Review Article

Applications of Ionic Liquids in Electrochemical Sensors and Biosensors

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Ionic liquids (ILs) are salt that exist in the liquid phase at and around 298 K and are comprised of a bulky, asymmetric organic cation and the anion usually inorganic ion but some ILs also with organic anion. ILs have attracted much attention as a replacement for traditional organic solvents as they possess many attractive properties. Among these properties, intrinsic ion conductivity, low volatility, high chemical and thermal stability, low combustibility, and wide electrochemical windows are few. Due to negligible or nonzero volatility of these solvents, they are considered “greener” for the environment as they do not evaporate like volatile organic compounds (VOCs). ILs have been widely used in electrodeposition, electrosynthesis, electrocatalysis, electrochemical capacitor, lubricants, plasticizers, solvent, lithium batteries, solvents to manufacture nanomaterials, extraction, gas absorption agents, and so forth. Besides a brief discussion of the introduction, history, and properties of ILs the major purpose of this review paper is to provide an overview on the advantages of ILs for the synthesis of conducting polymer and nanoparticle when compared to conventional media and also to focus on the electrochemical sensors and biosensors based on IL/composite modified macrodisk electrodes. Subsequently, recent developments and major strategies for enhancing sensing performance are discussed.

1. Introduction

ILs are a class of materials which have attracted many scientists as holding a great promise for green chemistry applications [1–3]. Paul Walden gave a definition to ILs that is still acknowledged today [4]. They are “materials composed of cations and anions, those melt around 100°C or below as an arbitrary temperature limit.” This definition identifies the difference from molten salts that have also been known for a long time and are inorganic salts with high melting temperatures [5]. A typical IL has a bulky organic cation (e.g., N-alkylpyridinium, N-N'-dialkylimidazolium) that is weakly coordinated to an organic or inorganic anion, such as BF_4^- , Cl^- , I^- , CF_3SO_3^- , and AlCl_4^- . The big difference in the size of a bulky cation and a small anion does not allow packing of lattice, which happens in many inorganic salts; instead, the ions are disorganized. This results in that some of these salts remain liquid at the room

temperature [2]. ILs are liquid electrolytes composed entirely of ions. Due to the high ionic conductivity, nonvolatility, low vapor pressure, thermal stability, hydrophobicity, and wide electrochemical window that ionic liquids possess, these compounds have become a novel solution to problems encountered with organic solvents and these molecules are a prospective solution to the limitations encountered in electrochemical systems [6, 7]. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new syntheses. Due to these unique properties, ILs have been widely used in different field of applications (Figure 1). These physical properties can be varied by selecting different combinations of ions [8, 9]. Since the electrochemical window of the pure ILs depends on the electrochemical stability of the cation and/or anion, understanding the ion behavior at the electrode surface leads to improvement and implementation of the IL to the desired

FIGURE 1: Applications of ILs.

system [10]. The presence of an abundance of charge carriers means that when ILs are used as solvents, no supporting electrolyte is required for electrochemical experiments and this minimizes waste towards greener site [9].

2. History of ILs

The field of ILs has been reviewed by several authors, including Welton [8], Holbrey and Seddon [9], and Seddon [2]. Moreover, ILs have been known for a long time, but their extensive use as solvents in chemical processes for synthesis and catalysis has recently become significant. The discovery date of the first IL is disputed, along with the identity of its discoverer. Ethanolammonium nitrate (m.p. 52–55°C) was reported in 1888 by Gabriel and Weiner [11]. The first RTIL [EtNH₃][NO₃] (melting point 12°C) was discovered in 1914 [12]. This material is probably the first described in the literature that fulfills the definition of ILs used today. In this context it should be noted that at that time Walden had of course no idea of this definition or the whole concept of ILs. Consequently, it is not surprising that at time no attention was paid to the potential of this class of materials. Moreover, Walden had reported the physical properties of ethylammonium nitrate, [C₂H₅NH₃]⁺ NO₃⁻, which has a melting point of 12°C, formed by the reaction of ethylamine with concentrated nitric acid, but interest did not develop until the discovery of binary ILs made from mixtures of aluminum(III) chloride and N-alkylpyridinium [13] or 1,3-dialkylimidazolium chloride [14].

In 1970s and 1980s, Osteryoung et al. [13, 15] and Hussey et al. [14, 16, 17] carried out extensive research on organic

chloride-aluminium chloride ambient temperature ILs and the first major review of ILs was written by Hussey [18]. The ILs based on AlCl₃ can be regarded as the first generation of ILs.

In the late 1990s, ILs became one of the most promising chemicals as solvents. An important property of the imidazolium halogenoaluminate salts is that their physical properties such as viscosity, melting point, and acidity could be adjusted by changing the alkyl substituents and the imidazolium/pyridinium and halide/halogenoaluminate ratios [19]. Two major drawbacks for some applications were moisture sensitivity and acidity/basicity. In 1992, Wilkes and Zaworotko obtained second generation of ILs with “neutral” weakly coordinating anions such as hexafluorophosphate (PF₆⁻) and tetrafluoroborate (BF₄⁻), allowing a much wider range of applications [20]. After the first reports on the synthesis and applications of air stable ILs such as 1-n-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF₆]), the number of air and water stable ILs has started to increase rapidly [21]. Unlike the chloroaluminate ILs, these ILs could be prepared and safely stored outside of an inert atmosphere. Generally, these ILs are water insensitive; however, the exposure to moisture for a long time can cause some changes in their physical and chemical properties. Therefore, ILs based on more hydrophobic anions such as tri-fluoromethanesulfonate (CF₃SO₃⁻), bis(trifluoromethanesulfonyl)imide [(CF₃SO₂)₂N⁻], and tris(trifluoromethanesulfonyl)methide [(CF₃SO₂)₃C⁻] have been developed [22–24]. These ILs have received extensive attention not only because of their low reactivity with water but also because of their large electrochemical windows. Usually these ILs can be well dried to the water contents of below as 1 ppm under vacuum at temperatures between 100 and 150°C.

3. Electrochemical Properties of ILs

ILs are made of positively and negatively charged ions, whereas water and organic solvents, such as toluene and dichloromethane, are made of molecules. The structure of ILs is similar to the table salt such as sodium chloride which contains crystals made of positive sodium ions and negative chlorine ions, not molecules. While salts do not melt below 800°C, most of ILs remains liquid at room temperature. Since these conventional molten salts exhibit high melting points, their use as solvents in applications is severely limited. However, ILs are liquid generally up to 200°C. ILs have a wide liquid ranges.

Researchers explained that ILs remain liquid at room temperature due to the reason that their ions do not pack well [25]. Combination of bulky and asymmetrical cations and evenly shaped anions forms a regular structure, namely, a liquid phase. The physical and chemical properties of ILs can be varied over a wide range by the selection of suitable cations and anions. Some of the properties that depend on the cation and anion selection include melting point, viscosity, and solubility characteristics [26]. Most widely

TABLE 1: List of some abbreviations.

Abbreviation	Name
[BEIm]	1-Butyl-3-ethylimidazolium
[BMIm]BF ₄	1-Butyl-3-methylimidazolium tetrafluoroborate
[BMIm]PF ₆	1-Butyl-3-methylimidazolium hexafluorophosphate
[BMIm]Tf ₂ N/NTf ₂	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMP]Tf ₂ N/NTf ₂	1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[BMMIm]Tf ₂ N/NTf ₂	1-Butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIm]TfO	1-Butyl-3-methylimidazolium trifluoromethanesulfonate
[EMIm]BF ₄	1-Ethyl-3-methylimidazolium tetrafluoroborate
[EMIm]Cl	1-Ethyl-3-methylimidazolium chloride
[EMIm]PF ₆	1-Ethyl-3-methylimidazolium hexafluorophosphate
[OMIm]Tf ₂ N/NTf ₂	1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[PMP]	1-Propyl-1-methylpyrrolidinium
TFA	Trifluoroacetate
Tf ₂ N/NTf ₂	Bis(trifluoromethylsulfonyl)imide
TfO	Trifluoromethanesulfonate
BF ₄	Tetrafluoroborate
PF ₆	Hexafluorophosphate

used ILs and their structures are given in Table 1. As solvents, ILs possess several advantages over conventional organic solvents, which make them environmentally compatible [27–34].

- (i) A diverse range of organic, inorganic, and organo-metallic compounds are soluble in ILs. The solubility of gases such as O₂, benzene, nitrous oxide, ethylene, ethane, and carbon monoxide is also good, which makes them attractive solvent system for catalytic hydrogenations, carbonylations, hydroformylation, and aerobic oxidations.
- (ii) Due to the large electrochemical window, they are especially suitable as reaction media for electrochemical (and also chemically induced) polymerization processes leading to conducting polymers.
- (iii) ILs are highly polar.
- (iv) ILs consist of loosely coordinating bulky ions.
- (v) Most of ILs have a liquid window of up to 200°C which enables wide kinetic control.
- (vi) ILs have high thermal conductivity.
- (vii) ILs are immiscible with many organic solvents.
- (viii) ILs are nonaqueous polar alternatives for phase transfer processes.
- (ix) The solvent properties of ILs can be tuned for a specific application by varying the anion cation combinations.
- (x) ILs tend to have good thermal stability and can be liquid over a range of 300°C. This wide liquid range is distinct advantages over traditional solvent system that have a much narrower liquid range; for example, water has a liquid range of 100°C or toluene 206°C.

- (xi) The majority of ILs have low volatility. This property makes them easy to contain, use, and transfer and in addition they can be used under high vacuum conditions. This is an important feature that reduces chronic exposure to solvent vapors.
- (xii) ILs can be recycled. Recovery and recycling of the catalyst are also possible with the ILs, thus keeping production of waste and loss of valuable catalysts to a minimum.

Properties such as nonflammability, high ionic conductivity, and electrochemical and thermal stability of ILs make them ideal electrolytes in electrochemical devices like in batteries [35–38], capacitors [39–41], fuel cells [42], photovoltaics [43–48], actuators [49], and electrochemical sensors. Recently, ILs have captured the attention of the analysts to use them in different analytical applications as well. ILs can improve separation of complex mixtures of both polar and nonpolar compounds when used either as stationary phase or as additives in gas-liquid chromatography [50–53], liquid chromatography [52], and capillary electrophoresis [54]. They are also used in optical sensors [55, 56] and also to enhance the analytical performance of the matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) [57]. The use of ILs in different applications is determined by their intrinsic properties.

3.1. Physical Properties of ILs

3.1.1. Conductivity. In electrochemical experiments, the conductivity of a solvent is of vital importance. ILs have reasonably good ionic conductivities compared with those of organic solvents/electrolyte systems (up to 10 mS cm⁻¹) [58]. At elevated temperatures of, for example, 200°C a conductivity of 0.1 Ω⁻¹ cm⁻¹ can be achieved for some systems. ILs have advantages over traditional organic solvents

as their conductivity is intrinsic and they do not require the addition of supporting electrolyte. However, at room temperature their conductivities are usually lower than those of concentrated aqueous electrolytes. Based on the fact that ILs are composed solely of ions, it would be expected that ILs have high conductivities. This is not the case since the conductivity of any solution not only depends on the number of charge carriers but also on their mobility. The large constituent ions of ILs reduce the ion mobility which, in turn, leads to lower conductivities. Furthermore, ion pair formation and/or ion aggregation lead to reduced conductivity. In fact, the change in conductivity with composition in ILs can be attributed almost directly to changes in the viscosity [59]. Hence, ILs of higher viscosity exhibit lower conductivity. Increasing the temperature results in increase in conductivity and decrease in viscosity.

3.1.2. Viscosity. The viscosity of a solvent is an important electrochemical property since high viscosities limit some applications and slow down the rate of diffusion-controlled chemical reactions [60].

As a result of the strong electrostatic and other interaction forces the viscosity of ILs is typically 10 to 100 times higher than that of water or organic solvents [61–64]. The viscosity of IL is affected by the nature of both the cations and anions. Alkyl chain lengthening in the cation leads to an increase in viscosity. This is due to stronger van der Waals forces between cations leading to increase in the energy required for molecular motion. The nature of the anion also affects the viscosity of the IL, particularly through relative basicity and the ability to participate in hydrogen bonding. It is found that PF_6^- and BF_4^- anions form much more viscous IL due to strong H...F interactions than those IL formed with the weakly basic $[\text{NTf}_2]^-$ anion, in which the negative charge is quite delocalized over the two sulfoxide groups [65]. Differences in viscosities may also be caused by the size, shape, and molar mass of anion with smaller, lighter, and more symmetric anions leading to more viscous ILs.

3.1.3. Density. ILs are composed only of ions; almost all ILs are denser than water, from 1.0 to 1.6 g cm^{-3} depending on their ion structure. The density has been found to decrease with increasing alkyl chain length on the imidazolium cation [66, 67]. Similarly, in the ammonium and sulfonium salts, the density decreases with increasing alkyl chain length. This clearly shows that the charged ion unit is heavier than the hydrocarbon chain. Accordingly, the density of ILs is tunable to some extent. The density of aromatic onium salts is higher than that of aliphatic ammonium salts. Generally, density decreases in the order of pyridinium salts > imidazolium salts > aliphatic ammonium salts and piperidinium salts. The densities of ILs are also affected by the anion species. Similarly to the trends for cations, the density of ILs decreases with increasing alkyl chain length of the anion. The density of ILs is increased on the introduction of a heavy chain such as fluoroalkyl chains. For example, 1-ethyl-3-methylimidazolium (EMIm) salts became heavier

with the following anion species: $\text{CH}_3\text{SO}_3^- < \text{BF}_4^-$ and $\text{CF}_3\text{COO}^- < \text{CF}_3\text{SO}_3^- < (\text{CF}_3\text{SO}_2)_2\text{N}^- < (\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$. It is easy to understand this order as an effect of formula weight of the ions. However, these tendencies are still empirical and a perfect correlation between ion structure and density is not available.

3.1.4. Thermal Stability and Decomposition Temperature. ILs can be thermally stable up to temperatures of 450°C with decomposition temperatures around $300\text{--}500^\circ\text{C}$. The thermal stability of ILs is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds, respectively [68]. The thermal decomposition temperature decreases as the anion hydrophobicity increases. Halide anions reduce the thermal stability of ILs, with decomposition occurring at least 373 K below corresponding ILs with nonhalide anions. Relative anion stabilities have been suggested by Huddleston et al. [69] as $\text{PF}_6^- [\text{BMIm}] \text{PF}_6 > \text{NTf}_2^- \approx \text{BF}_4^- > \text{halides}$. The ILs $[\text{BMIm}][\text{PF}_6]$, $[\text{BMIm}][\text{NTf}_2]$, and $[\text{BMIm}][\text{BF}_4]$ have decomposition temperature of 373 K higher than the corresponding halide IL $[\text{BMIm}][\text{I}]$. The trend of thermal stability with respect to cation species appears to go as follows: phosphonium > imidazolium > tetraalkyl ammonium pyrrolidinium [70].

3.1.5. Electrochemical Potential Window. The electrochemical potential window (potential region without significant background current) is a key criterion to be considered when any medium is used in electrochemical measurements. A general common feature of ILs is their inherent redox-robustness, because of the robustness of cations and anions employed for their preparation. ILs generally exhibit a wide potential window, which is highly desirable property for applying the ILs as electrochemical solvents. Typical windows of 4.5–5 V have been reported for the ILs [71, 72] and even an enlarged electrochemical window up to 7 V was found for some IL such as 1-butyl-3-methyl-imidazolium tetrafluoroborate [73]. On the whole, this potential window range is equal to slightly wider than that observed in conventional organic electrolytes but largely exceeds that accessible in aqueous electrolytes.

4. Applications of ILs in Conducting Polymer and Nanoparticle Syntheses

The utilization of ILs for the synthesis and use of conducting polymers (CPs) brings together two of the most exciting and promising areas of research from recent years. CPs are organic materials that can display electronic, magnetic, and optical properties similar to metals, but that also have the mechanical properties and low density of a polymer. They have the potential to allow the design and fabrication of a vast number of electrochemical devices including photovoltaics, batteries, chemical sensors, supercapacitors, conducting textiles, electrochromics, and electromechanical actuators [74–77].

Research into CPs has been increasingly intense for the last 3 decades, since MacDiarmid, Heeger, and Shirakawa

published their seminal work on polyacetylene, which demonstrated that the conductivity of these materials can be increased by several orders of magnitude by doping with anions [78, 79]. The importance of these materials and the progress made in this field is reflected in the award of the Nobel Prize for chemistry in 2000 to these founding researchers in this area.

ILs are new solvents for polymerization reactions. The potential benefits of using ILs as electrolytes in CPs devices have been investigated by a number of authors for applications such as actuators [80–88], supercapacitors [89–91], electrochromic devices [83, 92], and solar cells [93] with significant improvements in lifetimes and device performance reported.

The potential of the ILs as media for electrosynthesis of CPs was first demonstrated in the late 1980s for polyfluorene [94, 95], polythiophene [96], or polyphenylene [97] in chloroaluminate ILs. But the high sensitivity of these ILs towards water produced HCl that led to rapid decomposition of the polymer. One should remember that electrooxidative polymerization involves the coupling between two radical cations of the monomer or of the produced oligomers [98]. It is likely that stabilizing interactions should play a favorable role in the coupling between two charged species, explaining the good results noticed in ILs.

Electrosynthesis of polypyrrole (pPy) in [BMIm][PF₆] on iron and Pt [99, 100] and in [EMIm][OTf], [EMIm][BF₄], and [EMIm][PF₆] on Pt [101], poly(3,4-ethylenedioxythiophene) (PEDOT) in [EMIm][NTf₂], [BMIm][PF₆], and [BMIm][BF₄] on Pt [102–104], or in [EMIm][BF₄] on “K-glass” of poly(3-(4-fluorophenyl)thiophene) in [EMIm][NTf₂] and [EEMIm][NTf₂] on Pt [105], poly(paraphenylene) (PPP) in 1-hexyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate on Pt [106], poly(3-chlorothiophene) in [BMIm][PF₆] on Pt [107], and of polythiophene in [EMIm][NTf₂] on Pt [108] has been studied.

Lu et al. [109] reported significant improvements in device performance when the ILs 1-ethyl-3-methylimidazolium hexafluorophosphate, [C₂mim][PF₆], and 1-ethyl-3-methylimidazolium tetrafluoroborate, [C₂mim][BF₄], were used as supporting electrolytes for pPy and poly(aniline) actuators and for PEDOT in electrochromic devices, respectively. For the PEDOT study, the IL was also used as the growth medium for the electropolymerization.

Easier or more efficient preparation of CPs films in neat ILs as compared with conventional media was highlighted in some works [102, 107, 110, 111]. The electropolymerization of benzene could be achieved with milder conditions in ILs than in the usually employed concentrated sulfuric acid or liquid SO₂ [110]. As mentioned by the authors, the use of ILs would enable further studies on the nanoscale with *in situ* scanning tunneling microscopy (STM) that would be totally precluded in aggressive media like 18 M sulfuric acid or liquid SO₂ [110]. Comparison of electropolymerization of pyrrole in neat [EMIm][OTf], as well as in [EMIm][OTf] diluted in CH₃CN or H₂O (0.1 mol L⁻¹), demonstrated that the electropolymerization is more efficient in the neat IL [110]. This result strengthens the idea that ILs are powerful

media for the electrochemical generation of CPs films in a greener way.

The influence of the nature of the ILs towards the preparation, the morphology, and the electrochemical activity of polymers has been investigated [101, 102, 108]. The electropolymerization of pyrrole was found to be more efficient in [EMIm][OTf] than in [EMIm][BF₄] and [EMIm][PF₆], with a formation of smoother and more highly doped polymer films than those from the latter ILs. This result indicates a significant influence of the anion [103]. Thiophene, bithiophene, and terthiophene have been polymerized in imidazolium- and pyrrolidinium-based [NTf₂] ILs. Whatever the monomer, use of the pyrrolidinium salts led to polythiophene films that were smoother and denser and had a lower electroactive surface than those from the imidazolium salts [108]. Very striking differences between films grown in conventional solvents and those grown in ILs have been observed using scanning electron microscopy (SEM) [102, 112–116]. Generally, the films grown from ILs appear to be considerably smoother, which may also result in improved conductivities. SEM analysis of poly(thiophene) grown from [C₂mim][NTf₂] and [C₄mpyr][NTf₂] reveals a slightly smoother morphology for the poly(thiophene) films from the pyrrolidinium ionic liquid [105].

Dong et al. [117] have investigated the electrochemical polymerization of 1,2-methylenedioxybenzene (MDOB) in an IL 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF₆]. This polymer poly(1,2-methylenedioxybenzene) (PMDOB) showed good redox activity and stability even in concentrated sulfuric acid. In contrast to acetonitrile containing 0.1 mol/L Bu₄NBF₄, BMImPF₆ serves as both the growth medium and an electrolyte. Hence, enhanced electrochemical stability of PMDOB can be easily obtained on repetitive redox cycling; as formed PMDOB represented good electrochromic properties from green grass to opalescent between doped and dedoped states. SEM results demonstrated that smooth and compact PMDOB films composed of ordered nanostructures were obtained, implying their possible utilizations in ion-sieving films, ion-selective, and matrices for catalyst particles.

Sekiguchi et al. [118] reported the electropolymerisation of pyrrole in 1-ethyl-3-methylimidazolium triflate, both neat and as a 0.1 M solution in either acetonitrile, or water and observed an improvement in the morphology and electrochemical capacity of the films. Moreover, Pringle et al. [119] reported the electrochemical synthesis of inherently CPs such as polypyrrole in a molecular solvent/electrolyte system such as acetonitrile/lithium perchlorate and IL as well. We use ILs 1-butyl-3-methylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, and N, N-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl)amide, both as the growth medium and as an electrolyte for the electrochemical cycling of polypyrrole films. Use of the ionic liquid as the growth medium results in significantly altered film morphologies and improved electrochemical activities over traditional organic solvents.

Pyrrole was electropolymerized in ILs using a platinum wire that was vertically placed into the cell, completely immersed in the ILs and touching the bottom of the cell. It was observed that if the polymerization started as an initial layer on a section of the working electrode, prolonged electrosynthesis led to a growth of the polymer film along the surface of the ionic liquid. This solution-surface electropolymerization was found to occur with a large range of ILs [120]. Fibrils of polypyrrole, polythiophene, and PEDOT were obtained from closely related interfacial polymerization. Using this time a chemical polymerization route, a biphasic ionic liquid/water system with the oxidant dissolved in the aqueous phase and the monomers dissolved in the ILs, allows the polymerization to occur at this RTIL/water interface. The resulting polymers consisted of fibrils about 50 nm wide and several hundreds of nanometers long [121].

The introduction of the metal nanoparticles into the sensing interface to facilitate the electron transfer can significantly improve the sensitivity [122]. Nanoparticles of noble metals have attracted special interest because they differ from their bulk metal counterparts. Their size controllability, chemical stability, large surface area, thermal stability, good biocompatibility, high catalysis activity, surface tenability, and suitability for many surface immobilization mechanisms make them very advantageous for application in sensors [121, 123]. For example, CaCO_3 nanoparticles can offer a large surface area for adsorption of substances of interest due to their porous structure.

ILs possess pre-organized structures, mainly through hydrogen bonds [124–126] which induce 3D structure dimensionality in these systems. Conversely, aggregates of classical salts display charge-ordered structures. Since ILs can form extended hydrogen bond networks at the liquid state, therefore they demonstrate this very unique property of high self-organization on the nanomolecular scale and can be classified as supramolecular fluids. This nanoscale structural organization of ILs can be used to drive the spontaneous extended ordering of nanomaterials [127, 128]. Some of the classical examples that ILs as designer solvents for the synthesis of metal nanoparticles have illustrated this concept include IL-mediated synthesis of ordered mesoporous materials and microporous aluminophosphates, wherein ILs served as both the solvent and structure-directing agents [129, 130]. One another example in this category includes synthesis of protein and silica nanocapsules in $[\text{BMIm}][\text{BF}_4]$ IL via self-organization process, as was demonstrated recently by Suarez et al. [131]. It has also been established that the properties of imidazolium-based ILs are dependent on their organized nanoaggregates, rather than merely on their isolated cations and anions [132, 133]. The 3D arrangement of the imidazolium-based ILs is generally formed through chains of the cationic imidazolium rings, which generates supramolecular channels in which anions are typically accommodated as chains [126]. The formation of this 3-D ionic network entails high directional polarizability, which provides an opportunity to adopt a range of external species in either hydrophilic or hydrophobic regions of ILs [134]. Therefore, size and shape of the metal nanoparticles synthesized in ILs are typically modulated by

the volume of these 3-dimensionally arranged regions within IL environment. It would probably not be an overstatement to classify ILs as nanostructured solvents, with a potential to direct the tailored synthesis of nanoscale materials.

A series of studies in the literature suggests that ILs interact relatively strongly with the surface of metal nanoparticles, which have been summarized in a recent report [135]. In fact, transition metal nanoclusters and nanoparticles stabilization by imidazolium-based ILs are now considered as a classical stabilization method [135]. Therefore, in account of the previous points, unambiguously ILs are an appealing medium for the formation and stabilization of catalytically active transition metal nanoparticles.

5. Applications of IL in Gas Sensor

Extensive efforts have been made to develop new materials and transducers for gas sensing both at room and at high temperatures with particular emphasis on optimizing interface properties among the gas phase, the sensitive materials, and the transducer. IL thin films perform well as sensor interfaces and provide additional control over selectivity and sensitivity when interacting with analytes in the gas phase.

Due to the entire ionic composition, which eliminates the need to add supporting electrolyte, the intrinsic conductivity and negligible vapor pressure ILs are unique compounds to be used in the development of stable electrochemical sensors for gaseous analytes such as O_2 , CO_2 , and NH_3 [136–142]. The superoxide radical ($\text{O}_2^{\bullet-}$) which is generated *in situ* by the reduction of O_2 was found to be stable in ILs at glassy carbon, gold (Au), or platinum (Pt) electrodes [136–138]. This makes the amperometric detection of O_2 possible and the reported solid-state O_2 gas sensor based on porous polyethylene supported $[\text{EMIm}][\text{BF}_4]$ membrane has a wide detection range, high sensitivity, and excellent reproducibility [136]. With increasing levels of CO_2 in the sample, cyclic voltammetry shows an increased cathodic peak current from the production of $\text{O}_2^{\bullet-}$ radicals together with the decreased peak current from the reverse scan of oxidation. This indicates that the generated $\text{O}_2^{\bullet-}$ radical reacts irreversibly with CO_2 to form peroxydicarbonate ion, $\text{C}_2\text{O}_6^{2-}$ [138].

Cai et al. [143] have developed an SO_2 gas sensor resembling the Clark model that employs an IL as the electrolyte, while Wang and coworkers [136, 144] have reported a supported IL membrane-coated oxygen sensor, incorporating 1-ethyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_2\text{MIm}][\text{BF}_4]$) into a polyethylene membrane.

The oxidations of halides, Cl^- and Br^- , display some different behaviors in ILs than those observed in organic media. Oxidation of Cl^- in $[\text{BMIm}][\text{PF}_6]$, with large concentrations of $[\text{BMIm}][\text{Cl}]$, displays an irreversible process on both platinum and graphite electrode. The main feature was that this oxidation does not lead to chlorine gas evolution but to the formation of oxidation products that stay in the ILs in the form of complexes between Cl_2 molecule and chloride ion where the Cl_3^- is the major product [145–147]. Moreover,

the electrochemical oxidation of the nitrite ion (NO_2^-) and nitrogen dioxide gas (NO_2) in $[\text{EMIm}][\text{Tf}_2\text{N}]$ has been studied by cyclic voltammetry on Pt electrodes of various sizes [148]. From chronoamperometric measurements, the following solubility values were calculated: 7.5 mM for NO_2^- and 51 mM for NO_2 , indicating that this IL is a potential media for sensing NO_2 gas.

Determination of ammonia based on the electrooxidation of hydroquinone in dimethylformamide (DMF) and $[\text{EMIm}][\text{Tf}_2\text{N}]$ has also been reported [141]. Ammonia can remove protons from the hydroquinone molecules reversibly and thus facilitate the oxidation process giving a new wave at less positive potentials in the cyclic voltammogram (CV). Similar responses were found in both dimethylformamide and $[\text{EMIm}][\text{Tf}_2\text{N}]$. The detection limit of ammonia based on this method is 4.2 ppm in DMF. Solubility and thermodynamic properties of different gases such as CO_2 , H_2 , and O_2 in $[\text{BMIm}][\text{PF}_6]$ have been thoroughly studied [149]. ILs are also utilized as sensing materials for detection of organic vapors by using the quartz crystal microbalance (QCM) technique [150–152].

Yu et al. [153] have developed an integrated sensor that combines electrochemical and piezoelectric transduction mechanisms into a single miniaturized platform for explosives. The IL $[\text{BMIm}][\text{BF}_4]$ was used as both the electrolyte and the sorption solvent for the two-dimensional electrochemical and piezoelectric gas sensors. Jin and coworkers developed a high-temperature sensor array using a QCM-based sensor [151]. Thin films of seven ILs were employed to provide sensitivity to concentrations of various flammable organic vapors (i.e., ethanol, dichloromethane, benzene, heptane).

Schäfer and coworkers [154] developed a QCM-IL sensor for use as an artificial nose using the ubiquitous $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$. The IL was spin coated onto the surface of a 10 MHz AT-cut quartz crystal with gold electrode. The work specifically studied the response of the sensor to ethyl acetate. The deposition of the IL on the surface of the electrode decreased the resonance frequency of the QCM by 2017 Hz, demonstrating the popularity of QCMs for sensor applications. Goubaidouline and coworkers opted to entrap IL within nanoporous alumina deposited on the surface of the QCM to eliminate dewetting of the QCM and solving the problem of the soft IL surface [152]. The detection limits for the organic vapors ranged from 321 to 7634 mg/m^3 . Sensor response times were on the order of minutes.

6. Application of IL in Electrochemical Sensors

By far the most highly investigated aspect of IL-based electrochemical sensors is in the realm of electrochemistry, with most of them being based on IL modified electrodes [155–158] wherein the IL typically serves as both binder and conductor. Common attributes observed when incorporating ILs into electrodes include higher conductivity, good catalytic ability, long-term stability (including stability at elevated temperature), superior sensitivity, improved linearity, and better selectivity. Different electrochemical

sensors have been developed by using ILs. Several groups had used different kinds of ILs in electrode modification for the design of new electrochemical sensors or as novel electrocatalytic materials [159–164]. Lu et al. [165] used a novel chitosan/1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF_6) composite material as a new immobilization matrix to entrap the proteins and studied the electrochemistry behaviors of hemoglobin (Hb) on the glassy carbon electrode. Maleki et al. developed an IL-modified carbon paste electrode (CPE) with 1-octylpyrrolidinium hexafluorophosphate (OPFP) as binder and further used it for the detection of some electroactive molecules [166–168]. Sun et al. also applied the IL-modified CPE for the investigation of the direct electrochemistry of hemoglobin [169–171].

Sun et al. [172] have used hydrophilic IL 1-ethyl-3-methylimidazolium tetrafluoroborate $[\text{EMIm}][\text{BF}_4]$ as a modifier in the CPE to make a new kind of IL-modified carbon paste electrode (IL-CPE). The fabricated IL-CPE showed good electrocatalytic behaviors towards the oxidation of metol with the enhancement of the redox peak current and the decrease of the peak-to-peak separation with a detection limit of $2.0 \times 10^{-6} \text{ mol L}^{-1}$ (3σ). The established method was successfully applied to the synthetic samples and photographic solutions detection with good recovery.

Xiao et al. [173] described the carbon nanotube (CNT)/Ruthenium (Ru), Pd, and Au/IL composite electrode for the fabrication of a nonenzymatic glucose sensor. Electrochemical experiments show that the PtRu- (1:1, i.e., ratio of $(\text{H}_2\text{PtCl}_6)/(\text{RuCl}_3)$) multiwalled carbon nanotube- (MWNT-) IL nanocomposite-modified glassy carbon electrode (PtRu(1:1)-MWNT-IL/GCE) has smaller electron transfer resistance and larger active surface area than PtRu(1:1)/GCE, PtRu(1:1)-MWNT/GCE, PtPd(1:1)-MWNT-IL/GCE, and PtAu(1:1)-MWNT-IL/GCE. The PtRu(1:1)-MWNT-IL/GCE also presents stronger electrocatalytic activity towards the glucose oxidation than other electrodes. At -0.1 V , the electrode responds linearly to glucose up to 15 mM in neutral media, with a detection limit of 0.05 mM ($\text{S/N} = 3$) and detection sensitivity of $10.7 \mu\text{A cm}^{-2} \text{ mM}^{-1}$. Meanwhile, the interference of ascorbic acid, uric acid, acetamidophenol, and fructose is effectively avoided. The as-made sensor was applied to the determination of glucose in serum and urine samples. The results agreed closely with the results obtained by a hospital. This novel nonenzyme sensor thus has potential application in glucose detection.

Jabbar et al. [174] have found the excellent electrocatalytic reductive dechlorination of 1,1 bis(*p*-chlorophenyl) 2,2,2-trichloroethane (DDT) in the IL 1-butyl-3-ethylimidazolium tetrafluoroborate ($[\text{BMIm}][\text{BF}_4]$) in the presence of a cobalamin derivative afforded 1,19-(ethylidene) bis(4-chlorobenzene) (DDO) and 1,19-(ethenylidene) bis(4-chlorobenzene) (DDNU) with 1,19-(2-chloroethylidene) bis(4-chlorobenzene) (DDMS); the enhanced reactivity, as well as the recyclability of the cobalamin derivative catalyst in IL, makes the present system more efficient for the development of green technologies.

Safavi et al. [168] have constructed a nonenzymatic composite electrode by mixing the nanoscale $\text{Ni}(\text{OH})_2$ with

graphite powder and [Opyr][PF₆], which showed excellent electrocatalytic activity towards oxidation of glucose in an alkaline solution.

The mechanism of this catalytic detection is as follows:

Ding et al. [175] have used IL, 1-(2-hydroxyethyl)-3-methyl imidazolium tetrafluoroborate ([HEMIm][BF₄]), as the supporting electrolyte for direct electrochemical response of Myoglobin (Myb) at the basal plane graphite (BPG) electrode. Both anodic and cathodic peak currents increased linearly with the potential scan rate. Compared with the supporting electrolyte of phosphate buffer, [HEMIm][BF₄] played an obvious promotion for the direct electron transfer between Myb and the BPG electrode. Further investigation suggested that Myb was adsorbed tightly on the surface of the BPG electrode in the presence of [HEMIm][BF₄] to form a stable, approximate monolayer Myb film. Myb adsorbed on the BPG electrode surface showed a remarkable electrocatalytic activity for the reduction of oxygen in a [HEMIm][BF₄] aqueous solution. Based on these, a third-generation sensor could be constructed to directly detect the concentration of oxygen in aqueous solution with a limit of detection of 2.3×10^{-8} M.

Tu and coworkers [176] developed a composite material based on single-walled carbon nanotube (SWCNT), a water-insoluble porphyrin (hydroxyferriprotoporphyrin, hematin), and [BMIm][PF₆]. This composite material was used to modify a GC electrode in order to study the direct electrochemistry and electrochemical property of porphyrin. The porphyrin dissolved in [BMIm][PF₆] can be self-assembled on SWCNT by π - π noncovalent interaction, which leads to good dispersion of the SWCNTs in the [BMIm][PF₆] and a direct electrochemical response corresponding to the Fe^{3+/2+} redox couple. The presence of SWCNT and [BMIm][PF₆] produces a synergic effect that accelerates the electron-transfer between porphyrin and the electrode. As a consequence, the porphyrin/SWCNT/[BMIm][PF₆]-modified GC showed excellent electrocatalytic activity towards the reduction of trichloroacetic acid (TCA). This study provides a facile way for preparing biofunctional materials, accelerating electron-transfer, and extending the application of porphyrins/IL-based composite materials in sensor applications.

Singh et al. [177] developed a greener electrochemical method for a chemical warfare agent (CWA) using triethyl sulfonium bis(trifluoromethylsulfonyl)imide (TSBTSI). Addition of CWA nitrogen mustard-2 (NM-2) to TSBTSI showed a new peak in addition to an enhancement in peak current than observed for blank TSBTSI. The calculated diffusion coefficient for NM-2 in TSBTSI and Acetonitrile-TBAP was found to be 2.14×10^{-7} cm² s⁻¹ and 1.57×10^{-4} cm² s⁻¹, respectively. The linear response was obtained in the range of 2.94×10^{-5} to 1.17×10^{-3} M with the correlation coefficient 0.9977 and the detection limit of 1.47×10^{-5} M (s/n = 3) with chronoamperometric method. Electrochemical impedance spectroscopy results revealed an

enhancement of solution conductivity after the addition of NM-2 to TSBTSI. The large number of available IL based on the combination of anion and cation and their unique properties allows scope for the possible electrochemical detection of toxic CWAs in a greener way.

7. Application of IL in Electrochemical Biosensors

Biosensors are small devices employing biochemical molecular recognition properties as the basis for a selective analysis. The major processes involved in any biosensor system are (i) analyte recognition, (ii) signal transduction, and (iii) readout. In an electrochemical biosensor, a molecular sensing device couples a biological recognition element to an electrode transducer, which converts the biological recognition event into an electrical signal.

ILs have shown good compatibility with biomolecules and enzymes and even whole cells are active in various ILs. [BMIm][Cl] was found miscible with silk, which is an attractive biomaterial with excellent mechanical properties and biocompatibility. The patterned films cast from this silk-IL solution supported normal cell proliferation and differentiation [178]. Recently, some authors have reported increased stability of enzymes in ILs compared with stability in some organic solvents [179–181]. ILs were also found to act as agents to stabilize proteins effectively at elevated temperatures [182]. Laszlo and Compton have also reported the catalysis of hemin activated by an electron acceptor in IL solutions and it was found that the activity of hemin increased with the enhanced amount of IL in the methanol-IL system [179].

Dramatically enhanced activity and thermal stability of horseradish peroxidase (HRP) were obtained when it was immobilized in the [BMIm][BF₄]-based sol-gel matrix [183]. The IL was used as a template solvent for the silica gel matrix via a simple sol-gel method via hydrolysis of tetraethyl orthosilicate in [BMIm][BF₄]. This particular HRP-immobilized sol-gel matrix was further used in amperometric biosensors [184]. The novel amperometric hydrogen peroxide biosensor based on this ionogel exhibited excellent stability and sensitivity. The detection limit for hydrogen peroxide is reported to be 1.1 μ M.

Direct electrochemical reduction of hemin has been studied by cyclic voltammetry and chronocoulometry in the ILs, [BMIm][PF₆] and [OMIm][PF₆] [185]. N-Methylimidazole- (NMI-) ligated hemin had a lower $E_{1/2}$ than pyridine-ligated hemin in both ILs, which is consistent with the stronger electron donor characteristic of NMI. It was further discovered that while hemin is electrochemically active in IL, its behavior is modified by the ligand field strength and surface adsorption phenomena at the working electrode. Electrochemistry and electrocatalysis of a number of heme proteins entrapped in agarose hydrogel films in [BMIm][PF₆] have also been investigated [186]. UV-Vis and FTIR spectroscopy show that the heme proteins retain their native structure in agarose film. CV shows that the direct electron transfer between the heme proteins and glassy

carbon electrode (GCE) is quasireversible in [BMIm][PF₆]. The redox potentials for hemoglobin (Hb), myoglobin, HRP, cytochrome c, and catalase were found to be lower than those in aqueous solution, indicating the catalytic effect in the IL matrix. The heme proteins can catalyze electroreduction of trichloroacetic acid and tert-butyl hydroperoxide in [BMIm][PF₆] [186]. Direct electrochemical response of HRP [187], myoglobin [188], and Hb [169] has been observed on IL-modified electrodes.

Zhao et al. [155] mixed MWCNTs with the 1-octyl 3-methylimidazolium hexafluoro phosphate, by grinding them together in a mortar to create a gel-like paste which was then applied to the surface of a cleaned GC electrode. Using a platinum wire and a saturated calomel electrode as auxiliary and reference electrodes, respectively, CVs were measured for dopamine in phosphate buffer (PB) for both the MWCNT-IL-modified GC electrode and a bare GC electrode. In both cases, two pairs of redox peaks characteristic to dopamine were observed. An immediate advantage of the MWCNT-IL-modified electrode (ME) was a larger peak current with smaller peak separations, an indication of faster electron transport to the electrode surface. Similar measurements for ascorbic acid and uric acid revealed that the anodic peak potentials were, respectively, shifted more negative (by ~0.31 V) and more positive (~0.02 V), when employing the MWCNT-IL-modified electrode compared with GC. This feature helps to eliminate overlap between dopamine's anodic peak and the anodic peaks of ascorbic acid and uric acid as occurred at a GC electrode. Further resolution was achieved by using differential pulse voltammetry. At pH 7.08, the ascorbic acid and uric acid peaks are separated from dopamine by 0.20 and 0.15 V, respectively. Hence, dopamine could be determined in the presence of uric acid and ascorbic acid in 100-fold excess. The detection limit of dopamine was determined to be 1.0×10^{-7} M with a linear dynamic range up to 1.0×10^{-4} M.

In fabricating electrochemical biosensing layers, the CNT/IL-based composite materials are advantageous due to the following reasons: (i) retain inherent mechanical, electrical, and thermal properties of CNT (e.g., large surface area, good electroconductive nanowires, etc.), (ii) better solvent and conductivity property of ILs (e.g., large potential window, ion conductor, etc.), and (iii) proper interaction between CNT and ILs. Direct physical adsorption is one of the most widely used approaches to immobilize biomolecules on CNT/IL-modified sensing layers. However, the preparation of CNT/IL pastes and composites by direct mixing of the CNT with a suitable IL has been limited by the very high background currents which would limit monitoring the faradaic current, and hence, limit the use of such a combination. This increased capacitive charging current can be reduced using steady-state linear sweep voltammetry at rotating disk electrodes, as suggested by Compton group [189].

Most of carbon paste electrodes (CPEs) reported for electroanalysis are based on incorporation of a sensing material into the carbon paste. The carbon paste usually consists of graphite powder dispersed in a nonconductive mineral oil such as paraffin. Incorporation of mineral oil

gives some disadvantages. Mineral oil is not component fixed since it is derived from refining of petroleum and processing of crude oil. As a result, contaminants or matrix components may unpredictably effect on detection and analysis. In addition, the mechanical stability of CPEs rests somewhere between that of liquid membrane electrodes and solid state electrodes. CPEs have attracted attention as ion selective electrodes mainly due to their improved renewability, stable response, and low ohmic resistance when compared to membrane electrodes [190–193].

Musameh and Wang [194] have prepared IL-carbon composite glucose biosensor with the help of n-octylpyridinium hexafluorophosphate (nOPPF₆) and graphite powder and they found that the electrocatalytic properties of the ILs are not impaired by their association with the graphite powder. The marked electrocatalytic activity towards hydrogen peroxide permits effective amperometric biosensing of glucose in connection with the incorporation of glucose oxidase within the three-dimensional IL/graphite matrix. The prepared composite film shows accelerated electron transfer with low background current and improved linearity. A comparison was made between IL-based biocomposite devices and conventional mineral oil/graphite biocomposite and it is found that IL-based biocomposite devices performed well with good linearity. In this work the influence of the IL and glucose oxidase (GOx) loading was also studied towards the amperometric and voltammetric responses.

Kachoosangi et al. [195] developed a new composite material based on MWCNT and [Opyr][PF₆], which showed an extremely low capacitive and background current compared to graphite and mineral oil-based CPEs. The new composite material combines the unique and attractive electrocatalytic behaviour of CNTs and [Opyr][PF₆], with very low background current and mechanically robust structure compared to many other forms of composite and paste electrodes made from CNTs and other ILs. Wang et al. [196] prepared a composite material based on [BNIm][BF₄], MWCNT, and chitosan successfully used for the electrochemical oxidation of NADH.

CNT and carbon microbeads were incorporated into the water-immiscible [BMIm][PF₆] [197]. In particular, CNT has been demonstrated to be physically cross-linked in the viscous ILs, forming gels [198]. These carbon-composite materials mixed with HRP, Hb, or glucose oxidase were dropped onto gold or GCEs. The direct electrochemistry of heme proteins or glucose oxidase immobilized at these carbon materials has been investigated and this promising biointerface promoted direct electron transfer and biocatalytic performance [198–200].

CNT-modified GCEs showed enhanced sensitivity and stability in the oxidation of phenolic compounds [199]. The CNT-modified electrodes were also found to show good electrocatalytic ability to biomolecules such as dopamine (DA), ascorbic acid (AA), and dihydronicotinamide adenine dinucleotide (NADH) [199–203]. CNTs usually exist as tangled bundles that are difficult to dissolve in both aqueous and organic media. However, they can be well individualized in ILs due to "cation- π " interactions and a

CNTs-IL gel can easily be prepared using IL as the binder [204], where the CNTs greatly enhance the conductivity of the system. Electrochemical functionalization of single wall carbon nanotubes in [BMIm][PF₆] was used to make a glucose sensor by covalently binding glucose oxidase (GOD) to the modified nanotube [205].

Zhang et al. [206] have prepared a novel polyaniline-IL-carbon nanofiber (PANI-IL-CNF) composite by *in situ* one-step electropolymerization of aniline in the presence of IL and CNF for fabrication of amperometric biosensors for phenol. This biosensor exhibited a wide linear response to catechol ranging from 4.0×10^{-10} to 2.1×10^{-6} M with a high sensitivity of $296 \pm 4 \text{ AM}^{-1} \text{ cm}^{-2}$, a limit of detection down to 0.1 nM at the signal-to-noise ratio of 3, and applied potential of -0.05 V . According to the Arrhenius equation, the activation energy for enzymatic reaction was calculated to be 38.8 kJ mol^{-1} using catechol as the substrate. The apparent Michaelis-Menten constants of the enzyme electrode were estimated to be 1.44, 1.33, 1.16, and $0.65 \mu\text{M}$ for catechol, p-cresol, phenol, and m-cresol, respectively. The functionalization of CNF with PANI in IL provided good biocompatible platform for biosensing and biocatalysis.

Tao et al. [156] compared the interaction of [BMIm][BF₄] with three different types of carbonaceous material for use in MEs: acid-treated MWCNTs (AMWCNTs), pristine MWCNTs (PMWCNTs), and pyrolytic graphite powder (PGP). To prepare the MEs, each carbon material was ground with the water-miscible IL [BMIm][BF₄], resulting in AMWCNT-[BMIm][BF₄], PMWCNT-[BMIm][BF₄], and PGP-[BMIm][BF₄] composites which were then applied on to a polished GC electrode surface. The composite films were presumably attached through electrostatic adsorption between the negatively charged surface and the positive component of the IL. The conductivities and optical properties of each composite were compared using ac impedance and Raman spectroscopy. [BMIm][BF₄] formed a gel when ground with MWCNTs, whereas a viscous liquid resulted from the admixture of [BMIm][BF₄] with PGP. Raman spectroscopy demonstrated that both AMWCNs and PMWCNs electrostatically interact with [BMIm][BF₄] while no such interaction occurs between PGP and [BMIm][BF₄], accounting for the fact that PGP-[BMIm][BF₄] blend fails to form gel. Data from ac impedance and CV measurements (using potassium ferricyanide, K₃[Fe(CN)₆]) demonstrated that the ME conductivity increases in the following order: PGP-[BMIm][BF₄] < PMWCNT-[BMIm][BF₄] < AMWCNT-[BMIm][BF₄]. Thus, the AMWCNT-[BMIm][BF₄] ME system was selected for additional bioelectrochemical studies. For these experiments, the redox biocatalyst (i.e., hemin, hemoglobin (Hb), or HRP) was initially mixed with the IL prior to grinding with AMWCNTs and the ensuing gel fixed to the GC electrode by rubbing. CV measurements showed a pair of reversible peaks attributed to the heme Fe³⁺/Fe²⁺ redox couple for all three MEs. The hemin, Hb, and HRP-AMWCNT-[BMIm][BF₄] MEs all demonstrated electrocatalytic behavior towards H₂O₂, with the fastest electron transfer rate observed for the hemin-based ME. The MEs were reproducibly fabricated and reportedly exhibited

good stability, retaining $\geq 60\%$ of the peak current after 20 cycles.

A novel amperometric biosensor was fabricated based on the immobilization of cholesterol oxidase (ChOx) into a cross-linked matrix of chitosan- (Chi-) IL (1-butyl-3-methylimidazolium tetrafluoroborate) by Gopalan et al. [207]. In this study, the surface of bare electrode (indium tin oxide-coated glass) was modified with the electrodeposition of Au particles onto thiol- (SH-) functionalized MWNTs. The presence of Au particles in the matrix of CNTs provides an environment for the enhanced electrocatalytic activities. The MWNT(SH)-Au/Chi-IL/ChOx biosensor exhibited a linear response to cholesterol in the concentration range of 0.5–5 mM with a correlation coefficient of 0.998, good sensitivity ($200 \mu\text{AM}^{-1}$), a low response time (approximately 7s), repeatability (R.S.D value of 1.9%), and long-term stability (20 days with a decrease of 5% response). The synergistic influence of MWNT(SH), Au particles, Chi, and IL contributes to the excellent performance for the biosensor.

Kachoosangi et al. [195] prepared a new composite electrode using MWCNT and the IL n-octylpyridinium hexafluorophosphate (OPFP). One major advantage of this electrode compared to other electrodes using carbon nanotubes and other ILs is its extremely low capacitance and background currents. A 10% (w/w) loading of MWCNT was selected as the optimal composition based on voltammetric results, as well as the stability of the background response in solution. The new composite electrode showed good activity towards hydrogen peroxide and NADH, with the possibility of fabricating a sensitive biosensor for glucose and alcohol using glucose oxidase and alcohol dehydrogenase, respectively, by simply incorporating the specific enzyme within the composite matrix. The marked electrode stability and antifouling features towards NADH oxidation was much higher for this composite compared to a bare glassy carbon electrode. While a loading of 2% MWCNT showed very poor electrochemical behavior, a large enhancement was observed upon gentle heating to 70°C, which gave a response similar to the optimum composition of 10%. The ease of preparation, low background current, high sensitivity, stability, and small loading of nanotubes using this composite can create new novel avenues and applications for fabricating robust sensors and biosensors for many important species.

The composite film based on Nafion and hydrophobic IL 1-butyl-3-methyl-imidazolium hexafluorophosphate [BMIm][PF₆] was explored by Chen et al. [208]. In this work, nafion was used as a binder to form nafion-ILs composite film and help [BMIm][PF₆] effectively adhered on GCE. X-ray photoelectron spectroscopy (XPS), CV, and electrochemical impedance spectroscopy (EIS) were used to characterize this composite film, showing that the composite film can effectively adhere on the GC electrode surface through Nafion interacting with [BMIm][PF₆] and GC electrode. Meanwhile, doping [BMIm][PF₆] in Nafion can also effectively reduce the electron transfer resistance of nafion. The composite film can be readily used as an immobilization matrix to entrap horseradish peroxidase (HRP). A pair of well-defined redox peaks of HRP was obtained at the HRP/Nafion-[BMIm][PF₆] composite film-modified

GC electrode through direct electron transfer between the protein and the underlying electrode. HRP can still retain its biological activity and enhance electrochemical reduction towards O_2 and H_2O_2 . It is expected that this composite film may find more potential applications in biosensors and biocatalysis.

An organophosphorus hydrolase (OPH) immobilized on MWCNT/IL where IL = [BMIm][BF₄], [BMIm][PF₆], or [BMIm][NTf₂]-modified composite electrodes showed higher sensitivity and better stability in detecting organophosphate [209]. The modification of MWCNTs with these different ILs allowed high dispersion of CNT bundles and the formation of a 3D-network structure, good compatibility with OPH, and accelerated electron-transfer reaction at the interface. The electron-transfer rate of the three modified electrodes increased after the incorporation of OPH in the following order: OPH/[BMIm][PF₆] < OPH/[BMIm][BF₄] < OPH/[BMIm][NTf₂]. Sun et al. [210] developed two methods, namely, casting and rubbing methods to prepare the Fc-filled SWCNT-modified GC electrode which showed excellent mediation of H_2O_2 based on the Fc/Fc⁺ couple used as electron-transfer mediator for oxidation of H_2O_2 to O_2 and reduction of H_2O_2 to H_2O .

Gels of acid treated multiwall CNTs with water-miscible IL [BMIm][BF₄] were made by grinding them together [156]. GCE modified by this gel was used in direct electrochemical study of heme proteins (Hb and HRP). The heme proteins entrapped in CNTs-[BMIm][BF₄] gel exhibit good biocatalytic activity towards H_2O_2 due to the biocompatibility of [BMIm][BF₄]. This composite material has shown to keep the bioactivity and to facilitate direct electron transfer of heme proteins. Carbon fiber microelectrode has also been modified by CNTs-IL gel and used in bioelectrochemical studies [158]. The carbon fiber microelectrode modified by CNTs-IL gel promotes greatly the direct electron transfer of glucose oxidase and exhibits effective catalytic activity to biomolecules, such as DA, AA, and NADH. IL has also been used as binder to modify electrode surface of multiwall carbon nanotubes. This construction has better electrochemical properties than by chitosan or Nafion-modified electrodes. The GOD adsorbed at this modified electrode shows good stability and electrocatalytic activity to glucose with a broad linear concentration range up to 20 mM [155].

Rahimi et al. [211] developed a nanocomposite material consisting of amine functionalized multiwalled carbon nanotubes and an IL, 1-butyl-3-methylimidazolium tetrafluoroborate and further it was used in construction of a novel catalase-based biosensor for the measurement of hydrogen peroxide. The modified electrode exhibited a quasireversible CV corresponding to the Fe²⁺/Fe³⁺ redox couple in the heme prosthetic group of catalase with a formal potential of -460 mV in 0.1 M phosphate buffer solution at pH = 7.0. The nanocomposite film showed an obvious promotion of the direct electron transfer between catalase and the underlying electrode. The apparent charge transfer rate constant and transfer coefficient for electron transfer between the electrode surface and enzyme were reported as 2.23 s⁻¹ and 0.45, respectively. The immobilized catalase exhibited

a relatively high sensitivity (4.9 nA/nM) towards hydrogen peroxide.

Graphene [212], known as single layer graphite, has attracted intensive scientific interest in recent years due to its two-dimensional and unique physical properties, such as high intrinsic carrier mobility at room temperature ($\approx 10^5$ cm²/V·s), excellent mechanical strength, and electrical and thermal conductivity comparable to the in-plane value of graphite [213]. Owing to the unique properties [214, 215] graphene/IL-based composite materials have been widely used in fabricating electrochemical biosensors [216].

Shan et al. [217] reported the first graphene-based glucose biosensor with graphene/polyethylenimine-functionalized IL nanocomposites-modified electrode which exhibits wide linear glucose response (2 to 14 mM, $R = 0.994$), good reproducibility (relative standard deviation of the current response to 6 mM glucose at -0.5 V was 3.2% for 10 successive measurements), and high stability (response current +4.9% after 1 week). In this work, direct electron-transfer of GOx and electrocatalytic activity towards the reduction of O_2 and H_2O_2 at the polyvinylpyrrolidone-protected graphene/polyethyleniminefunctionalized IL/GOx-modified electrode has been demonstrated.

IL-graphene-based biosensors have been reported for direct electron transfer and detection of different targets also such as NADH and guanine [218, 219]. These results suggest that IL-graphene hybrid nanosheets due to good dispersibility and long-term stability are expected to be useful materials for enhancing the electrochemical performance for the detection of different target molecules in electroanalytical applications.

8. Conclusions

ILs are solvents that can be designed for special applications either by synthesizing new ILs or by pairing different cations and anions to fine-tune the properties of a particular IL. In this review article we have tried to give an overview on the importance of ionic liquids for the synthesis of conducting polymers and nanoparticle. Moreover, electrochemical methods such as potentiometry, voltammetry, and QCM have been used in ILs to develop new generation of ion selective sensors, voltammetric devices, gas sensors, and electrochemical biosensors.

The good catalytic ability of IL-based composite materials together with the simple preparation procedure greatly promotes the development of highly sensitive, selective, and reproducible microelectrode to be used in electrochemical biosensors and other bioelectrochemical devices. Taking advantage of the fact that ILs could be used as both immobilizing matrices to entrap heme proteins and enzymes as the electron-transfer promoters to achieve direct electron-transfer between the redox proteins and underlying electrodes hence provided a good electrocatalytic sensing platform for various substrates. The fundamental understanding of the underlying biochemistry, surface chemistry, electrochemistry, material chemistry, and technological advances is needed in order to enhance the capabilities and improve

the reliability, portability, and functionality of IL-based biosensors to bring the biosensors in real applications. The still rising interest in ILs in various fields of chemistry will surely lead to a rising output of products papers, stimulating further studies. It can be expected that ILs in electrochemical sensing are a promising and exciting area of research and definitely need further exploration. Combination of ILs with electrochemical sensors has the potential to broaden or even revolutionize the range of analytical methods.

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