, ILs containing quaternary ammonium ions are preferred as they are more resistant to reduction and oxidation [37, 38].

Inorganic anions with which the ILs decompose endothermically, while organic anions lead to exothermic thermal decomposition [39]. The thermal stability of halides is substantially lower (300°C). Many of these imidazolium salts display supercooling and are liquid at room temperature. More symmetric cations lead to higher melting points and vice versa. A longer alkyl chain (propyl as compared to ethyl) lowers the melting points and branching of the chain (i-propyl) raises the melting point [39]. Considering the aforementioned features, ILs synthesized by changing the boron anion and cation are potential candidates for the field of energy.

Boron anion and boron cation-based ILs are described in further depth in the next section.

1.2.1 Boron anions based ILs

Over the past few decades, boron anion families of ILs have been prominent in the field of energy due to their high thermal stability, low flammability, negligible vapor pressure, and wide electrochemical window [8, 40–53]. One of the liquid salts borates is the most commonly used negatively charged boron compound as anions in BBILs [22, 23, 35–37]. **Figure 2** illustrates examples of tetrahedral boron (borate) anions in ILs. The negative charge of ILs produced with tetrahedral boron anions is

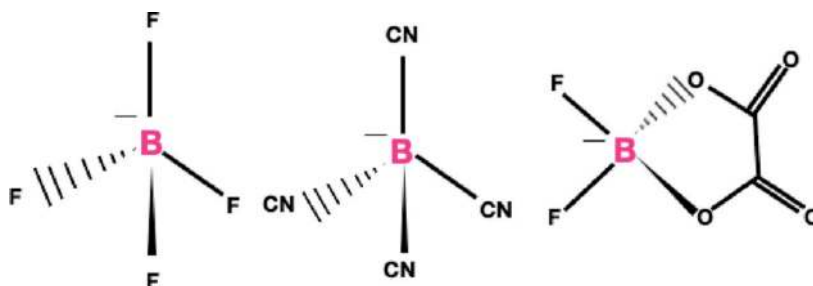


Figure 2. Tetrahedral boron anions (adapted from Refs [22, 31, 35]).

compensated for by positively charged groups such as ammonium. Mixed borates containing $[\text{BF}_4]^-$ as an anion can react with trimethylsilyl ethers of acids to generate IL, as shown in the figure.

The $[\text{BF}_4]^-$ anion is uncoordinated in an aqueous solution; therefore, they are called weakly coordinated anions. A modest negative charge and strong charge delocalization are some desirable features for weakly coordinated anions. Nonnucleophilicity and the minimally base surface of the anion also lead to poor coordination [8, 21, 40].

Anions should not be divided into small moieties in ILs, such as $[\text{BF}_4]^-$ which loses a fluoride when attacked by a nucleophile. Therefore, kinetic and thermodynamic stability are also significant points. Anions must also resist oxidation because the corresponding electrophilic cation often acts as an oxidizing agent [8].

As an alternative to Lewis acid/base pair anions that function in a combination of a Lewis acidic boron component and a Lewis base, derivatives of polyhedral anions such as 1-carba-closo-dodecaborate ($[\text{CB}_{11}\text{H}_{12}]^-$) are used (see **Figure 3**) [1, 8, 40].

Polyhedral borane clusters and three-dimensional carboranes have attracted attention in recent years with an increasing interest in ILs as materials and building blocks because of their great chemical and thermal stability [35].

Because of their inertness, dipolarity, and high symmetry, carboranes (most known: closo ($[\text{C}_2\text{B}_n\text{H}_{n+2}]$), nido ($[\text{C}_2\text{B}_n\text{H}_{n+4}]$), arachno ($[\text{C}_2\text{B}_n\text{H}_{n+6}]$)) as a new class of weakly coordinating anions can be considered three-dimensional analogs of benzene. Carboranes are promising candidates in ILs as anions due to their size, spherical shape, remarkable chemical stability, and only weakly coordinated B-H groups [41]. Carboranes are electron-delocalized organometallic clusters composed of carbon (C), boron (B), and hydrogen (H).

Carboranes are promising candidates in ILs as anions due to their size, spherical shape, remarkable chemical stability, and only weakly coordinated B-H groups [41]. Carboranes are electron-delocalized organometallic clusters composed of carbon (C), boron (B), and hydrogen (H). The general formula of carboranes is represented by $\text{C}_2\text{B}_n\text{H}_{n+m}$, in which n is an integer; n range from 3 to 10. Carboranes are synthesized by adding one-carbon reagents (i.e., cyanide, isocyanides, and formaldehyde) to boron hydride clusters. For example, monocardodecaborate ($[\text{CB}_{11}\text{H}_{12}]^-$) is produced from decaborane and formaldehyde, followed by the addition of borane

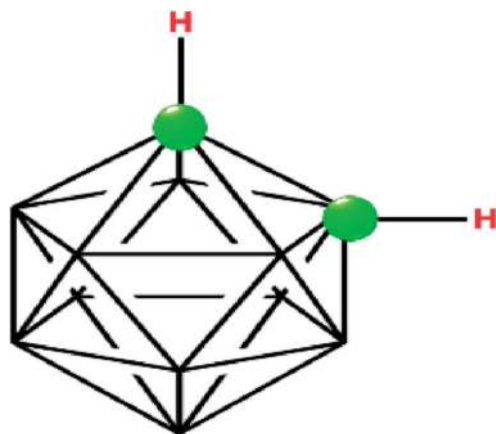


Figure 3.

Closo carborane (a green circle represents a C-H unit or a C in the cases where a charge is specified. And another corner one B-H unit closo-Carborane. Adapted from Refs [41, 42, 45]).

dimethylsulfide [42–45]. Monocarboranes are precursors of poorly coordinated anions [41, 42]. The resulting poor coordination is established in a charge distribution over the entire 12-cornered carborane anion. The 10-sided anion $[\text{CB}_9\text{H}_{10}]^-$ and its halogenated and methylated derivatives coordinate more strongly than the 12-sided carboranes. Due to their specific properties, these boron molecules are some of the most inert and least nucleophilic anions currently known.

Cyanoborate anions ($[\text{B}(\text{CN})]^-$) (see **Figure 4**) have become an important class of building blocks in materials science, especially for ILs that are used as components of electrolytes for electrochemical devices. Also, in recent years, low viscosity room temperature cyanoborate based ILs have been studied in EAs, especially dye-sensitized solar cells (DSSCs) and as a fuel additive for hyperbolic liquids. Cyanoborate chemistry has been popularized as an important topic in the last years, beginning with two independent research on the successful synthesis of the tetracyanoborate anion $[\text{B}(\text{CN})_4]^-$ in 2000 [53–56].

A wealth of $[\text{B}(\text{CN})_4]^-$ with different substituents in addition to CN group (s) bonded to boron, such as hydrogen, halogen, alkyl, and alkoxy, have been developed, which makes possible the tuning of features of compounds. The easily accessible alkali metals are convenient starting materials for the preparation of cyanoborates with various organic, and inorganic compounds.

Furthermore, cyanoborates are promising starting compounds for the synthesis of other boron species, for example, the weakly coordinating tetrakis(trifluoromethyl) borate anion $[\text{B}(\text{CF}_3)_4]^-$ and the boron-centered nucleophile $\text{B}(\text{CN})_3^{2-}$. Detailed studies on this subject will be described in more detail in the next section.

Moreover, recent studies have shown that orthoborate anion-based ionic liquid combinations possess outstanding electrolyte characteristics and are attractive solvents for lithium-ion battery solvents. **Figure 5** depicts the simplest orthoborate ion, $[\text{BO}_3]^{3-}$. Orthoborate is an anion derived from orthoboric acid ($\text{B}(\text{OH})_3$). It is a very weak monobasic that functions solely by hydroxyl-ion acceptance rather than proton donation. Many organic molecules have boron-oxygen bonds (B-O), europium borate ($\text{Eu}(\text{BO}_2)_3$), chromium borate (CrBO_3), beta barium borate ($\beta\text{-BaB}_2\text{O}_4$), gadolinium

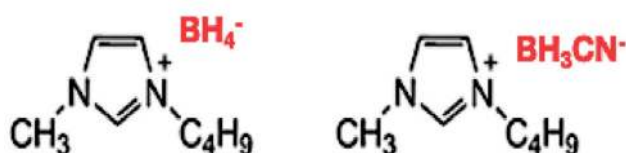


Figure 4. Borohydride and cyanoborate anion-based ionic liquid (adapted from Refs [53, 55]).

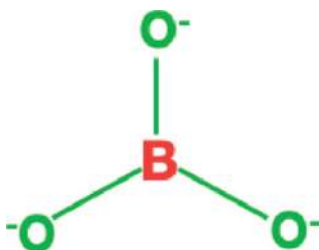


Figure 5. Simplest orthoborate anion.

orthoborate (GdBO_3), and polyborate $[\text{B}_3\text{O}_9]^-$ ion as anions are examples of such compounds [54, 55].

1.2.2 Boron cation based ILs

Studies indicate boron has a significantly higher electropositive charge than most of the donor elements in the ligand (L). After the discovery of cationic boron species, the developed ILs are hard-to-find, highly electrophilic species with high Lewis acidity and reactivity, which are essential in boron chemistry [28, 47]. Boron cation-based ILs, which have high melting points, are used as electrolytes that must be liquid at sub-zero temperatures for electric vehicle applications that must be liquid at ambient temperature battery applications and electrochemical devices due to their relatively low viscosity. Furthermore, the integration of cationic boron centers in organic heterocycles or transition-metal metallocenes is also providing opportunities for the discovery of novel redox-active and optical materials [28].

In recent years, tetracoordinate borocations have had relative stability, which arises from a filled octet and a complete coordination sphere. Because of their larger electronic deficiency and coordinative unsaturation, they are also known to be more reactive than neutral borates [23, 28, 41]. In literature, commonly boron cations are divided into three main groups [28]: Borinium (two-coordinate), borenium (three-coordinate), and boronium (four-coordinate) cation ions (see figure, where: L is a Lewis base; R is substituents, based on the coordination number at boron) [28, 34–47] (see **Figure 6**).

Borinium cations are typically bi-coordinate species bonded by two R that can compensate for the electron deficiency in boron via p donation. Since these species can only have two valence electrons, an additional electron pair must be ensured by an electron donor L (i. e., N or O). That is, at least one L capable of p-bonding must be present to stabilize these cations [46]. In addition, borinium compounds are quite reactive compared to borenium and boronium.

On the other hand, borenium cations are tri-coordinate species containing two bonded R, one L and a third coordination site [28].

The boroniums are the third and most prevalent class of boron cations. The simplicity with which the boronium ions are manufactured and the structural diversity embodied in them provide an essential pragmatic basis for formulating IL. In 2010, R  ther et al. [48] brought out boronium-cation-based RTILs as novel electrolytes for rechargeable lithium batteries. These boronium-containing RTILs exhibited good conductivities and electrochemical windows (4.3–5.8 V). They are stable up to 238

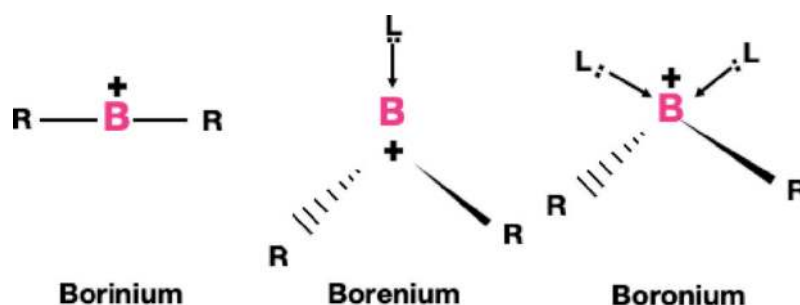


Figure 6.
Boron cation species (adapted from Ref. [44].)

and 335°C, respectively, and have enabled reversible charge–discharge cycles in batteries with high-capacity retention [48]. Among the boron cations, borinium ions have the most electron deficiencies and are the most chemically unstable species. Thus, while extensive research has been conducted on three- and four-coordinate boron cations, there are only limited examples of borinium ions. Borinium ions generated by electron ionization of borane or borate precursors have been reported to react aggressively and selectively with organic substrates in several cases. However, only a few ionic products are produced, which give valuable structural information on the substrates [46]. Donor ILs in boronium and borinium often serve to extinguish the boron's positive charge. Boronium cations, on the other hand, are better ideal for energy investigations because of the additional stability and electron density offered by donor L. This is evident in the number of studies that describe the production of species or use them as intermediates in various chemical processes [46–48]. Finally, cationic boron compounds are an uncommon but important species in boron chemistry. Emerging research shows that cationic boron compound chemistry is on the verge of a quantum leap in activity; we hope that this review will motivate additional effort in this interesting area of EA.

2. Boron-based ionic liquids for energy-related applications

2.1 Dye sensitized solar cells

Dye-sensitive solar cell technologies continue to be the focus of scientific and industrial research as one of the photovoltaic devices that provide the opportunity to benefit from the sun, which is one of the renewable energy sources. The DSSC projects are widely oriented toward increasing power generation and low-cost generation. The numerous critical processes for DSSC power production mainly occur at the nanocrystal/dye/electrolyte interface (see **Figure 7**), which is now a significant research focus in this field. The maximum efficiency (14.3%) [51] has been obtained using a ruthenium complex in combination with an electrolyte [52, 53]. However, the limited supply of ruthenium and volatile organic solvents are a significant concern for the long-term stable operation of DSSCs. Due to their ideal properties of minimal

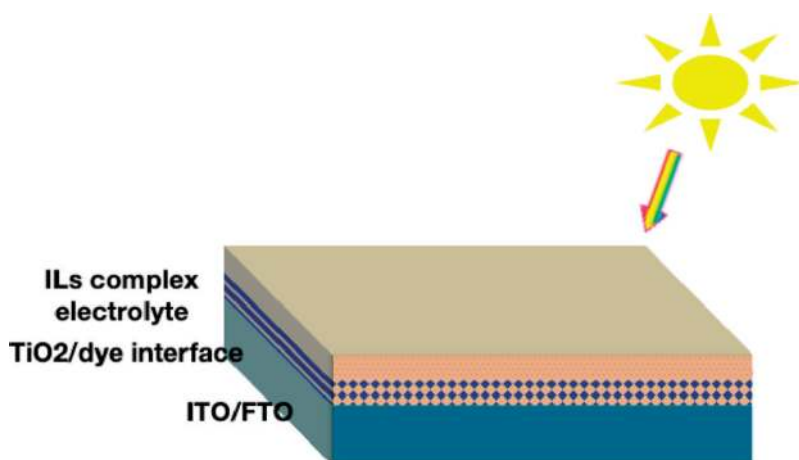


Figure 7.

A systematic view of functionalization ILs in DSSCs (adapted from Ref. [49–53]).

vapor pressures, high conductivity, and thermal stability, RTILs have emerged as a possible choice for enhancing the efficiency of DSSCs. ILs-based DSSCs with ruthenium complexes as sensitizers have already demonstrated impressive photovoltaic performance and stability.

The properties of ILs make them appropriate for use in perovskite solar cells to address significant device efficiency and stability issues, as in DSSC. It was proposed that ILs form a protective layer on the perovskite film to provide the device with moisture and thermal stability. However, no extensive research on boron-containing ILs used in perovskite solar cell technology has been conducted [54, 57]. The DSSC conversion efficiency still lags behind that of organic solvent-containing DSSCs. The fundamental cause of this poor performance is the ILs' high viscosity, which results in mass transfer constraints on the photocurrent under sunlight. To overcome this problem, it uses a combination of a low viscosity IL and a redox-active salt as the electrolyte to optimize the diffusion rate of the redox couple. These additives optimize the kinetics of the processes of electron injection that occur at the photoanode. The nature of IL, especially basic anions such as dicyanamide, can significantly affect the position of the conduction band edge and thus the open-circuit voltage (V_{oc}) of the device. The most efficient IL-based system reported to date employs the I^-/I_3^- redox couple in conjunction with one of a eutectic solution of imidazolium iodide salts [C2mim], yielding good stability $[B(CN)_4]^-$ [53–56, 58]. According to research, when combined with titania/electrolyte in DSSCs, $[B(CN)_4]^-$ exhibits a higher photocurrent response. $[B(CN)_4]^-$ anions cause a downward displacement of an electrolyte-immersed film's conduction-band edge, resulting in a more favorable energy balance at the titania/dye interface and thus a better exciton dissociation efficiency [53].

Organic dye-sensitized $[B(CN)_4]^-$ IL-based solar cells were reported by Daibin Kuang et al [55]. It has been claimed that the first rapor and organic DSSC combined with these newly developed ILs (without solvent) obtained a conversion efficiency of 7.2% to electrical power. A molecularly tailored indoline sensitizer with 1-ethyl-3-methyl-imidazolium tetracyanoborate ($[EMIB(CN)_4]$) was used in the electrolyte. This is the first time an ionic-liquid electrolyte has been used to achieve such high efficiency for organic dye-based ILs.

Magdalena Marszalek et al. [56] prepared and characterized the $[B(CN)_4]^-$ anion-based series of ILs for use in DSSC applications. These new fluorine-free ILs were composed of $[B(CN)_4]^-$ anions and cations such as imidazolium and ammonium. Synthesized and characterized novel BBILs were evaluated as electrolyte additives in DSSC, with obtained efficiencies of 7.35 and 7.85% under 100 and 10% sun, respectively, in combination with the standard Z907 dye [56].

Promising alternative electrode materials with BBILs may include nanostructures that may have lower charge transfer resistance for I^-/I_3^- relative to a molecular solvent in an IL electrolyte. However, reducing the charge transfer resistance to obtain acceptable performance under full solar radiation is extremely important for device development, and this field of study remains open to considerable advancement.

2.2 Boron-based ionic liquids in advanced battery technologies (Lithium, sodium and magnesium ion batteries)

The properties of ILs, such as inflammability, extremely wide liquid range, and especially the stability of some types of cations and anions at high anodic potentials, make them suitable for lithium batteries. ILs are mixed with appropriate lithium salts to make electrolytes for lithium-ion batteries. The choice of electrolyte used for

lithium battery production is critical and determined by a variety of factors, including safety and “greenness.” Because RTILs are non-volatile and non-flammable, they are more appealing as lithium battery electrolytes than conventional organic liquid solvents. The structural chemistry of boron and oxygen compounds, the building blocks of orthoborates, is characterized by extraordinary complexity and diversity. Lithium borate (see **Figure 8**), one of the metal borates, is one of the building blocks of IL, which is used as a lithium-ion battery electrolyte. Orthoborate-based ILs have been reported to be more efficient than conventional salts such as LiPF_6 as they offer several advantages such as halogen-free, non-toxic, good thermal stability, and high compatibility with cathode materials [59–62].

Faiz Ullah Shah et al. [61] described the ion transport mechanism of a ternary combination of phosphonium bis(salicylato)borate IL, diethylene glycol dibutyl ether, and a lithium bis(salicylato)borate ($\text{Li}[\text{BScB}]$) salt for lithium-ion batteries. The ion transport properties and viscosity of the orthoborate-based halogen-free ionic liquid hybrid electrolytes were investigated. In the investigation, the lithium bis(salicylato)borate salt was dissolved in a combination of IL and diethylene glycol dibutyl ether. Diethylene glycol dibutyl ether has a flashpoint at 118°C and is miscible with ILs. This research is the first to look at the ion transport processes of orthoborate-based ionic liquid hybrid electrolytes. As a consequence, the maximal solubility of $\text{Li}[\text{BScB}]$ salt in a combination of ILs and diethylene glycol dibutyl ether at room temperature was determined to be 1.0 mol kg^{-1} . The viscosity of the combination was 1000 times lower than that of the neat phosphonium bis(salicylato)borate ionic liquid. However, no differences in ionic conductivity were observed between the combination and the neat phosphonium bis(salicylato)borate ionic liquid.

Liang, Fuxiao et al. [62] have investigated a novel BBIL electrolyte for high voltage lithium-ion batteries with outstanding cyclic stability. According to the study, adding an appropriate amount of N-propyl-N methylpiperidinium difluoro(oxalate)borate ($\text{PP}_{13}\text{DFOB}$) to an electrolyte containing lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) results in a high discharge capacity. In addition, a promising strategy is presented to mitigate aluminum corrosion of boron-based ionic liquid electrolytes and further improve the cycling performance of lithium-ion batteries at high cut-off voltages in the paper.

The construction of electrochemical cells requires the use of target carrier ions such as lithium cations, protons, or iodides. That is, a matrix that transports these target ions is essential for such applications. Several solutions have been suggested

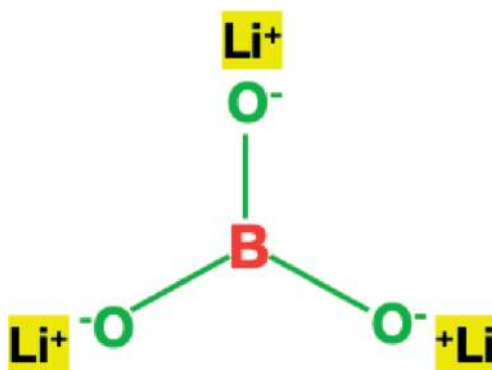


Figure 8.
Lithium orthoborate.

to facilitate selective lithium-ion transport in ILs. Several techniques have been described to accomplish selective lithium-ion transport in ILs. For instance, zwitter ions, which have a cation and an anion in the same molecule, have been proposed to inhibit IL component ion movement under an electrical potential. An IL with alkyl borane units has been synthesized to trap anions by the interaction between boron and the anion [63].

A few publications have subsequently explored variations of IL cation (dominated by small aliphatic and cyclic ammonium cations) and anion (dominated by bis-(trifluoromethanesulfonyl)-imide [TFSI]⁻ or [BF₄]⁻ combinations with a range of lithium battery anodes and cathodes.

Clarke-Hannaford et al. [64] have conducted enhanced cycling performance in lithium metal batteries of boronium-cation-based ILs. They investigated using a combination of density functional theory calculations and ab initio molecular dynamics simulations, the chemical stability and reaction mechanisms between the Li surface and [NNBH₂]⁺[TFSI] and dihydroborate ([NNBH₂]⁺) to understand the existence of the solid electrolyte interphase layer formed using boronium-cation-based ILs. Simulations showed that the surface interaction with the [NNBH₂]⁺ cation is weak, and its anions easily dissociated to create numerous chemical species (LiF, Li₂O, and Li₂S). The results provided evidence that the [NNBH₂]⁺ cation is stable against a lithium metal surface and that self-dissociation of the cation is unlikely to occur. Enhanced cycling performance in lithium metal batteries, a stable solid electrolyte interphase [NNBH₂]⁺ cation, usually formed on the Li surface, has been shown to have similar properties compared to commonly used cations, helping to explain the positive performance of boronium cation-based ILs.

Research has been done on Na metal to make second-generation batteries a safer, lower-cost option for energy storage. Regarding sodium batteries, Nikitina et al. [49] [bmim] showed that sodium salt, unlike lithium, has only a minor effect on the conductivity, dielectric properties, and viscosity of sodium tetrafluoroborate (NaBF₄) in ILs. Electrical conductivities, densities, viscosities, and molar conductivities of [bmim][NaBF₄] ionic liquid were measured in the wide temperature range of (278.15–358.15) K and (238.15–458.15) K, respectively. The values for viscosities and conductivities were described by the Vogel-Fulcher-Tammann equation. The Walden plots, log(Λ) vs. log(η -1), for the NaBF₄ solutions, coincide with the straight line found for neat [bmim][BF₄], indicating that the solute had only a limited impact on the structure of the ionic liquid. Also, they found that the dielectric properties of the most concentrated NaBF₄ solution (0.1739 mol·kg⁻¹) are identical to those of pure [bmim][BF₄].

Basile et al. [21] reported on room temperature ionic liquid comprising the dicyanamide anion as a successful electrolyte system for sodium metal batteries that do not contain expensive fluorinated species. At a current density of 10 μ A cm⁻², the effects of sodium plating and stripping from Na metal electrodes were examined in a symmetrical Na|electrolyte|Na configuration. The presence of residual water molecules in the ionic liquid electrolyte was seen to have a significant impact on the surface film and plating/stripping behavior. The increase in moisture content from 90 to 400 ppm has hampered both electrodeposition and electrodisolution of the Na⁺/Na. They also used cyclic voltammetry on Ni electrodes at various Na salt concentrations to further understand the mechanism. As a result, the water concentration in this pyrrolidinium ionic liquid alters the Na electrochemistry.

For rechargeable magnesium batteries, Guo and colleagues [18] have developed a boron-based electrolyte system with outstanding electrochemical performance,

formed through the reaction of tri (3,5-dimethylphenyl)borane (Mes_3B) and PhMgCl in tetrahydrofuran. In the study, the structure-function correlations of the novel electrolyte were investigated, as well as the identification of the equilibrium types in the solution using NMR, single-crystal XRD, fluorescence spectra, and Raman spectroscopy. Moreover, the electrochemical stability of various current collectors, air sensitivity, and charge-discharge performance of a $\text{Mg-Mo}_6\text{S}_8$ battery in the electrolyte are analyzed. As a consequence, fluorescence and Raman spectroscopy investigations revealed that the $\text{Mes}_3\text{B}-(\text{PhMgCl})_2$ electrolyte's strong anodic stability (about 3.5 V vs. Mg reference electrode) is due to non-covalent interactions between the anion $[\text{Mes}_3\text{BPh}]^-$ and Ph_2Mg . Motivated by this finding, the researchers proposed a reversible electrochemical technique of Mg intercalation into a Mo_6S_8 cathode, indicating that the novel boron electrolyte may be used in rechargeable Mg battery systems.

Carter TJ et al. [19] studied a combined carboranyl magnesium halide and closo-borane electrolyte for unconventional electrolyte system optimization in Mg batteries. In the results, they found that closo-borane compounds can function as high-oxidative-stability magnesium-battery electrolytes while maintaining compatibility with magnesium-metal anodes. Also, the carboranyl magnesium halide demonstrated compatibility with magnesium-metal anodes and outstanding oxidative stability (3.2 V vs. Mg) on non-noble-metal electrodes in the study.

2.3 Hypergolic fuels

The concept of hypergolicity is that one chemical (fuel) reacts spontaneously when it comes into contact with another (oxidizer). Hypergolic ILs tend to have low volatility and high thermal and chemical stability that could allow the utilization of these substances as bipropellant fuels under different conditions. Meanwhile, the adjustment of the oxidizer/fuel ratio, the order of adding the fuel and oxidizer, and the ignition temperature should be considered when evaluating new hypergolic fuels.

In the formation of hypergolic boron-based ILs, boron compounds act as triggers, while cations (such as imidazolium) promote hypergolic firing. Recently BBILs frequently have been investigated as components in hypergolic fuel for rocket applications. In order to improve ignition performance and hydrolytic stability, electron-withdrawing moieties such as -CN group and nitrogen heterocyclic ring are often used to tune anions. A strategy of bridging another BH_3 moiety or adding phosphorus atoms to anions can also improve the physico-chemical properties of hypergolic ILs.

According to studies in the literature, $[\text{BH}_4]^-$ and $[\text{B}(\text{CN})\text{H}^{-3}]$ were commonly used as anions.

In the design of hypergolic [65–70], hypergolic fuels with $[\text{BH}_4]^-$ and $[\text{B}(\text{CN})\text{H}]^{-3}$ (ultra-fast spontaneous combustion with HNO_3 oxidizers) and amines with borane-based ILs (low ignition delays) are promising.

Zhang et al. [67] reported the synthesis of water-stable hypergolic ILs ($(\text{B}(\text{CN})^-$ based) in aqueous media. The B-H bond is unquestionably accountable for the hypergolic nature of compounds based on borohydride and cyanoborate. They stated that dicianoborate-based ILs exhibited similar phase transition temperatures, analogous thermal breakdown temperatures, and lower densities when compared to other hypergolic ILs containing amine anions. As a result, the novel boron-containing anionic ILs had substantially lower viscosities (12.4 mPa s) and ignition delays (4 ms) than nitrocyamide and dicyanamide hypergolic ionic liquids.

Bhosale et al. [69] synthesized boron-based B-H single bond-rich ILs and investigated hypergolic reactivity. Notably, 1-ethyl-3-methyl imidazolium borohydride ([EMIM][BH₄]⁻ IL) distinguished itself by having a short ignition delay time of 18.5 ms. The ignition delay time of [EMIM][BH₄]⁻ and methyl imidazolium borane (1:1, w/w) as a combination of IL and fuel was determined to be around 35 ms. In addition, two algorithms were utilized to calculate the gas-phase heat of formation and the specific impact. One of the most promising possibilities for next-generation green hypergolic fluid and hybrid rocket propulsion has been identified as ILs rich in B-H single bonds.

Another hypergolic fuel study belongs to Li et al. [70]. They employed borane derivatives as additives to enhance the ignition delay of borohydride-based hypergolic ILs. First, they synthesized borohydride-based ILs (Amim-BH₄ and Bmim-BH₄) and then investigated the ignition delay time of these ILs with borane additives. The synthesized borohydride-based hypergolic ILs exhibited the shortest ignition delay time compared to any known hypergolic IL in the study. Also, they discovered that the triethylamine-borane combination is the most effective hypergolic additive studied to date. While the ID times of borohydride-based ILs are as short as 2 ms, IL solutions of borane-based additives have the lowest ID of 3 ms.

Based on the above explanations, borohydrides and boranes have great potential not only for ignition acceleration but also for alternative fuels due to their higher densities, lower vapor pressures, and adjustable heats of formation and viscosities. Although hydrazine and its derivatives are poisonous and carcinogenic, this new IL family offers a more environmentally friendly option. The increasing use of boron and its analogs to treat hypergolic ILs has resulted in more cost-effective solutions. However, in propellant systems, hydrazine and its derivatives remain the fuel of choice, despite containing a class of acute carcinogens and toxicants that exhibit extremely high vapor pressures and require expensive handling procedures and costly safety precautions.

2.4 BBILs for hydrogen storage and production

Having excellent hydrogen densities, safety, and release rate characteristics, many boron molecules can retent substantially more releasable hydrogen by weight and volume than pure liquid hydrogen [22]. Boron compounds are used as anions in ILs for hydrogen-containing applications, along with cations such as N,N'-dialkylimidazolium, N-alkylpyridinium, tetraalkylammonium, and tetraalkylphosphonium [35]. Particularly for commercially accessible sodium borohydride (NaBH₄), hydrogen technologies provide easy and compact power for portable devices and backup power systems.

Amir Doroodian et al. [71] conducted one of these investigations. They presented the first ionic liquid based on methylguanidinium borohydride ((N₃H₈C)C + BH₄) with effective hydrogen storage capacity. It is stated in the study that a liquid electrolyte is an ionic liquid that releases 9.0% by weight H₂ under both thermal and catalytic conditions.

Developing technologies based on metal borohydrides (M(BH₄)_n) and amine boranes (AB, NH₃BH₃) on the other hand, have the potential to produce greater power densities than established sodium borohydride systems [72]. AB (see **Figure 9**) is a class of borohydride and one of the leading candidates for chemical hydrogen storage, which can release 19.6 wt% H₂ when heated (at 85°C) due to its high hydrogen

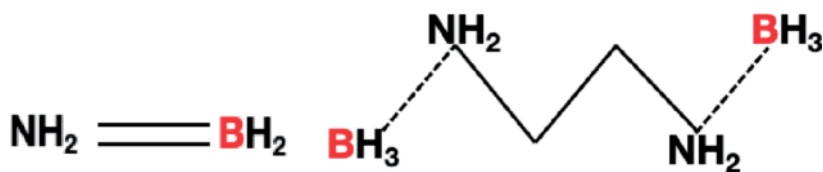


Figure 9.
Structure of aminoborane and diamine bisborane.

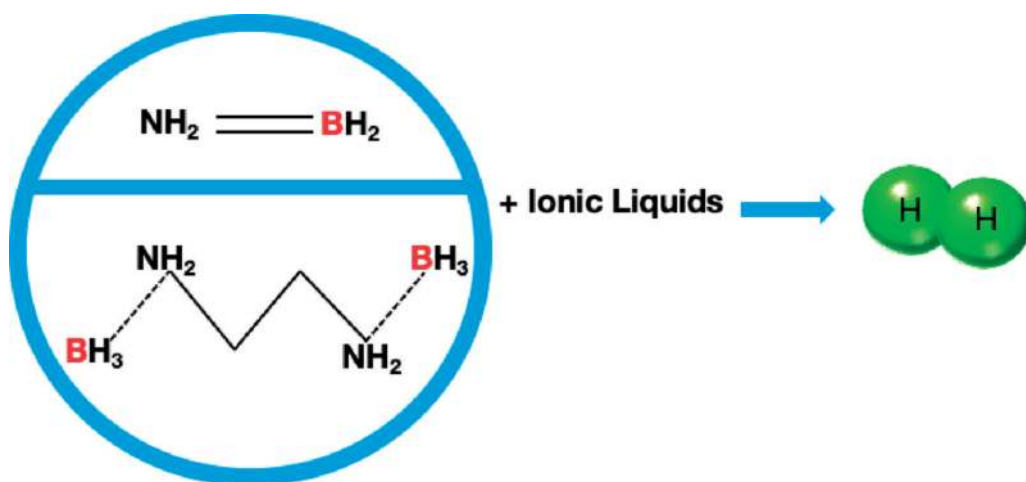


Figure 10.
Aminoborane and diamine bisborane mix ILs for degeneration of hydrogen.

content [73]. A feasible AB regeneration technique, as well as a quick and regulated H_2 release rate are required for AB mix ILs to be suitable for hydrogen storage. Several approaches can accelerate the release of AB H_2 mechanically, including activation with transition metal catalysts. **Figure 10** depicts the systematic figure of AB and diamine bisborane mix ILs for the degeneration of hydrogen.

Daniel et al. [74, 75] showed that base-supported AB increases the rate of H_2 release in ILs by promoting the anionic dehydropolymerization mechanism. They reported AB reactions in 1-butyl-3-methylimidazolium chloride that took 171 min at $85^\circ C$ and only 9 min at $110^\circ C$ to produce equivalents of H_2 . Moreover, ionic-liquid solvents were shown to be more beneficial than other solvents because they minimized the development of unwanted compounds like borazine.

The effect of ethylenediamine bisborane (EDAB), one of the AB derivatives, on the hydrogen release rate in combination with ILs has been studied in the literature. Many research have been conducted to improve dehydrogenation, reduce dehydrogenation temperatures, and enhance equivalent H_2 production [75–77]. In one of these studies, Debashis Kundu et al. [77] reported thermal dehydrogenation of EDAB in [BMIM] sulfate-based ILs. The time-resolved and temperature-resolved dehydrogenation of EDAB/IL systems have been carried out and characterized by NMR characterization in the study. Also, the equal quantity of equivalent hydrogen created per mole of EDAB injected into the system was computed. The results showed that IL-facilitated dehydrogenation released a higher amount of equivalent hydrogen than dehydrogenation with pure EDAB at $120^\circ C$. At $100^\circ C$, the EDAB/[BMIM] $[HSO_4]$ system released 3.92 cumulative equivalent hydrogen.

2.4.1 Hydrogen generation by water splitting

A significant trend in the creation of hydrogen by electrolysis from a mixture of ILs and water, a renewable resource, has lately emerged. Water splitting includes the simultaneous oxidation and reduction of water [78–80]. Water ILs serve as an electrolyte and a solvent in the water-splitting process reactant. Water is merely one of several solutes present in the reaction mixture. When used in water separation, IL electrolytes have produced unique and surprising outcomes.

Roberto F. de Souza et al. [80] tested different electrocatalysts (molybdenum, nickel, and chromium) using aqueous ILs such as [BMIMBF₄] for hydrogen production by water electrolysis. The hydrogen evolution reaction (HER) was carried out at ambient temperature with a potential of -1.7 V. For the Mo electrode, a Hoffman cell apparatus with a current density value of 77.5 mA/cm^{-2} in water electrolysis was used. The system efficiency for all tested electrocatalysts was found to be very high, ranging between 97.0 and 99.2%. The findings indicate that hydrogen production in BMIM[BF₄]⁻ aqueous solution can be performed with inexpensive materials at room temperature, making this process economically viable.

Hydrogen bonds are more readily broken when water molecules are dissolved in a suitable IL, thus increasing the free energy and resulting in a lower energy input required in the water-splitting reaction. The free energy can approach that of gaseous water, which requires a lower free energy input of around 10 kJ mol^{-1} . Such a process must include a thermodynamically endothermic water dissolution process. As an example, [C₂mim] [B(CN)₄] based ILs have been proposed. However, no data on the thermodynamic process in BBILs is yet available. Also, the four-electron water oxidation reaction (see **Figure 11**) is much heavier than the water reduction reaction. That is why there has recently been a significant effort focused on developing and understanding water oxidation electrocatalysts.

2.5 Non-aqueous boron-based electrolyte for electrodeposition

This section discusses the electrodeposition of metals from non-aqueous BBILs. The application of non-aqueous BBILs makes it feasible to obtain cathodic residues of metals or metallic alloys that cannot be deposited by conventional electrolysis of aqueous solutions. Since the hydrogen overpotential is relatively low, it does not allow some electrodeposition reactions to occur in aqueous solutions. Due to the intrinsic conductivity of ILs, many metals and semiconductors may be electrodeposited directly from an IL solution of metal ions or metal-ILs ion complexes using standard electrowinning techniques. Because of the low volatility of IL, the procedure may be carried out at high temperatures exceeding 100°C . The number of studies published on non-aqueous solution electrodeposition has grown in recent years [33].

Yanna NuLi and colleagues [81] investigated highly reversible magnesium precipitation and dissolution processes in the ionic liquid of $1 \text{ Mg} (\text{CF}_3\text{SO}_3)_2$ and 1-butyl-3-methylimidazolium tetrafluoroborate [BMIMBF₄]. According to the scanning electron microscopy (SEM) data, micrometric-sized, virtually pyramidal-shaped magnesium deposits appeared, and when the magnesium dissolved, the electrode became clean and film-free. Cyclic voltammograms of Mg accumulation-dissolution also show that these reactions are reversible. [BMIMBF₄] demonstrated especially promising properties in terms of electrochemical window (Pt vs. 4.2 V) and

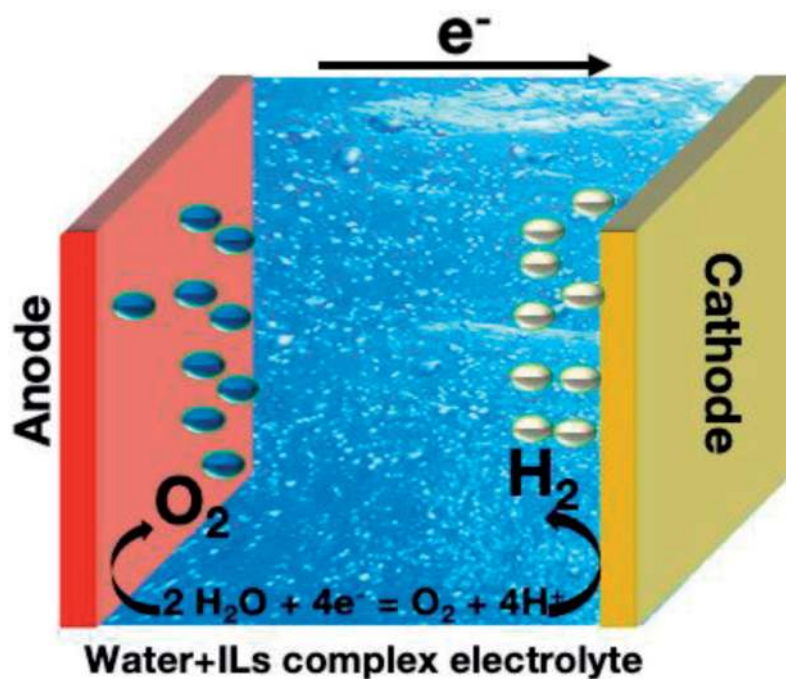


Figure 11.
Water electrolysis in ILs electrolyte mixture.

magnesium deposition-dissolution efficiency. As a result, this method may be acceptable for application in rechargeable Mg batteries.

Survilien et al. [82] studied the electrodeposition of the chromium from the ionic liquid [BMIMBF₄] and chromium chloride. The cathodic process of chromium electrodeposition procedure from the ionic liquid used was as follows: electrochemical reduction of water molecules, followed by chemical degradation of [BF₄] ions. According to the findings of this investigation, [BMIMBF₄] can be deemed promising for hazardous Cr (VI) baths for black chrome plating.

Menzel et al. [83] examined the development of the mechanism of the ZnO nanowire growth model by studying [BMIMBF₄] as an ionic liquid. They concentrated on the effects of IL sources on nanowire development in this work. They discovered that because B is an n-type source of ZnO material, IL-promoted growth may be employed to recruit donors. Electrical measurements of XPS and ZnO nanowires validated these hypotheses. Electrical measurements revealed that ionic liquid-assisted growth improved electrical conductivity (=0.09 cm). [BMIMBF₄] IL-assisted nanowire growth showed that boron was significantly involved in the alteration of nanowire growth properties compared to pure ZnO nanowire growth.

For electrodeposition, another IL, [C₂mim][BF₄], was utilized. Steichen M and Dale P [84] investigated the electrodeposition of trigonal selenium (t-Se) nanorods from [C₂mim][BF₄]/[C₂mim]Cl at high temperatures ($T > 100^{\circ}\text{C}$). phase, morphology, and crystallinity of Se residues vary, the choice of precursor salts also controls the electrodeposition of selenium. They demonstrated for the first time that t-Se nanorods may be made at high temperatures using a template electrodeposition route from [C₂mim][BF₄]/[C₂mim]Cl. The crystal quality of t-Se nanorods improves when the temperature rises above 100°C.

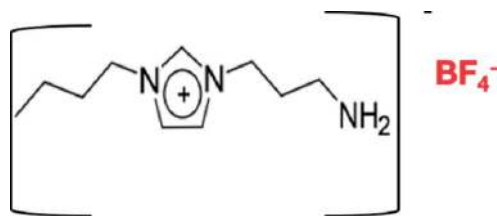


Figure 12.
Structure of ILs designed capture of CO₂ (adapted from Ref. [85, 86]).

According to the researchers, photoactive t-Se nanorods with p-type conductivity have been detected in an ionic liquid for the first time. Photoelectrochemical measurements performed in ionic liquid confirmed the p-type conductivity of t-Se nanorods.

2.6 Carbon dioxide capture using BBILs

The use of ILs to help separate CO₂ from other gases has recently become a hot topic of activity both in academia and industry. ILs' lack of volatility is a particular advantage in CO₂ absorption over molecular liquid absorbers. Carbon capture has become legally mandatory for electric power plants to operate. However, there is a net cost of carbon capture, and these costs are passed on to consumers. For this reason, it is critical to design and synthesize efficient CO₂ capture ILs made from the most basic and inexpensive building blocks, especially since the volumes required to achieve CO₂ capture using ILs would be prohibitively expensive at envisioned scales [85, 86]. In recent years, many publications have appeared on IL-CO₂ interactions of one kind or another (**Figure 12**).

Certain functional groups in the ionic liquid, such as anions of the amide family, absorb CO₂ up to 0.5 mol/mol IL through the traditional carbamate reaction. CO₂ absorption is enabled via similar functionalization through direct contact with amine or anionic functional groups. In addition, several ionic liquids also show potential in other environmentally conscious applications, such as CO₂ capture. Some of these novel "task-specific" ionic liquids have shown promise in CO₂ capture.

Using the ionic liquids 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [BMIM] [PF₆⁻] and [BMIM] [BF₄⁻], Anthony et al. [87] investigated CO₂ capture. They also compare CO₂ collection utilizing these ILs to conventional monoethanolamine-based technologies. According to the findings, [BMIM] [PF₆⁻] is particularly effective in capturing CO₂ from a mixture of N₂ or CH₄. As a result, these ILs are a viable choice for CO₂ capture in order to create an ionic liquid with a carrying capacity comparable to monoethanolamine.

3. Conclusion

Because as the fields of energy transmission, storage, and conversion continue to grow technologically, IL-based systems can provide a platform for safe, clean, durable, and high-energy-density materials, especially halogen-free and fluorine-free. Currently, there are limited studies based on boron atoms or particles, although millions of IL combinations with existing cations and anions are possible. In the field of energy storage, this focus has been mainly on fluorinated anions because of their stability.

There is a need to design halogen-free anions and cations with high electrochemical stability. However, in the context of energy science and technology, it is also necessary to quantitatively assess toxicity, recyclability, and biodegradability, for which there is insufficient information in most cases. For most energy applications of ILs, the cost is another issue for those with high electrochemical stability.

In this context, this review, recent advances in the synthesis of boron-containing ILs and various materials derived from them provide a powerful opportunity for further investigation in the field of energy research to improve and develop the properties of these BBILs. With this perspective, the article can guide further research and development of the unique properties of green and halogen-free BBILs.

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