

Synthesis, Analysis and Thermochemical Applications of Ionic Liquids

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Abstract

New materials, which are eco-friendly and have unusual characters, are so attractive with the increasing demand and harmful pollutants amount all over the world. As a solvent, non-evaporate ionic liquids (ILs) have recently captured notable interest due to their magnificent properties. They have been used for distinct purposes such as electrochemistry, separation, lubrication, catalyst, and energy applications. Adding functional groups and/or anion or cation tunability can ensure improved efficiency ILs depends on the application type. The present paper is primarily focused on the ionic liquids (IL) synthesis, development of functionalized ionic liquids, and their purification process. It also provides a review of the use of ionic liquids as electrolytes in the thermochemical cells due to the immediate necessity in areas ranging from waste heat conversion to electricity in modern life. Because ionic liquids have hazardous environmental effects, incur high costs, and require complex synthesis and purification process, all must be under control, recovered and optimized. Therefore, understanding their nature has become more important. Additionally, viscosity and conductivity of ILs are an obstacle in experimental studies; besides, the use of redox couples in IL electrolytes must be improved to use in thermochemical cell applications.

Keywords: Ionic liquid; Purification; Functionalization; Synthesis; Analysis; Thermochemical

Introduction

Ionic liquids (ILs) are defined as a multipurpose salt forming ion pairs with melting points below 100 °C or sometimes at or around room temperature (RT). Ion pairs generally consist of asymmetric organic cations (e.g. pyridinium, imidazolium, alkylphosphonium or alkylammonium ions) and weakly coordinating inorganic/organic anions. In ILs, anions and cations have been connected with strong Coulombic interactions in the free movement charge field unlike conventional salts [1]. Other chemical interactions such as hydrogen bonding

and van-der-Waals interactions between ions are very important to determine IL structure [2,3]. The main reason for liquidity of ILs at RT is the fact that ionic interactions with small lattice enthalpies reduce due to inorganic ions replaced with large sized organic ions [4]. They are called molten salts, neoteric solvents, designer solvents, green solvents, liquid electrolytes, ionic fluids, fused organic salt, eco-friendly solvents, greener selects, third group of solvents, etc. [5,6]. Hazards of ILs have not been identified on the living body; therefore, contact with skin, eyes, and any other body parts should be avoided [7].

Nature and cation-anion design of ILs can primarily affect their acidity-basicity and hydro-characteristics.

Depending on this classification, ILs may be categorized as in Table 1.

Type of IL	Example	References
Hydrophobic	1-alkyl-3-methylimidazolium ions with hexafluoro-acetylacetonate anions	Mehdi, et al. [8]
	$N(SO_2CF_3)_2^-(NTf_2^-)^{2,3}$	Bhatt [9]
Hydrophilic	1-Ethyl-3-methylimidazolium ions with choline	Hayakawa, et al. [10]
	2-methacryloyloxy ethyl with trimethyl-ammonium chloride	Jiao, et al. [11]
Acidic	1-(3-propylsulfonic)-3-methylimidazolium chloride	Amarasekara [12]
	1-(4-butylsulfonic)-3-methylimidazolium hydrogensulfate	Amarasekara [12]
Basic	3-amino-propyl-tributyl-phosphonium glycine	Hajipour, et al. [13]
	1-butyl-3-methylimidazolium hydroxide	Hajipour, et al. [13]
Neutral	Hexafluorophosphate	Li, et al. [14]
	bis(trifluoromethanesulfonyl)amide	Kimble, et al. [15]

Table 1: Classification of ILs depending on their acidity-basicity and hydro-characteristics.

Because of their tunable and unique properties, they can arouse much more interest in research and development of media activities. These properties can be listed as follows:

1. good thermal stability (up to 400°C)
2. high chemical stability
3. polarity
4. non-volatility
5. dissolvability
6. non-flammability
7. wide electrochemical potential window
8. viscosity
9. adjustable miscibility
10. high gas solubility to separate gases
11. less toxicity than conventional salts

The most important property of ILs is the fact that their negligible vapor pressure causes a replacement of volatile organic solvents in organic reactions, supplying a huge contribution of green chemistry compared to traditional solvents. Additionally, they ensure a good control over all chemical processes especially in the catalysis. These properties make them different compared with water or organic solvents.

Ionic liquids are characterized by the structural design of anions and cations, structural functionalization of their side chains, and/or mixture of two or more ILs. Especially anion alteration exerts an effect on the physicochemical properties such as viscosity, density, conductivity, and melting point [16]. In order to obtain more specific and intended ILs, arrangement of new ion families (approximately $\sim 10^{18}$ as assumed) and understanding ILs' interactions with other species are mandatory [17]. Besides, purification and functionalization are necessary steps to develop task-specific ILs.

There are many industrial fields to use ILs in as a technological material. Some are showed in Figure 1 Their applications can become diversified over the years with the increasing demand and amount of functionalized ILs [18]. They can be divided further into subcategories in themselves such as separation (gas separation, extractive distillation, extraction, etc.), electrochemistry (batteries, fuel cells, solar panels, metal plating, double layer capacitors, sensors, electro-optic devices, etc.), pharmaceutical (vaccination, drug delivery, active pharmaceutical ingredients, perfume, etc.) and green chemistry (water splitting, green solvents, high-energy materials, thermoelectro-chemical cells, fuel additives, bio-ionic liquids, capturing of CO₂, SnO₂, H₂S, CO, or NO_x etc.) [19,20]. Out of these applications, the use of IL as a solvent is widespread in different type chemical reactions such as Diels-Alder, Friedel-Craft, Heck, hydration, oxidation, alkylation, hydroformulation, esterification, dimerization, polymerization, etc [21].

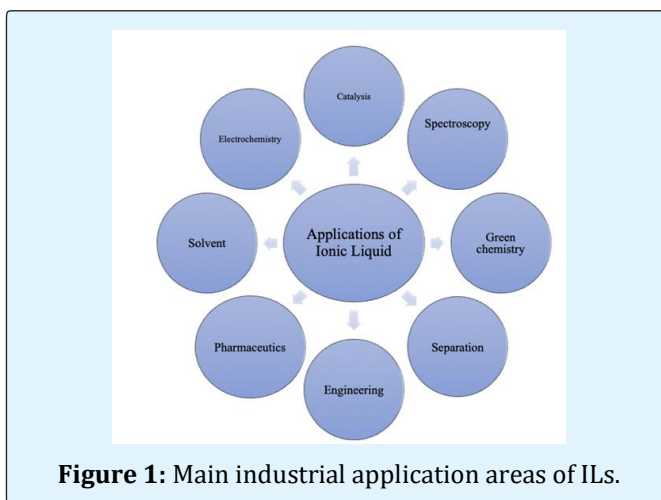


Figure 1: Main industrial application areas of ILs.

Although ILs have a considerable variety of applications, their production strikingly limited, which arises from some adverse properties that they have. Thanks to their potential allowing for varied structural designs, each IL has characteristic solvent properties accompanied by several advantages and disadvantages. For example, mass production results in decreased outlay, but purification is a crucial issue in this procedure. Limitations and disadvantages of ILs may be listed as low biodegradability, ecotoxicity, biocompatibility, high viscosity, sustainability, and cost in the practical applications [22]. These complications are dependent on the cation and anion types/natures and the length of alkyl side chains. When standard OECD tests are run to determine biodegradability, short alkyl chains can cause a decrease in the microbiological decomposition [23]. Additionally, hydrolyzable groups, oxidized groups, and carboxylic acids affect the biodegradability level of ILs [24]. As explained by Mutabil, longer cation alkyl chain length adversely affects toxicity of microorganisms, e.g. marine bacterium *V. fischeri* [25]. Trophic level of the test organisms determines the susceptibility of ILs [26].

In order to reduce production cost of ILs in the industry, they are mixed with other proper materials, such as cellulose, carbon nanotube, epoxy resin, polymers, etc [27]. Additionally, another problem concerned with ILs is that they are petroleum derivatives. Therefore, biobased ILs have been increasingly synthesized recently [28].

In the history of ILs, the first synthesized ionic liquid was ethanalammonium nitrate, reported by Gabriel and Weiner in 1888 [29]. The first protic IL at RT was ethylammonium nitrate with a melting point of 12 °C, which was reported by Walden in 1914 [30]. Back then, this topic did not receive much attention from the scientific community because of its instability, poor solubility in water, and limited application areas. Binary ILs (aluminum (III) chloride with N alkylpyridinium) challenged and broke down this prejudice [31]. Between the 1960s and 1980s, electrolytes containing ionic liquids in battery cells were developed by U.S. Force Academy by using the conductivity nature of chloroaluminate-based ionic liquids with pyridinium or imidazolium cations as known dual intercalating molten electrolyte [32].

After the 1st (1980s) and 2nd (1990s) generation stable ILs were discovered in water and air, the 3rd generation (2000s) ILs called as task-specific ILs were developed by Davis, et al. based on organic cations that were extracted from miconazole, an antifungal agent [33]. Chemical reactions involving imidazole quaternization and anion

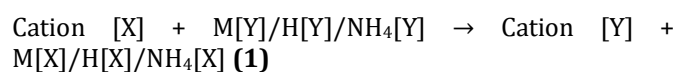
metathesis were used to synthesize the 1st and 2nd generation ionic liquids, respectively. ILs through the separation of CO₂ from gas streams have been investigated since 1999 [34]. Nanotechnological application (Pd-nanoparticle) of ILs was first observed by transmission electron microscopy (TEM) as described by Srinivasan, et al. [35]. In 2002, ionic liquid functionalization protocol was first reported by Zhaou with a specific reference to functional groups in the cation [36]. Dai, et al. were the first to use ILs as a solvent [37]. Moreover, polymer science and green chemistry applications of ILs have been studied since 1998 and 2004, respectively [38]. These mark milestones in IL-based technology. The first functional 1,1,3,3-tetramethylguanidinium lactate ([TMG]L) was synthesized by SnO₂ capturing in 2004 [39]. Ionic liquid crystals in flexible electronics and ion gels have attracted substantial attention particularly in the last years.

Synthesis and Analysis of Ionic Liquids

The type of synthesis is gravely important to obtain the desired ILs. They can be utilized in very different ways such as homogeneously, heterogeneously, multiphase, and in bio-transformations and in organo-catalysis. Until now, many research groups have investigated IL synthesis routes by using different methods.

There are three basic chemical reactions to prepare ILs as shown in Figure 2:

a) Metathesis reaction: After the cation design, anion exchange is performed by a metathesis exchange reaction by using metal salts (silver nitrate, silver thiocyanate) or Brønsted acid to obtain alkylammonium, pyridinium and imidazolium halides. It is probable that the most preferred method for the synthesis of ionic liquids is metathesis reaction. They are equilibrium-controlled, reversible, and under kinetic control [40]. A small amount of impurities occurred after this reaction, which may react with solute materials. In equation (1) related to metathesis reaction, M[Y] is inorganic metal salt, H[Y] is conjugate acid of the desired anion, and NH₄[Y] is ammonium salt



b) Acid-base neutralization: This procedure is very simple, non-contaminated, and inexpensive. It is known that ILs consist of proton acceptor and proton donor sites and stronger acids have much more effects on the proton transfer than bases. Protic ILs are generally prepared by neutralization with proton transfer between

a Bronsted acid and a Bronsted base according to Equation 2:



In protic ILs, neutralization produces active protons, having H-bonds. Near-pure organic tertiary amines with halide acids or some organic acids may be obtained by acid-base neutralization. As explained by Kirchner, acid/base equilibrium is so important in neutralization such as an anion amino acid with [C₂mim][OH] reacted by neutralization [41]. Liu, et al. reported that the electronic environment of the anion could be tuned with the increased basicity of the anion or acidity of the cation [42].

c) The reaction of imidazole carbenes as strong bases: Imidazole-based ILs have no N-H bonds and are reactive towards basic salt, potassium, and bases. Imidazolium cation are conjugate acid-base couples and carbene acts as a base and regenerates its parent ion. Non-contaminated ILs with halide ions or metal ions may be obtained by using imidazole carbenes [43]. Alcohols, carbonic acid, acetic acid, and alkyl sulphonic acid are used to carry out this reaction process. In some reviews, metathesis reaction and acid-base neutralization are considered due to the lack of data about imidazole carbenes reaction [44].

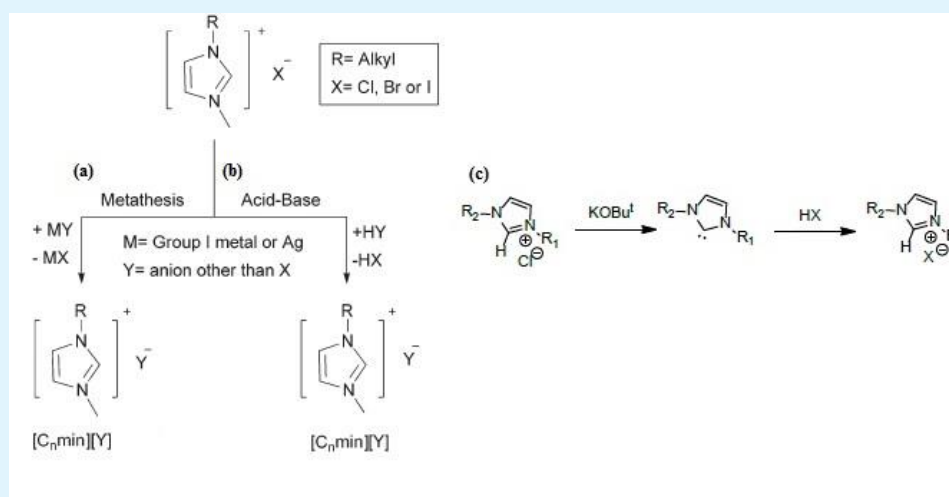


Figure 2: Basic chemical reactions to prepare ILs: a) metathesis reaction, b) acid-base neutralization and c) reaction of imidazole carbenes. Reprinted with permission from Ferraz, et al. [44] and Srouf, et al. [45].

In general, IL synthesis consists of two stages except for cation and anion formation from their starting materials, called as 'simple salts' or '2nd generation ILs', as in Equation 3;

Lewis Base \rightarrow ^D [Cat]⁺[A]⁻; D: triflate, tosylate (for direct synthesis) (3)

Cation Design (Imidazole quaternization): There are two types of cation synthesis: one is protonation of an amine by a free acid and the other is quaternization reactions of amine or phosphine. The described main cations are imidazolium, pyridinium, pyrazolium, pyrrolidinium, ammonium, phosphonium, and cholinium. Sometimes, only quaternization reactions are enough for IL synthesis. They generally do not contain acidic protons. Recently, cation-based ILs have become an attractive

subject due to the ton-scale production opportunity in the industry, inexpensiveness in the preparation step, and thermal/chemical stability [46]. The most used cation design alkylation reaction is 1-methylimidazole, which includes cheap haloalkanes and requires relatively mild temperatures. Besides, it contains specifically halide impurities, which reduce catalyst performance of ILs. Imidazolium compounds contain cations such as 1-ethyl-3-methylimidazolium [C₂mim]⁺ or 1-butyl-3-methylimidazolium [C₄mim]⁺ that make ILs stable and possess low melting points and high viscosities, as reported by Depuydt, et al. [47]. In the use of alkyl halides in quaternization reactions, alkyl chain length and reactivity of the halide determine reaction rate [48].

Anion Design (anion metathesis): Anion formation can be carried out by treating halide salts with Lewis acids or

by anion metathesis. The most common types of anions are halides, nitrate, chloroaluminates, hexafluorophosphate, tetrafluoroborate, alkyl sulphate, alkylcarboxylates, tosylate, triflate, dicyanamide, tris(trifluorophosphate), metal complexes, etc. Symmetrical tetraalkylammonium salts and trialkylsulfonium iodide are the samples which can be produced by this process alone. In Lewis acidic ILs, the molar excess of AlCl_3 can determine the type of acidic, basic or neutral IL where AlCl_3 is the most preferred.

IL synthesis properties, which contain the appropriate combination of cations and anions, may be listed as below:

- The reaction time should be short.
- The reaction should not be multi-step.
- The reaction medium must be designable.
- The yield should be high.
- The need for starting material should be minimal.
- It should be environmentally friendly and safe.
- Impurities such as halides, protic impurities, water, etc. should be minimal.
- In the catalyst applications, the catalysts may be recovered and reused several times.

Classical conventional methods via quaternization of amines were employed in the stirred tanks. This was time-consuming. The highest starting material demand occurred under high vacuum condition. Additionally, solvents were highly needed due to the purification of ILs. Therefore, research groups tried other successful methods. Microwave assisted preparation in solvent and solvent-free medium have been used by many researchers since 2001 [49]. The quaternization reaction have been improved by the use of microwave by heating reactants and superheating solvents to a temperature well in excess of their normal boiling points [50]. Ultrasonic irradiation is another option for synthesis of ILs. Ultrasonic irradiation includes simplicity, lower costs, decreased reaction time, higher yields, and pure cation-anion combinations compared to the classical conventional protocol [51]. However, ILs' decomposition under sonochemical signals is a problem in this procedure. Imidazolium-based ionic liquid derivatives (1,3-dibutylimidazolium-based ILs) were synthesized by Ameta, et al. using the sonochemical (ultrasound-assisted) procedure [52]. A combination of microwave and ultrasound processes was used by Leveque for the synthesis of RT ILs. This incorporation can ensure improved chemical and physical properties [53]. Fang, et al. developed a synthesis type, consisting of flexible reaction scales, so that time efficiency was ensured compared to the conventional heating synthesis [54]. The two-step process among them is the most common route

to synthesize ILs, including the formation of an organic halide salt via alkylation using a haloalkane and then a metathesis reaction introducing the weakly coordinating anion [55].

Besides, the synthesis of metal nanoparticles in ILs was achieved by a number of methods such as chemical reduction, photochemical reduction, ultrasound reduction, electrochemical reduction, gas-phase, etc. [56]. Thus, ILs gain enhanced properties with metal modification. Additionally, polymerized ionic liquids with various structures have been synthesized by direct polymerization of ionic liquid monomers or through post-modification of precursor polymers such as conventional free radical polymerization, versatile-deactivation radical polymerization, etc. [57].

In the related literature, there are a number of classifications of ILs depending on their different properties, anion/cation-based type, acidic/basic type, synthesis type, catalysis performance, chemical reaction procedures, etc. [58]. The most interesting aspect about the classification is that protic ILs, aprotic ILs task-specific ILs, polarizable ILs, bio-ILs, chiral ILs, metal-containing ILs, etc. depend on the generation of ILs. In order to obtain these high-quality ILs, purification is a necessary step in the overall synthesis process because a small amount of impurities have great impacts on the physico-electro-chemical properties (diffusion, viscosity, thermal stability, melting point, dielectric constant, etc.), thereby performance of IL in implemented technology. For example, halide impurities cause a decrease in the thermal stability and stability of the inter-ionic network as well as electrochemical window. Although many studies are provided in the literature, the analytical protocols about the purification are still complicated. Before the synthesis, starting materials must be highly non-contaminant. Additionally, IL preparation must be completed in a short while to minimize impurities such as volatiles, alkylating agents, inorganic halides, protic impurities, organic amines, water, etc. [59]. The most common impurities in ILs are halide ions such as fluoride, chloride, bromide, and iodide. The main reason for their existence is unreacted starting materials and unexpected product reactions or/and side reactions in low probability [60]. Although there is no proper method to obtain halide-free ILs, multiple washing steps (prevent to crystallization of halide salts) and drying are generally preferred under high vacuum conditions. In addition, reversed-phase liquid chromatography, ion pair chromatography, hydrophilic interaction chromatography, capillary electrophoresis and ion chromatography were used to obtain halide-free IL. Transformation of imidazolium-

based zwitterions is another way. Synthesis of some halide-free ILs are more difficult than that of other ILs due to their miscibility with water [61]. In the halide-free purification of ILs, generally activated charcoal is used in the last step of IL synthesis [62]. However, Srivastava showed that activated charcoal was not suitable for iodide-based imidazolium IL purification [63]. Petrovic used rotary evaporation followed by vacuum method to purify [C₄mim][Sal], [HOC₃mim][Sal], [HOC₃mim][Cl] and [HOC₂OC₂mim][Sal] [64]. Distillation and zone melting techniques have been used for the purification of protic ionic liquids and [C₂mim][OTf], [C₂mim]NTf₂, respectively [65]. Sorbent materials such as activated carbon, alumina, and silica (water as a solvent) are widely used to remove organic and/or colored impurities from ILs. The sorbents require a preparation process before ILs are purified. Francesco, et al. reported that 5% residual impurities were detected in RT IL purification [66]. High viscosity of ILs may cause a decrease in the velocity of

purification as reported by Gnahn [67]. During the quaternization reaction process, the oxygen in air could result in the occurrence of colored compounds, thus the quaternization reactions should be carried out in an inert atmosphere [68]. The use of grease, silica, carbon, and alox is known to cause increased impurities.

The most interesting property of ILs is anion or cation that can be tailored depending on the specific application. Such ILs are described as 'task-specific IL' or 'functionalized IL'. A number of interesting reviews about the functionalized ILs have appeared dealing with their specific applications [69,70]. Functionalized ILs have certain desired chemical, physical, or biological properties. Functional groups, namely -OH, -OR, -SH, NH₂, -PPh₂, -Si(OR)₃, SO₃H, urea, or metal complex, are generally tethered covalently to anion or/and cation or zwitterion. The usual method of functionalized ILs is shown in Figure 3.

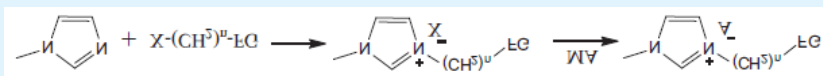


Figure 3: General synthesis route of functionalized ILs where FG: -OH, -OR, -SH, NH₂, -PPh₂, -Si(OR)₃, SO₃H, urea or metal complex. Reprinted with permission from H. Olivier-Bourbigou, et al. [71].

Functionalized ILs with the functional group on the cation have attracted considerable attention since the compounds may easily turn into cations and carbon side chains in IL cations such as guanidinium-based ILs, hydroxyl ammonium-based ILs, imidazolium/pyridinium-based ILs, quaternary ammonium-based ILs, phosphonium-based ILs. Cation-based functionalized ILs have been synthesized by quaternization reaction, Michael-type reaction, ILs containing both amino and carboxy groups, which can be obtained starting from amino acids or amines etc. [72]. Gao, et al. reported that the cation was designed by introducing the functionalized group of -SO₃H to the cation of the IL, so a salt of N,N,N-trimethyl butylsulphonate ammonium hydrosulfate was designed [73]. Yonenaga, et al. reported that tetrapropylammonium and tetrabutylammonium cation-based ILs exhibited significant amphiphilic characteristics with strong hydrophobic and equally strong hydrophilic contributions with the use of the 1-propanol probing methodology [74]. Fujiwara, et al. synthesized ILs including imidazolium, ammonium, and phosphonium cations with aromatic amino acid anions [75].

Anion-based functionalized ILs are used especially in CO₂ and SO₂ capture applications. Gurkan, et al.

synthesized amino acid-based ILs, including trihexyl(tetradecyl)phosphonium prolinatate ([P₆₆₆₁₄][Pro]) and methioninate ([P₆₆₆₁₄][Met]) [76]. Che, et al. prepared fluorescent IL [P₆₆₆₁₄][HBO] by using the acid-base neutralization between 2-(20-hydroxyphenyl)benzoxazole and a solution of phosphonium hydroxide in ethanol that was obtained from trihexyl(tetradecyl)phosphonium bromide by using the anion-exchange method [77]. Cui, et al. designed several kinds of acylamido-based anion-functionalized ILs [78]. Montano, et al. synthesized modified sodium montmorillonite with nine different methylimidazolium-based ionic liquids and each 1-alkyl-3-methylimidazolium cation was moreover modified with HO⁻, Br⁻ and BF₄⁻ anions [79]. Lethesh, et al. showed that nitrile functionalized ILs with thermal stability, especially triflate and trifluoro acetate anion containing ILs, are promising solvents for the dissolution of biomass [80].

Synthesis procedure of functionalized IL is crucial to achieve pure, cost-efficient, and sustainable functionalized ILs. Muthyala, et al. synthesized functionalized ILs by using solid-phase synthesis and fluororous phase synthesis [81]. In the esterification, ricinoleic acid [RA] with methanol was used to synthesize

six different functional ILs as received by Sun, et al. [82]. Fu, et al. designed alkoxysilyl-functionalized ionic liquid by ultrasonic/microwave synergistic method [83]. Alamdari used anion exchange of IL-Br salt for synthesis diacidic hydroxyl functionalized ionic liquid to be used in the synthesis of diester plasticizers [84]. Turgis, et al. synthesized various functionalized hydrophobic ionic liquids based on piperidium, imidazolium, or pyridinium cations bearing ketone moieties which have been synthesized for the liquid/liquid extraction of Ta(V) [85].

Furthermore, the first dysfunctional RT ILs from the 1,2-bis(chlorosulfonyl)tetrafluoroethane were reported in 1998, another example with direct methylation of imidazole using methylated dysfunctional or tetrafunctional perfluorosulfonyl as received by Hickman [86].

Understanding ILs' properties is important to determine their purity and efficiency/stability in the application field. Molecular organization and/or dynamics of ILs as a function of the cation and anion nature and interactions between other molecule groups or metal complexes have been determined by proper analysis techniques [87].

Basic analysis types of ILs for the characterization are listed below:

-NMR: Nuclear magnetic resonance spectroscopy (NMR) is a useful method for a basic understanding of IL interactions and their supramolecular liquid structures. Based upon the earlier IL NMR studies, many ILs have an ordered internal structure in the liquid phase. The most common types of NMR are $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ in the synthetic chemistry using ILs. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ indicated notable differences in the chemical shifts depending on the used anion. The most efficient method is $^1\text{H-NMR}$ to detect the reagents and the resulting ionic liquid with a quaternization reaction. However, monitoring metathesis reactions with it is difficult because only the anion is changed. Therefore, the combination of MS(ESI) and $^1\text{H-NMR}$ analysis are conductible to monitor both the quaternization and the metathesis reaction [88].

-TGA and DSC: The thermal stability of ILs and its upper temperature limit are characterized by thermal decomposition temperature (T_{onset}) (clough). Glass transition and T_{onset} of the ILs are determined by thermo gravimetric analysis (TGA) method. The thermal stability of ILs mainly depends on the ILs' natures such as cation or anion type, yet anion type is more important because decomposition temperature could rise from 200 to 400 °C

with the changing anion type [89]. Thermal conductivity is measured by thermal conductivity analyzer at different temperatures. Melting points are measured with DSC or a different melting point apparatus, but it is not reliable due to the supercooling condition [vadapalli]. The melting point of ILs with unsymmetrical cations and a delocalized charge depends on the hydrogen-bonding presence, packing efficiency, and cation/anion composition [90].

-SEM: IL droplet gives a dark contrast scanning electron microscope (SEM) images because the ILs are not charged by electron beam irradiation without any noise until the applied highly accelerated voltage. Clear ILs images have been obtained by low accelerated voltage under 1 kV to solvate electrons and allow them to move in the liquid. With their liquid form and low vapor pressure, ILs can be directly observed by SEM [91]. Several attempts have been made for SEM observations using IL treatment especially in biological and medical studies. Because biological specimens have complex surface structures, metal or carbon deposition cannot perfectly deposit conducting films on the surfaces [92].

-XRD: In general, X-Ray diffraction can be used to determine solid (crystal) structure and to obtain data about the "liquid" structure. The structure factors and the radial distribution functions can be obtained from diffraction patterns as a fingerprint of the ionic liquid. This method is especially useful when thin film is intercalated with ionic liquid materials [93].

-XPS: X-ray photoelectron spectroscopy (XPS) is a useful method to allow for the detection of species dissolved in the IL, enabling in situ analysis of chemical reactions. Depending on the change in electronic environment of a certain element present in ionic liquids and the cation-anion interaction in ionic liquids, the surface composition of ionic liquids is determined by XPS [94].

-CV: Cyclic voltammetry (CV) is a tool to investigate electrochemical properties and also to determine diffusion coefficients of ILs as an electrolyte in the electrochemical cells such as batteries, fuel cells, thermoelectrochemical cells. In general, it has been performed by using three electrode cells (counter electrode, working electrode, and pseudo-reference) with non-isothermal cells. AC impedance spectroscopy is used to evaluate the conductivity of solvents with it.

Thermoelectrochemical Applications of Ionic Liquids

Thanks to tremendous demand for renewable energy sources and because of increasing pollution, growing

human population, and greenhouse effect, thermal energy devices significantly contribute to sustainable energy technology. Nearly 63% of global energy consumption occurs due to waste heat [95]. As an alternative energy generation, thermoelectrochemistry studies deal with this waste thermal energy to reconvert it into useful electricity. Harvesting thermal energy has wide accessibility and abundance such as heat body, power station waste heat, geothermal activities, car dashboard, industrial waste streams, etc. Thermal energy converting methods may be categorized as thermoelectrics, thermocouples, and stirling engines and thermoelectrochemical cells.

Thermoelectrochemical cells (TECs), sometimes called thermogalvanic or thermocells, are interesting to research due to the waste heat/electricity conversion (conversion of temperature gradient to reliable electrical voltage) as an alternative to traditional energy conversion devices. No emissions and consuming materials are produced; rather, direct and continuous conversion are observed.

TECs rely upon an entropy difference between the two electrodes, where dissimilar temperature sides with a redox reaction, so a potential difference can be generated across two electrodes accompanying proportional to the temperature difference. One electrolyte is located between and contact two electrodes on both sides. The thermoelectric (open circuit) voltage is directly linked to the temperature dependence of the redox potential. Increased temperature difference between the two electrodes causes an increased output of cell voltage. The resulting temperature-dependent potential difference is typically summarized as the Seebeck coefficient (S_e) as shown by Equation (4).

$$S_e = \Delta E / \Delta T \quad (4)$$

where E is the potential and T is the temperature. Standard high S_e is around mVK^{-1} and the negative sign indicates that the hot electrode behaves as the anode [96]. When equation (4) is modified according to thermodynamical rules, electrochemical thermopower of thermocell can be given by equation (5);

$$S_e = \partial E / \partial T = -\Delta S / nF \quad (5)$$

where E is full-cell voltage, T is temperature, n is the number of electrons transferred in the reaction, F is Faraday's constant and ΔS is the entropy change for the cell reaction under the standard condition.

In an ideal TEC, the small temperature difference in waste heat between the heat source, and the surrounding ambient equal a high electric voltage. The main purpose is to achieve high power density output and conversion efficiency; therefore, cell design must be improved and optimized with electrode materials and electrolyte materials and by redox process through oxidation and reduction reactions and adjustment of the quantity and mobility of the redox couples, etc. The responsibility of electrolytes is ion transfer between anode and cathode during charge-discharge processes depending on the charge transport and diffusion capability of ions.

There are a great number of studies having investigated dissolving redox couples in a suitable solvent or electrolyte. The most common aqueous thermocells contains generally 0.4 M. ferrocenium/ferrocene ($[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$) due to the highest Seebeck coefficient (1.4 mV K^{-1}), where ferrocene solubility is rather low. This value ranges between 1 mVK^{-1} and 1.7 mVK^{-1} for dissolution in water and depends on the supporting electrolytes that have high boiling temperatures such as DMSO, *g*-butyrolactone, DMF and IL and spin state changes [97]. ILs are very suitable with their low vapor pressure, which allows for longer service lifetimes and chemical stability, which allows for the harvest of higher-temperature waste heat. Cobalt, iodine, iron, nickel and sulfur-based redox couples in ionic liquids are being increasingly investigated [98]. Functionalized ILs can be used to increase solubility of redox-active compounds. Han, et al. tethered ferrocene and quaternary ammonium or phosphonium cations and these IL salts showed soluble and non-volatile properties [99].

Besides, solid state TECs are the first examined membranes and also typically semiconductors and their working principles based on Seebeck effect, its 2D-schematic representation are shown in Figure 4. Compared to solid-state TECs, liquid types involving various redox couples in solutions are preferred in the practical applications because solid-state TECs have low Seebeck coefficient (S_e) ($\mu\text{V/K}$), high preparation costs, relatively low efficiency and long-term production. In liquid-based TECs, the solutions may be aqueous (e.g. containing the ferrocyanide/ ferricyanide redox couple), organic (3-methoxypropionitrile (MPN)), gelled (agar agar) or ionic liquid [100]. Aqueous-based electrolytes restrict their operating temperatures to less than $100 \text{ }^\circ\text{C}$ due to the parasitic heat transport and they have limited electrochemical window less than $\sim 1 \text{ V}$, so device performance decreases.

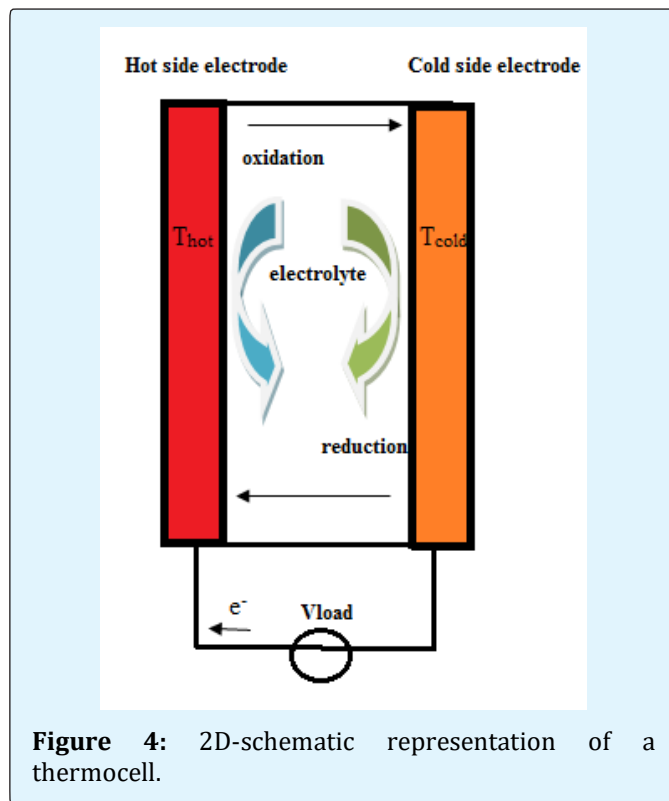


Figure 4: 2D-schematic representation of a thermocell.

ILs are new alternative materials as solvents or electrolytes in energy technology with their incredible properties. Energy technology device types may be subcategorized as advanced batteries (e.g. lithium batteries, sodium ion cells, magnesium batteries), dye-sensitized solar cells, double layer capacitors, actuators, fuel cells, hydrogen storage systems, and thermo-cells. Common IL ion families using energy applications are described by Macfarlane, et al. in Figure 5.

As an electrolyte, ILs are attractive thanks to their good thermal and electrochemical stability, high ionic conductivity, very high electrochemical window of $\sim 3\text{--}4\text{ V}$, non-volatility, and non-flammability properties [101]. In the mid- to high-temperature range, the operating temperature of ILs (up to $\sim 300\text{ }^\circ\text{C}$) is higher than aqueous and organic solutions particularly, so they are suitable solutions to harvest in thermal energy applications. Additionally, low thermal conductivity allows a larger temperature difference to be maintained across the cell. Seebeck coefficient is directly related to the structural changes of the redox species and the solvent during the redox reaction. Wide liquid temperature range of ILs allows high voltage due to the larger temperature differences between the two electrodes. At this point, ILs'

influence on the redox couples must be understood so can obtain higher Seebeck coefficients.

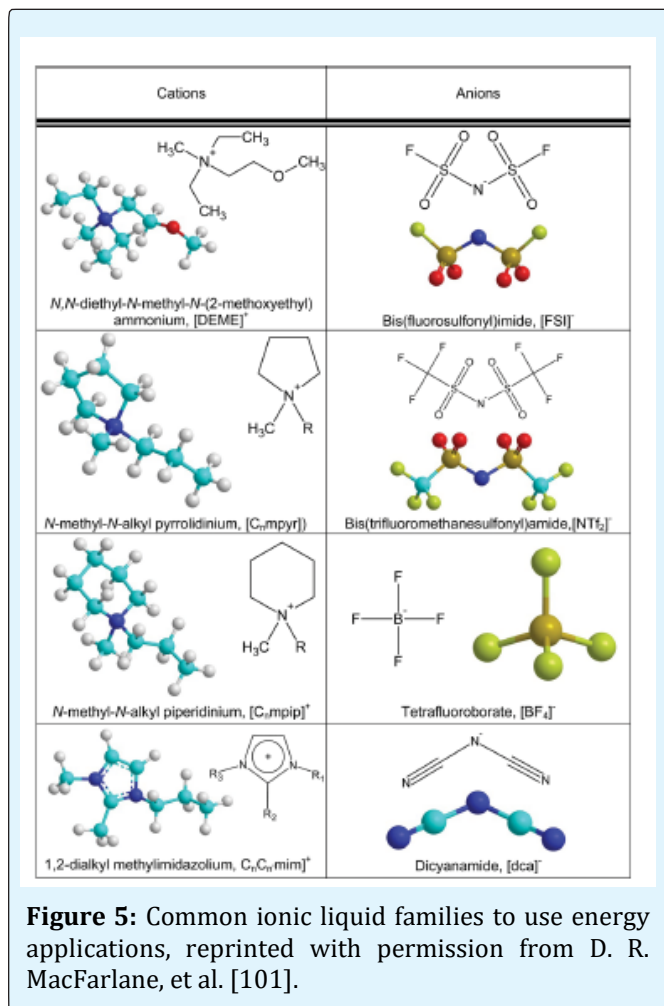


Figure 5: Common ionic liquid families to use energy applications, reprinted with permission from D. R. MacFarlane, et al. [101].

In 1968, for the first time Cornwell, et al. showed the use of ILs in TECs, but the ILs' effects were not fully understood [102]. In 1980, Chum, et al. contributed with a similar study [103].

The first reported functioning TEC with an ionic liquid was produced by Abraham, et al. [104]. As an electrolyte, The $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple in choline $[\text{H}_2\text{PO}_4]$ combined with water and single-walled carbon nanotubes (SWNTs) as an hot-cold electrodes were used. In another study conducted by Abraham, IL electrolyte was achieved using $\text{Co}^{\text{II/III}}$ tris(bipyridyl) redox couple in 1-ethyl-3-methylimidazolium tetracyanoborate IL that showed the highest power density (240 W m^{-2}) [105]. Aldous, et al. investigated that the ferrocenium|ferrocene redox couple in an ionic liquid and redox centre had been covalently

tethered to either the 1-ethyl-3-(methylferrocenyl)imidazolium[EimFc]⁺ cation or ferrocenylsulfonyl (trifluoro-methylsulfonyl)imide anion, [FcNTf₂]. It was showed that tethering a fixed charge to a desirable redox centre could simultaneously improve solubility and entropic changes [106]. Black, et al. showed that lithium bis(trifluoromethylsulfonyl)imide (Li[NTf₂])/tetraglyme(G4) mixing resulted in thermo-electrochemical electrolytes when combined with lithium metal electrodes [107]. S_e results of the I⁻/I³⁻ redox couple in ILs for TEC were found to be 0.03, 0.26, and 1.67 mV K⁻¹ corresponding to [P_{2,2,2,(101)}][NTf₂], [C₂mim][BF₄] and [C₂mim][NTf₂], respectively [108].

Cabral, et al. investigated that electrochemistry of redox couple ([Co(bpy)₃]^{2+/3+}) in four types of ILs and three aprotic molecular solvents. The diffusion coefficient of [Co(bpy)₃]²⁺ was related to solvent viscosity and the k⁰ values of [Co(bpy)₃]^{2+/3+} in the ILs were high on GC working electrode. The [Co(bpy)₃]^{1+/2+} reaction was not chemically reversible in 3-methoxypropionitrile [109].

The [Co^{II/III}(bpy)₃](NTf₂)_{2/3} redox couple in a range of different ionic liquids was investigated by He, et al. to determine ILs' effects on the thermodynamic properties and they showed that addition of propylene carbonate to the ILs significantly caused an increase in the current and power densities. In this comprehensive study, the selected ILs were (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C₄mim][NTf₂], 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide, [C₄dmim][NTf₂], 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonate, [C₄dmim][OTf], 1-butyl-3-methylimidazolium tetrafluoroborate, [C₄mim][BF₄], 1-butyl-3-methylimidazolium methanesulfonate, [C₄mim][MeSO₃], 1-ethyl-3-methylimidazolium methanesulfonate, [C₂mim][MeSO₃], 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [C₄mim][eFAP], trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide, [P_{6,6,6,14}][NTf₂], trihexyl(tetradecyl)phosphonium p-toluenesulfonate, [P_{6,6,6,14}][Tos], and trihexyl(tetradecyl)phosphonium tetrafluoroborate, [P_{6,6,6,14}][BF₄].

In a study by Anari in 2016, the thermoelectrochemistry of mixed redox couples (ferrocene and iodine) were investigated for the first time and the value of 1.67 mV K⁻¹ for [DiBoylFc][I₃] being one of the highest reported Seebeck coefficient for a solute in the ionic liquid [Emim][NTf₂]. Siddique, et al. received that the power and current output density of I⁻/I³⁻ redox couple in ammonium-based protic ILs for TEC and the

highest reported Se value was 420 mV K⁻¹ for I⁻/I³⁻ redox process. These protic ILs were Bis(2-ethylhexyl)ammonium trifluoroacetate (BEHA TFA), Bis(2-ethylhexyl) ammonium methanesulfonate (BEHA MS), Bis(2-ethylhexyl)ammonium trifluoromethanesulfonate (BEHA TFMS), Bis(2-ethylhexyl)ammonium tosylate (BEHA tosylate), Tris(2-ethylhexyl)ammonium trifluoroacetate (TEHA TFA), Tris(2-ethylhexyl) ammonium methanesulfonate (TEHA MS), Tris(2-ethylhexyl)ammonium trifluoromethanesulfonate (TEHA TFMS), and Tris(2-ethylhexyl)ammonium tosylate [110].

Anion or cation intercalation-based energy storage systems have been investigated by many researchers [111]. As electrode material using graphite with a combined non-aqueous electrolyte was first developed by Carlin, et al. They adapted the reductive and oxidative intercalation from ionic liquid electrolytes without any additional salt such as 1-ethyl-3-methylimidazolium hexafluorophosphate (EMI⁺PF₆⁻) [112]. Lastly, in the study by Agiorgousis, Al-graphite electrochemical cell involving IL as an electrolyte was detected to have high voltage due to the thermodynamic instability of the AlCl₄⁻ intercalated graphite [113]. Before this, a similar study was reported by Choi on the destructive intercalation of MMDMEA cations that contributed to the enhancement of cycling performance in graphite/LiCoO₂ cells with DMC/MMDMEA-TFSI/1 M LiPF₆ in Li-ion battery [114]. The ability to perform similar experimental studies in TECs can lead to the achievement of successful results.

A more detailed electrochemical model involving IL as an electrolyte is needed for future studies and the influence of the nature of cation or anion of IL on the TECs performance is not yet well understood, especially in relation to functionalized ILs.

Conclusion

Until today, a great number of scientific papers and books with ionic liquids (ILs) have been reported. Undoubtedly, their desirable and functional properties have increased the interest in them. Due to the wide application areas of ILs and many IL synthesis processes for this purpose, IL is a comprehensive research field that needs to be investigated from various perspectives.

The increase in people's demand for sustainable technology devices leads to the introduction of such applications to everyday life. Of them, thermoelectrochemical cells (TECs) are very important as alternative and cheap renewable energy devices. Recently,

development and research activities concerning this topic have increased.

Electrolyte type and electrolyte/electrode interaction play important roles in electrochemical cells. Especially over the last years, ILs as an electrolyte have been shown to enhance performance in the electrochemical cells (batteries, actuators, fuel cells, thermoelectrochemical cells) that were widely adapted to our lifestyle. ILs transform into liquid form over a wider temperature range, which offers advantages for the electrochemical devices.

In this chapter, we have introduced some useful reviews about ILs, especially as an electrolyte in TECs. Additionally, it is also planned to lay the groundwork for similar future studies on functionalized ILs, recovery of the redox couple, electrode material and various IL electrolytes and the use of redox couples in ionic liquid (IL) electrolytes.

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