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Ionic liquids as tailored media for the synthesis and processing of energy conversion materials

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Though in its infancy stage, ionic liquid (IL)-assisted synthesis and processing of energy conversion materials is triggering a wide interest to eco-friendly production of already existing and novel materials. ILs possess the potential of overcoming the limitations of conventional synthesis approaches. Due to their unique characteristics such as high chemical and thermal stabilities, nearly negligible vapour pressure, wide electrochemical window, broad liquidus range, tunable polarity, hydrophobicity/hydrophilicity, ionic liquids are opening new frontiers in the ionothermal synthesis of tailored materials, enabling products that are difficult or impossible to achieve by using other, more conventional preparation routes. Trying to offer an exhaustive review on the burgeoning role of ionic liquids for the synthesis and processing of energy conversion materials, this perspective article focusses on IL-assisted production of electrode materials and catalysts for fuel cells, photo-induced water splitting and dye-sensitized solar cells. A brief excursion on the use of ionic liquids for the processing of natural fuels for biofuel cells is also made. The state-of-the-art research endeavours are firstly evaluated, followed by the exploration of future research directions with some thoughts on emerging challenges and opportunities.

1. Introduction

Global environmental issues associated with climatic changes induced by greenhouse gases are dramatic concerns of today's energy-conscious society.[1–4] The ever-increasing world population and its better affluence to energy put huge pressure for expanding our current energy infrastructure, which has been, and still is, heavily relying on limited and environmentally unfriendly sources, such as coal, oil and gas. The increasing atmospheric pollution, global warming, depletion of fossil-fuels and lack of energy security, represent the most important imperatives to be urgently addressed for a sustainable future. These challenges can only be met through the development of new materials, systems, and technologies enabling the transformation of environmentally friendly and renewable energy sources, such as sunlight, wind, and biomass. However, all these sources rely on the availability of novel materials and systems capable of exploiting their full-spectrum shares to the grand energy challenge. For instance, electrical energy is converted from chemical energy in fuel cells and from light in photovoltaics. Chemical energy, on the other hand, can be generated from water splitting by using appropriate catalysts. Keys to the effective performance of all the aforementioned conversion systems are the materials that rule the primary process, such as catalysts and electrode materials in fuels cells, semi-conductors in photovoltaics, processing strategies in bio-fuels and so on. In this respect, the procedure for the materials fabrication plays a key role in tuning their properties and performance. Amid the synthetic routes reported in literature, the ionothermal method is expected to be economically competitive due to the low process temperature coupled with its eco-friendliness. Indeed, this method has gained great attention in the materials science community since it allows obtaining and processing a wide-range of attractive high performance energy conversion materials, otherwise not accessible via conventional synthesis approaches. As a result, ionothermal synthesis routes, utilizing ionic liquids (ILs) as tailored and green reaction media, have opened new frontiers in the field of energy storage and conversion devices. In a recent review,[5] we have shown the impact of IL-based synthesis and processing on electrochemical energy storage devices, such as batteries and super capacitors. Here we complete the information by critically discussing the role of ionic liquids on the preparation of materials for the development other classes of timely important technologies, including fuel cells (comprising PEMFCs, DMFCs and SOFCs), dye sensitized solar cells (DSSC), water splitting and bio-fuel systems and processing.

ILs can be broadly defined as molten salts formed by the combination of weakly coordinating cations and anions, with a melting point well below 100 °C.[6–10] The small lattice enthalpies and large entropy changes, resulting from the large size and conformational flexibility of the weakly coordinating ions, favor the occurrence of the liquid state.[9,11] Accordingly, some ILs possess unique physical properties compared to conventional electrolyte media, e.g., organic solvents, including, among others, negligible vapor pressure (thus, low flammability), high thermal stability, broad liquidus range, tunable electrochemical window, and ability to dissolve and process a wide range of materials (e.g., synthesis precursors, enzymes) as well as to stabilize metastable compounds.[10–13] Such wide range of unique properties endows ILs as suitable alternatives to molecular solvents for the synthesis of engineered materials, by acting as advanced solvents, reactants, dopants, as well as capping, templating agents and catalysts. For instance, owing to a series of beneficial aspects, electrochemical deposition is usually rated as the most convenient method to fabricate semiconducting materials for energy conversion (e.g., water splitting). However, electrodeposition is strongly temperature-dependent since throwing power and film quality are enhanced by operating at high temperatures in order to prevent yields of discrete materials affected by poor oxygen evolution efficiency, as instead is the case for low temperature operations. Conventional aqueous, and even, non-aqueous electrolytes (e.g., used in the SIGAL process[14]), do not stand high deposition temperatures, and, consequently, the search for thermally stable media has been one of the top priorities in the field. In this regard, IL-based electrolytes have been identified as perfect candidates due to their high thermal stability, as well as to their ability to allow atom diffusion on the surface during growth, a factor which positively influences the quality of the final film.[15–19] Another bonus of ILs is that theoretically they can be formed by unlimited cations/anion combinations. While the number of conventional solvents used in industry is of the order of about $6*10^2$, that of ILs that can be simply prepared in laboratory exceed 10^6, this resulting in more than 10^{12} binary and about 10^{18} ternary combinations. This in turn provides the opportunity to generate the required system of ILs of improved reactivity, viscosity, solubility, purification and recyclability, and thereby open their way towards industrial applications. However, the life-cycle cost, sensitivity to contaminants, more efficient and scalable commercial synthesis, precise recyclability data, green and optimized distillation and recyclable strategies are still crucial in evaluating ILs viability in commercial applications. In other words, there is a long way to go before large-scale implementation of ILs for the fabrication energy conversion materials and their eco-friendly processing. However, despite the excitement behind the use of ILs-mediated syntheses, the methodology is yet at its early stage being still affected by a series of issues, such as high cost and lack of well documented toxicity data. However, these apparent drawbacks appear to be compensated by recyclability and re-usability, actions that can be performed without affecting the quality of the resulting products, as in fact demonstrated in practice by the well-known BASIL process, see also later discussion in section #3.

Here we will critically evaluate these aspects by discussing the use of ionic liquids for the synthesis of various timely and relevant materials outlining the technological importance, as well as the issues which may possibly affect their application for large scale production and at the same time, providing suggestions on how to successfully address them.

For the sake of convenience for readers, the acronyms/abbreviations along with the descriptions of ionic liquids utilized in this review manuscript are provided in table 1.

<Table 1 here>

Table 1. Inclusive list of acronyms/abbreviations and descriptions of ionic liquids used in this review

2. Synthesis of energy conversion materials

2.1. Catalysts for Fuel Cell technologies (FCs)

General aspects

Among the various sustainable energy conversion systems, Fuel Cells (FCs) are gaining increasing popularity due to their higher environmental compatibility compared to conventional combustion-based power generation systems.[20–22] FCs are in fact not restricted by the Carnot cycle, thus, intrinsically capable of providing higher efficiency combined with the advantage of heat cogeneration or hybrid applications. As well known, a fuel cell operates by oxidizing the fuel (usually hydrogen, but also methanol or glucose and other carbon and hydrogen containing compounds) at the anode (+) and reducing oxygen at the cathode (-) to produce water (sometimes CO_2) as the only waste. Fuel cells (FCs) can be classified into various categories according to the choice of electrolyte and operating temperature, the most common being Proton Exchange Membrane Fuel Cells (PEMFCs); Direct Methanol Fuel Cells (DMFCs), and Solid-Oxide Fuel Cells (SOFCs).[22] In general, FCs are very appealing as energy conversion devices and this accounts for the extensive research and development activities devoted to their practical development. Although fuel-cell powered cars are already in the market, there still various issues to be solved for assuring a wide commercial impact for these devices. A major one is in the availability of effective catalysts, both for the oxygen reduction (ORR) and oxidation (OER) reactions, namely of catalysts characterized by low price/performance ratio at moderate temperatures. This condition does not apply for PEMFCs where the cost of the most commonly used catalysts (e.g., Pt or Pt-based compounds) contributes for more than 55% of the total cost.[21,23] In addition, these precious metal catalysts are also affected by low durability, scarce resistance carbon monoxide poisoning. While for the description of the basic electrochemistry which rules the fuel cell operation we refer the reader to other, more specialized reviews,[21,22] here we may only reiterate that a wide commercial output of fuel cells is obviously hampered by the lack of proper catalysts and that, consequently, current research trends are targeted at developing electrocatalysts of acceptable performance with minimal Pt- loading or, ideally, precious metals-free, with particular attention on the ORR, which is six or more orders of magnitude slower than OER.

From the synthesis methodology perspective, ILs have emerged as tailorable media for the fabrication of highly active, molecularly engineered electrocatalysts, since they benefit by a series of relevant specific advantages, including: (i) the production of materials with very low particle size, due to low surface tension resulting in a slow coarsening during the growth phase; (ii) electro-deposition at high temperature, due to the high thermal stability; (iii) flexibility in the solubility of precursors, due to the tunable polarity, and (iv) rapid crystal growth in microwave (MW) synthesis with a high susceptibility. In the following paragraphs, the role of IL-based synthesis is discussed for the various types of fuel cells.

2.1.1. Proton Exchange Membrane Fuel Cells (PEMFCs)

In general, the aforementioned peculiar features of ILs enable the synthesis of tailored materials of improved catalytic activities, such as carbon supported Pt nanoparticles with low Pt loading. In this respect, Zhao *et al.*[24] reported the use of novel ILs for the synthesis of carbon-nanotube-supported platinum (IL-Pt/CNT) catalyst for PEMFCs. This synthetic procedure implied first the activation via acids of the chemically inert CNT with the goal of generating surface functional groups for optimizing metal dispersion on the CNTs surface. However, the key aspect of this particular synthesis, i.e., decorating the CNTs with metal particles, keeping homogeneous size distribution and dispersion while preventing agglomeration without additional pre-treatment, can only be achieved with the use of ionic liquids as reaction media, see **Figure 1**. The Pt-decorated CNTs obtained by IL-assisted microwave ionothermal synthesis provide materials with improved catalytic activity due to a series of beneficial features associated with: i) high degree of disorder of the

CNTs and ii) large number of surface defects and the mono-dispersion of Pt particles, as demonstrated by the fact that IL-based Pt/CNTs catalyst showed considerable improvement in the specific current resulting from their electrochemical surface area, being 21% higher than that of commercial Pt/C catalysts.

Carbon nanomaterials (e.g., graphene) doped with heteroatoms, due to a series of specific features, which include excellent electro catalytic activity, high conductivity, and large surface area,[25–27] are among the strongest contenders for use as metal-free catalysts in PEMFCs. However, the available synthetic methods such as chemical vapor deposition (CVD), arc discharge, segregation growth, Hummer's oxidation followed by hydrazine (N_2H_4) reduction or N-doping by nitrogen plasma treatment, require rigorous reaction conditions like high temperature and vacuum, as well as the use of highly toxic and explosive reagents and possible metal contaminants. Thus, the fabrication of trace-metal-free N-doped-graphene via low energy and benign synthesis conditions is of paramount importance. In this regard, Lu et al.[28] showed a clever way of fabricating N-doped graphene via electrochemical exfoliation, followed by in-situ nitrogen doping of graphite, using nitrate (ethyl ammonium nitrate-EAN)-based ILs, serving both as exfoliating and doping agent. The electrochemical exfoliation of graphite in the presence of EAN, containing 10% (v/v) water, resulted in a metal-free, N-doped graphene having an excellent catalytic activity towards ORR. The presence of water facilitates the degree of exfoliation via oxidation, generating oxygen species. While the nitrate ions of the ionic liquid are responsible for the fast and low stage intercalation, the ethyl ammonium cations serve for the in-situ N-doping of the electro-generated intermediate material.

The sluggish ORR kinetics can be further improved by engineering the coating of the nanoparticle catalysts via ionic liquids, as demonstrated in the case of IL-impregnated nanoporous Ni-Pt, where ILs have been efficaciously applied to engineer metal-Pt alloy coatings.[29] It is important in this respect to point out that the incorporation of the hydrophobic, but protic [MTBD][BETI] into the pores of the high surface-area Ni-Pt alloy nanoparticles leads to consistent improvements in the kinetics of ORR.[29,30] The high O_2 solubility in [MTBD][BETI] combined with the confined environment (due to encapsulation in Ni/Pt nanoparticles) boosts the attempt frequency, namely the parameter that characterizes the rate of surface diffusion through a jumping process of adatoms residing at adsorption sites to nearer-neighbour ones, thus finally enhancing the ORR rate. Indeed, the IL-impregnated Ni-Pt carbon-supported nanoporous nanoparticle catalyst (IL-Ni-Pt/C) shows a catalytic activity one order of magnitude higher than that of commercial Pt/C. Another evidence of the key role of ILs for the synthesis of PEMFC catalysts is provided by the work of Hasche *et. al*[31], who evaluated mesoporous N-doped, carbon-supported Pt catalysts, synthesized in n-butyl-3-methylpyridinum dicyanamide, [BMP][DCA], which acts as N and C precursor. Compared to the benchmark commercial Pt ones, the new catalyst fabricated via the IL-assisted method presented a comparable activity, however, with a consistent enhancement in the electrochemical active surface area (ECSA) and long-term stability, thus, finally confirming its suitability for promoting ORR. Finally, improvements in the ORR kinetics in PEMFCs, have been also reported for other electrocatalysts such as Pt-loaded carbon aerogels,[32] and IL-functionalized MWCNTs decorated with Au nanoparticles.[33]

<Figure 1 here>

Fig.1 Schematic drawing of the synthesis of Pt/MWCNT electro catalyst with and without ionic liquids. The use of IL promotes the homogeneous dispersion of Pt nanoparticles, by preventing agglomeration as, e.g., when only ethylene glycol is used. This is due to the specific interactions between the IL and the carbon material, resulting in the surface modification of the MWCNTS.

2.1.2. Direct Methanol Fuel Cells (DMFCs)

DMFC, due to its high energy density, ease of refuelling, and low environmental impact, is among the most promising fuel cell technologies. However, the sluggish ORR kinetics and the methanol crossover are the crucial issues that still have to be successfully addressed to allow a full commercialization of this important power generating system. Moreover, in DMFCs, CO species are formed and adsorbed during the electro-oxidation of methanol, inferring that the catalyst for the methanol electrode also requires to be CO-tolerant. The most commonly used electrocatalysts in DMFCs are again Pt-based compounds; however, the high cost and CO-poisoning have also in this case hindered their large-scale application, calling for low-cost and high-performance alternative materials. In this respect, bimetallic particles are very attractive since the shape, size, and composition of their structures significantly influence the catalytic activity. In this scenario, Li et. al.[34] have recently demonstrated that core-shell-structured Au-Pt bimetallic particles may be successfully obtained by an ionothermal synthesis using [C_4mimBr] IL and a mixture of $HAuCl_4.4H_2O$ and $H_2PtCl_6.5H_2O$ (1:3 ratio) at room temperature. When tested as catalyst in a DMFC, these particles showed a much superior peak current density than that obtained by using a single element, i.e., 9.56 mAcm^{-2} versus 0.17 mAcm^{-2} (Au only) and 1.93 mAcm^{-2} (Pt only). The corresponding mass activity of the Au-Pt catalyst is 3.2 times higher than that reported for the Pt/C, i.e., 133.5 mA mg^{-1} versus 41.1 mA mg^{-1}. The key role of the IL in promoting the synthesis of the Au-Pt bimetallic particles was finally demonstrated by comparing their catalytic activity when prepared by a similar, but [C_4mim][Br]-free procedure.

As part of the research efforts towards the development of metal-free catalysts, it worth to stress that heteroatom (N, S, or B)- doped carbon-based catalysts have shown promising features, such as high immunity towards methanol crossover (i.e., they do not catalyze the oxidation of CH_3OH directly by oxygen), long-term stability, low cost and high electrocatalytic activity for ORR. Han *et al*.[35] successfully demonstrated the synthesis of N-doped hollow carbon spheres using ILs with a nitrile group anion/cation as carbon precursor and silica as the templating agent. The obtained material, having high nitrogen content (~10.9%) and degree of graphitization, combined with other features, demonstrated an excellent electro-catalytic activity with ~4e- transfer, super immunity towards methanol crossover and a stability superior to commercial Pt/C. In addition, also high surface area S, and N-co-doped hierarchical porous carbon, obtained using [BMP][TF_2N] as N, S, and C precursors, showed improved catalytic activity, high methanol crossover tolerance, and good thermal stability.[36] The ORR potential peaks were found to be directly related to the heteroatom loading, demonstrating the need to have a N/S optimal ratio for obtaining the best catalytic activity when both dopants were used.

It has been reported that graphene, due to its high surface area, can be exploited as an active support to load noble metals, such as Pt, Au, Ag, or bimetallic alloys (e.g., PtAg), for use as catalysts in DMFCs. For example, PtAg nanostructures decorated on reduced graphene oxide (PtAg/RGO) have been synthesized again using an IL, [C_{16}mimBr], which serves both as surface-capping and structure-directing agent.[37] The IL-prepared PtAg/RGO nanocomposite has a large electrochemically active surface area, namely, 92% and 16%, higher than that of Pt/C and Pt-black, respectively, as well as higher catalytic activity, methanol tolerance and long-term durability for ORR in alkaline solution. **Figure 2** illustrates the IL-based synthesis of PtAg-decorated graphene.

Another promising approach towards the fabrication of highly efficient hybrid nanocatalysts for DMFC sees the direct mixing of IL-functionalized carbon nanotubes (CNTs) with metal (e.g., Pt) precursors.[38] The imidazolium group, attached through N,N'-dicyclohexylcarbodiimide (DCC) coupling with the counter anion ($PtCl_4^{2-}$), plays a crucial role in the formation of IL-CNTs/Pt hybrid materials. More recently, Do *et al*.[39] reported the synthesis of GnP-supported Pt catalysts (Pt/GnP) by using a microwave process based on [C_4mim][PF6] and [C_4mim][CH_3CO_2] and using $H_2PtCl_6.6H_2O$ as Pt precursor and ethylene glycol (EG) as reducing agent. The IL addition to EG-GnP after that of the Pt precursor assured a uniform distribution of Pt on GnP, as promoted by the direct interaction of Pt ions with the π sites on the GnP basal plane and residual oxygen groups at the GnP edge surface. The size of Pt nanoparticles was found controlled by the polarity of the ILs, as well as by the IL-/GnP molar ratio. For instance, deposition in $[C_4mim][CH_3CO_2]$ produced small Pt nanoparticles, due to the higher basicity of the $CH_3CO_2^-$ anion with respect to PF_6^-, this being associated with its unsymmetrical arrangement of the oxygen atoms. Electrochemical comparisons of IL-assisted Pt/GnP and commercial Pt/XC-72R catalysts towards methanol oxidation revealed that the former exhibited much higher (an 80% increase) catalytic activity, in turn ascribed to the higher dispersion of Pt particles and more favorable Pt-support interaction with GnP. Finally, it is here worth noting that a large number of electro catalysts for use in DMFCs have been obtained via the ionothermal synthesis route. The most important of them are PtRu,[32] Pt/C,[40] C-PtAu-nanoparticle hybrids,[41] flower-like Pd nanoparticles, Pt-WC/TiO_2,[42] polymeric ionic liquids (PIL)/Pt nanoparticle hybrids,[43] CuPt-/IL-graphene,[44] Pt/XC-72 coated N-doped carbon (Pt/XC-72@C-N),[45] mixed ILs/graphene-supported Pt nanoparticles,[46] Pt-Ru/C,[47] and Pd/C.[48]

<Figure 2 here>

Fig.2 Illustration of the fabrication of PtAg/RGO composite electro catalyst via ILs-mediated approach. The IL plays the role of structure directing agent and surface capping, leading to high electrochemically active surface area and, thus, high catalytic activity.

2.1.3. Solid Oxide Fuel Cells (SOFCs)

The SOFC, a viable high temperature (500-1000°C) technology, has recently received large attention as a major source of electrical energy storage system, mainly owing to its efficiency which overpass that of Carnot Cycle power sources.[49,50] Similar to the aforementioned FCs, the efficiency of SOFCs is also highly dependent on the quality of the employed electro-catalyst,[51] usually of the rare earth-type. Among them, dysprosium oxide (Dy_2O_3) is the one so far reported having the best catalytic behaviour. However, due to its negative potential and high reactivity with atmospheric components, dysprosium cannot be electrodeposited from aqueous solutions. Once again, ionic liquids have been successfully employed for addressing the issue. Indeed, by a single electro-deposition step from an IL based on eutectic choline chloride/urea in a 1:2 molar ratio, followed by controlled oxidation, a highly performing nanostructured Au-Dy_2O_3 composite electro-catalyst could be easily obtained.[51] In general, though fuel cells are considered as relatively exotic technologies, they are not yet a major commercial success. This is mainly attributed to their high cost, durability and related issues. ILs-mediated synthesis has demonstrated to enable the synthesis of designable catalysts, one of the critical issue that need to be solved with FCs. Moreover, the question of how well the synthesis methodology can be scaled up from the laboratory to large scale need to be critically addressed.

2.1.4. Photo-electrochemical water splitting

The effective capture of sunlight and its subsequent conversion into chemical fuels, such as hydrogen, represents a significant step towards the exploitation of a truly sustainable and environmentally benign energy source.[52] The production of H_2 by photo-splitting of water based on the following reaction series:

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (1)

$4H^+ + 4e^- \rightarrow 2H_2$ (2)

$2H_2O \rightarrow 2H_2 + O_2$ (3)

is an important alternative to the current industrial process, primarily relying on reforming fossil fuels. Photo-electrochemical water splitting can be regarded as cost-effective, convenient, and simple technique, which involves the simultaneous oxidation/reduction of oxygen (eqn. 1) and hydrogen (eqn. 2) with the production of the two gases (eqn, 3). Compared to that associated with hydrogen production, the oxidation reaction, also called oxygen evolution reaction (OER), is the most sluggish and rate-determinant step, indeed requiring an overpotential exceeding 0.45V to drive the reaction at useful rates, which results in a substantial energy loss, usually as heat. This clearly accounts for the tremendous efforts recently devoted to the search of effective and tailor-made electro-catalysts based on earth-abundant elements (e.g., Mn, Co), aimed to allow the replacement of the precious metals (e.g., RuO_2, IrO_2, ...)-based catalysts currently used in commercial electrolysers.

In this scenario, particular attention has been addressed to manganese oxides, MnOx (x=1.5-2), which have been synthesized using a number of approaches, including precipitation, hydrothermal, sol-gel, classical aqueous electrode deposition, etc. Once again, ILs have shown fascinating outcomes as solvents/electrolytes for the preparation of MnOx and related catalysts. A relevant example is provided by Zhou, *et al*.[53] who recently reported the use of ethyl ammonium nitrate as electrolyte for the electro-synthesis of MnOx layers at moderate temperatures (100-150^{o}C). This process was made possible only by exploiting an ionic liquid (ethylammonium nitrate, EAN), which in fact, allows the use of water (reactant) at high temperatures without need of a high-pressure vessel. As it can be seen from **Figure 3**, the IL-synthesized catalyst presented a very good electrochemical performance, allowing significantly high currents at low overpotentials with an energy loss limited to 5.8%, i.e. a value much lower than the 23.5% associated with the production of MnOx-based catalyst via conventional synthesis routes. Unfortunately, the practical application of this catalyst is still hindered by its degradation over a relatively short operation time due to the fact that MnO_x, as the majority of the transition metal-based oxides, is penalized by oxo-anions solubility under prolonged exposure at high (oxidizing) potentials in aqueous solutions. This issue has been addressed attempting the stabilization of the metal oxide–based catalyst by developing water-insoluble multi-layer structures, again with the assistance of ionic liquids, as in fact shown by Iygorodin *et al*.[54] who demonstrated the incorporation of phosphates into the MnO_x surface at high concentration of phosphate ions, enabling a proper stabilization of the oxide surface, hence assuring its prolonged catalytic activity.

Still with the support of ethylammonium nitrate, EAN, Zhou *et al*.[55] succeeded in electrodepositing a variety of MnO_x phases having different catalytic performance, depending on the acidity and/or alkalinity of the IL used as the electrolyte. In this respect, while the film deposited from a highly basic medium mainly resulted in the hausmannite, spinel-structured (Mn_3O_4), those from slightly alkaline, acidic, and neutral electrolytes, yielded Mn_2O_3 and birnessite-like MnOx films, having the highest catalytic activity for water oxidation among all those deposited from a neutral electrolyte. Recently, a rational design of highly performing boron (B)– and fluorine (F)–doped 2D-graphitic carbon nitrides (g-CN) via self-polymerization of urea in $[C_4mim][BF_4]$ IL has also been reported.[56] In this synthesis, the urea is used as delamination agent, while the IL serves as a multi-functional modifier to control the texture and surface chemistry, as well as to tune the semi-conductor properties of the g-CN imparted by B and F doping. Finally, IL-assisted of efficient electrocatalysts, such as self-organized TiO_2 nanotubes,[57] TiO_2 nanotube arrays,[58] Ag/Pd nanoalloys,[59] etc. have also been reported to be effective novel catalysts in the photo-induced water splitting.

<Figure 3 here>

Fig.3 Performance of various MnO_x-based electro catalysts synthesised in 1M NaOH (right), 0.4M di(butyl ammonium)sulphate (BAS, pH=10) (center), and 2M di(butyl ammonium) sulphate – ethylammonium nitrate (BAS-IL, pH= 10) (left). Preparation of MnO_x films from ILs electrolytes enables obtaining films with less water, higher conductivity, and improved water oxidation performance.

The standard Gibbs free energy change (ΔG) for the water splitting into H_2 and O_2 is +237.2 kJ mol^{-1}, which corresponds to 1.23 eV per electron transferred, indicating that to run the overall process, a semi-conductor photoelectrode with a band gap wider than 1.23 eV, along with suitable band edge positions, is needed. Owing to its chemical and photo stability, environmental-friendly nature and low cost, titanium oxide, TiO_2, is in principle a very appealing candidate. However, its wide band gap (over 3 eV) and the rapid recombination rate of photo-generated electron-hole pairs, reflect in a very low efficiency of the overall H_2 production. The recombination issue has been addressed by developing carbon-TiO_2 composites, which provide enhanced interfacial contact with adsorbates. A recent example is provided by a TiO_2/reduced graphene oxide (RGO) nanocomposite, prepared via the hydrothermal method using [C_4mimPF_6] IL as a solvent. While the graphene sheets act as electron transfer channels, reducing the recombination of the photo-generated electron-hole pairs, ILs serve as tailorable solvents for yielding to a material with engineered morphology and boosted properties. The obtained TiO_2/RGO showed in fact, a much higher efficiency of hydrogen production than that achievable by composites synthesized making use of traditional solvents.[60]

Surface modification of TiO_2 by doping with heteroatoms is another proposed way to improve its photo-catalytic activity. This strategy involves the preparation of nitrogen (N) and carbon (C) co-doped mesoporous TiO_2 via evaporation-induced self-assembly method using [C_2mim][Cl] ionic liquid, as schematically shown in **Figure 4**. C and N co-doping are expected to tune the band gap, making it decreasing to a value of 2.92 eV, compared to 3.2 eV of the commercial TiO_2, reflecting in a significant increase in the absorbance edge and intensity of visible light.[61] All these material improvements lead to a photo-catalytic hydrogen generation of 81.8 µmol g-1 h^{-1}, which is ~37 times higher than that achievable by commercial TiO_2. Other important and highly performing electro catalysts that have been obtained by IL-assisted synthesis include: mesoporous TiO_2 (using [C_4mim][PF_6][62,63] and [C_4mim][BF_4][64]), mesoporous CeO_2-TiO_2 ([C_{16}mim][Br][65]) and TiO_2/RGO ([C_4mim][PF_6][66]).

<Figure 4 here>

Fig.4 Schematic representation of the synthesis of carbon (C) and nitrogen (N) co-doped TiO_2 from ionic liquids. The IL serves both as C and N source and mesopore creator via interaction with the titania surface.

2.2. Dye sensitized solar cells (DSSC)

The dye-sensitized solar cell (DSSC), also occasionally referred to as the "2nd generation PV" or "Gratzel" cell,[67] prospective to be technically and economically more viable than traditional semiconductor-based photovoltaics (PVs). A typical DSSC device consists of three components: the dye-sensitized, nanoparticle TiO_2 photo-anode, the redox electrolyte (most commonly iodide/triiodide), and the conducting, electro-catalytic layer, acting as counter electrode. Even if DSSCs use a number of the above described advanced dye and electrode materials, they are still less costly compared to the silicon-based solar cells, especially in terms of manufacturing steps.

Due to these expected favorable properties, DSSCs have attracted considerable attention both in academic and industrial laboratories. However, despite the large efforts spent in developing the related technology, DSSCs are only commercialized on a small scale, since the required improvements in efficiency (presently limited to 13%[68]) and the stability (<10% drop in performance after 1000 hours aging at 60°C) are still key targets to be met. One promising strategy to address these issues is to optimize the porous-structured oxide film photo-anode with the aim of enhancing its light absorption. In this scenario, a number of binary (e.g., TiO_2, ZnO, SnO_2) and ternary (BiOX, X=Cl, Br, I) oxide photo-anodes have been developed, using IL-assisted fabrication, either alone or in synergy with microwave, ultrasound and other similar synthesis techniques.[69]

Optimized anatase TiO_2, i.e., the photoanode of choice for DSSCs, may be prepared by sol-gel using [C_4mim][BF_4] IL as templating agent, so as to obtain a material characterized by high surface area, stable crystal structure, controlled porosity, tailored-designed pore size distribution, and good thermal stability.[70] Due to these unique structural and morphological features, this modified TiO_2 photoanode could benefit by larger absorption of dye molecules and longer electron life-time, compared to commercial, non-porous TiO_2, this finally allowing its operation with higher photocurrent, photovoltage and efficiency. In addition, the photocatalytic activity of this IL-prepared nanocrystalline TiO_2 was found be at 100 °C comparable with that of standard TiO_2, however obtained at the much higher temperature of 400°C.

The best DSSC performance, in terms of short-circuit photocurrent (13.15 mA cm^{-2}) and power conversion efficiency, was in fact achieved using TiO_2 films having a nano-flower morphology, as that obtained with a [$C_x$mimHSO_4] IL-assisted synthesis.[71] Another electrode choice for application in DSSCs is zinc oxide, ZnO, a material that also greatly benefits by IL-based synthesis. In this respect, it was found that the morphology of the IL-assisted prepared ZnO material varies from rod-like to star-like and flower–like depending on the nature of the ILs utilized.[72]. The control of the surface, which is assumed to play an important role in favouring the charge transfer mechanism at the ZnO-based hetero-junction, is another aspect recently receiving attention. Amongst all the suggested strategies to enhance the surface properties, the fabrication of ZnO-organic hybrid materials has been reported to be a very promising approach because of the complementary benefits of ZnO and the organic moieties can judiciously be combined to tune the formed material.[73] In this regard, ILs can again be the electrolytes of choice, not only because of their self-assembling and templating properties, but also as nifty sources of ions which may interact electrostatically with the inorganic solid oxide surface, so as to promote its tuneable functional properties. An impressive proof of concept on the use of ILs as all-in-one (i.e, reaction media, morphology templating agent, and surface modifier) media was recently reported by Azaceta *et al.*[73], who, by exploiting this route succeeded in preparing a nanostructured ZnO/ [C_4C_1py][TF_2N] having very promising properties as DSCC anode in terms of power conversion efficiency, electrochemical performance, extended absorption edge and open circuit voltage. For instance, the power conversion efficiency recorded for the ZnO-IL hybrid film increased by a factor of about 2, compared to the IL-free ZnO one.

2.3. Ionic Liquids for Bio-Fuel processing

Bio-fuel cells, see scheme of **Figure 5**, are attracting a continuously growing interest. There are few different strategies to prepare these cells whose function and performance depend on the materials used as catalysts, among which, enzymes are the most efficient ones. There are many studies on the fabrication and performance analysis of enzyme-based bio-fuel cells, but all of them are carried out in aqueous (buffer) solutions. In spite of being the best medium for biosystems, water is not a suitable solvent from the viewpoint of the required performance. Aqueous solutions, in fact, easily evaporate and require pasteurization to keep cleanliness, especially when used under open air. Accordingly, the challenge in the field is to replace these solutions with more efficient solvents. Ionic liquids, due to their properties of non-volatility and high ionic conductivity, are potentially excellent candidates. However, there is a critical requirement for the use of IL-based bio-fuel cells, namely whether they can allow the operation of enzymes. At present, there is no ionic liquid that completely satisfies this tough condition; however, several studies on enzyme-based bio-fuel cells are under way to address this issue. There are several challenges to dissolve proteins in ionic liquids. For instance, while lipase, a rather strong enzyme, can be stably dispersed in some polar ionic liquids still keeping its enzymatic activity, there are only few reports on the dissolution of active proteins, such as cytochrome C, in pure ionic liquids. Though few chloride-based ILs have a low melting point, chloride generally forms strong H-bonds with proteins amide linkages which favour dissolution. Along this line, 1-allyl-3-methylimidazolium cation was coupled with a chloride anion to prepare a low melting point polar ionic liquid in which cytochrome C was reported to be soluble at 80 °C with a redox activity detected up to 140 °C.[74] It was also reported that both the π^* and β values, i.e., the Kamlet - Taft parameters representing polarizability and hydrogen bond basicity, respectively, of ionic liquids are in fact sufficiently high to dissolve cytochrome C. On the other hand, the overall stability of proteins is not sufficiently long in pure ionic liquids.

Therefore, various strategies have been attempted to address this issue. Fujita et al. have reported that cholinium dihydrogen phosphate mixed with small amount of water (Hy-IL) is an excellent solvent for proteins.[75] Such a Hy-IL contains 3-5 water molecules per ion pair, all of them strongly hydrated to ions. Consequently, Hy-IL has no unbound water and thus, it can be regarded as one of ionic liquid derivatives. It has been reported that the electron transfer activity of cytochrome C dissolved in cholinium dihydrogen phosphate, containing small amount of Hy-IL, is maintained for more than one year. This exceptional long shelf life is suitable for application in enzyme-based bio-fuel cells. Indeed, Fujita et al. succeeded, for the first time, to obtain the enzymatic oxidation of cellobiose with cellobiose dehydrogenase (CDH) in the Hy-IL, with two electrons taken from cellobiose to the CDH, and further transferred to cytochrome C, to finally promote its reduction, as in fact spectroscopically demonstrated.[76] It was also shown that some metallo-proteins, such as horse-radish peroxidase, ascorbate oxidase, azurin II, and fructose dehydrogenase, all dissolve in the Hy-IL with enzymatic activity.[77] Although some property changes depending on their species cannot be excluded, most of these enzymes in the Hy-IL showed an improvement in thermal stability respect to that obtained in buffered aqueous solutions. Harvesting electrons from saccharides by corresponding dehydrogenases in the Hy-IL, was also reported to be a successful strategy to obtain prototypes of enzyme-based bio-fuel cells.[78] Ohno et al. reported that ionic liquids may dissolve cellulose,[79] as well as promoting its extraction not only from biomass,[80,81] but also even from wood,[82] finally demonstrating that exploiting ionic liquids is a powerful method to make bio-fuel cells may a practical reality. On this line, it is expected that in the near future grass, wood chips, used papers and even cotton T-shirts may be thrown into ionic liquids to generate electrons with the aid of enzyme-based bio-fuel cells.

<Figure 5 here>

Fig. 5 Schematic representation of the operating mechanism of a bio-fuel cell. The bio-fuel requires preliminary processing which can be proficiently done in ILs media.

3. Challenges, Prospects and Opportunities

In this review, we have shown that tailorable ionic liquids show some potential for assisting the production and processing of energy conversion materials. Table 2 summarises all materials presented in this review.

<Table 2 here>

Table 2. Summary of materials for use in electrochemical energy conversion devices produced in IL media. The used IL as the materials functional roles are also illustrated.

Indeed, ILs can play multiple roles, such as functional solvents, electrolytes for electrode-position, structure-directing agents, stabilizers and precursors, opening a low temperature and eco-friendly synthesis approach, and new avenues towards the synthesis of highly effective materials for fuel cells, photo-catalytic water splitting and dye sensitized solar cells. In addition, ILs have capability to process biofuels, a newly emerging area of potential practical importance. However, the research accounts that have been so far observed represent the tip of an iceberg and intensified research work is still needed to fully understand the effect of the IL structure in promoting advancements of the above listed materials. For instance, the interactions between ILs and precursors/intermediate products, as well as the detailed mechanism of enzyme dissolution in ILs are matters to be methodically investigated. Understanding of the governing mechanisms of the ILs towards tuning the reaction conditions via theoretical modeling is also another desirable, but not yet achieved goal. As announced by BASF in the large-scale and multi-ton BASIL (biphasic acid scavenging using ILs) process, ILs are starting to leave academic labs and find their way into industrial-scale applications.[83] However, for the not yet fully commercialized technologies (e.g., FCs, DSSCs, water splitting) a proper approach of scaling up of the IL-assisted ionothermal synthesis and processing need to be well thought and developed. As the concepts and paradigms of IL-assisted synthesis in the aforesaid applications is new, a very close cooperation between academia and industry is necessary towards their deployment in large-scale applications. Considering the research work in this field is still at its early stage, there hopes that these aspects will be successfully clarified in the near future.

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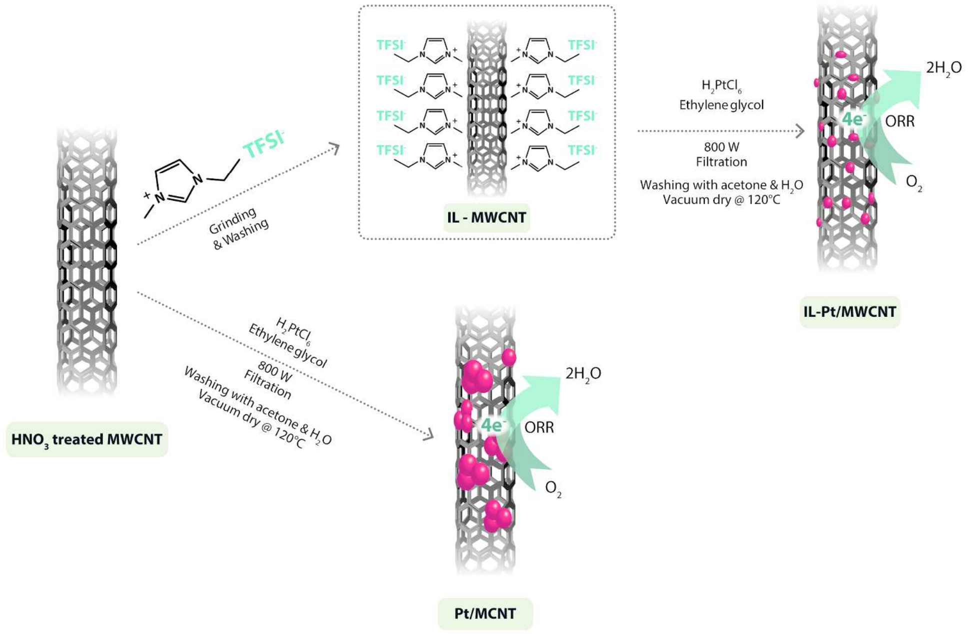

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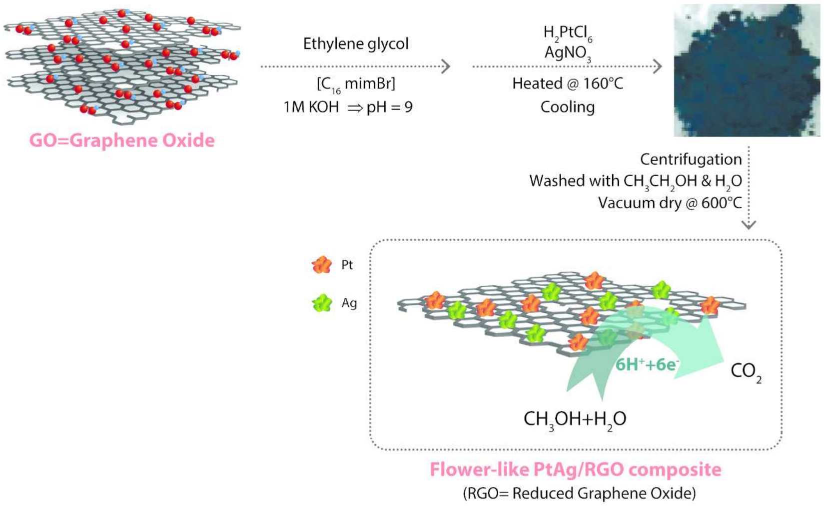

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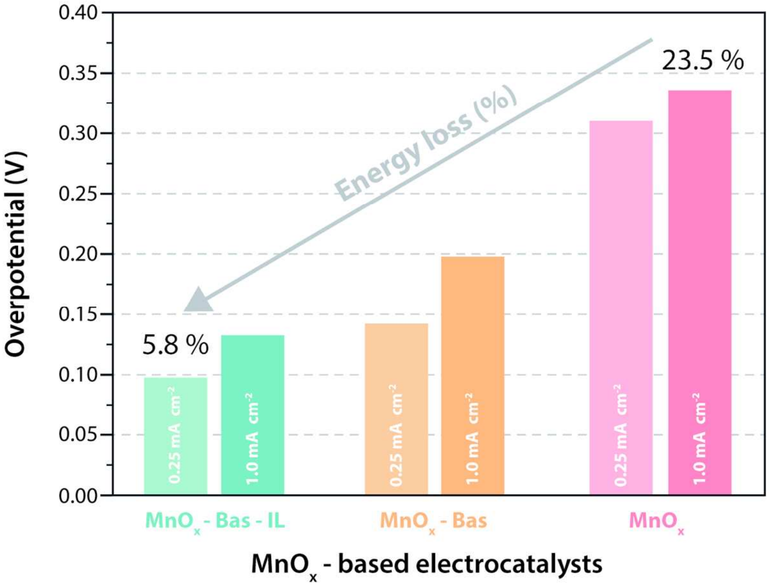

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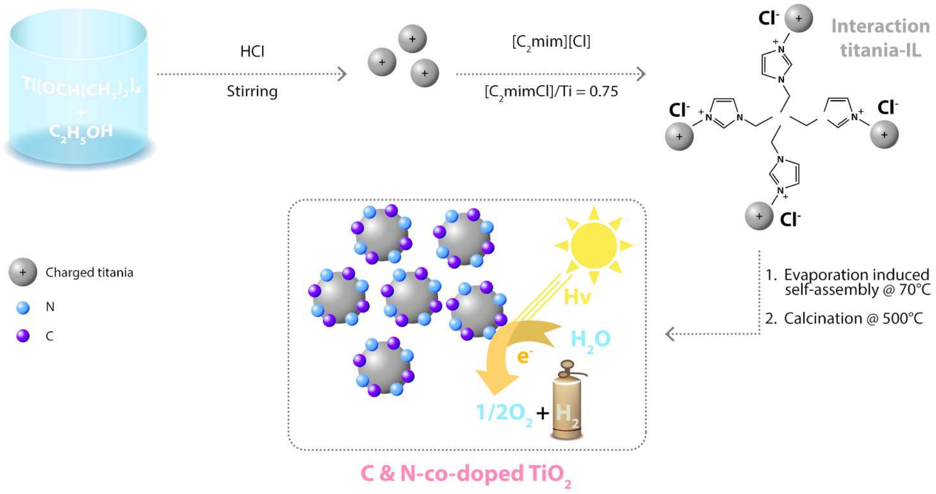

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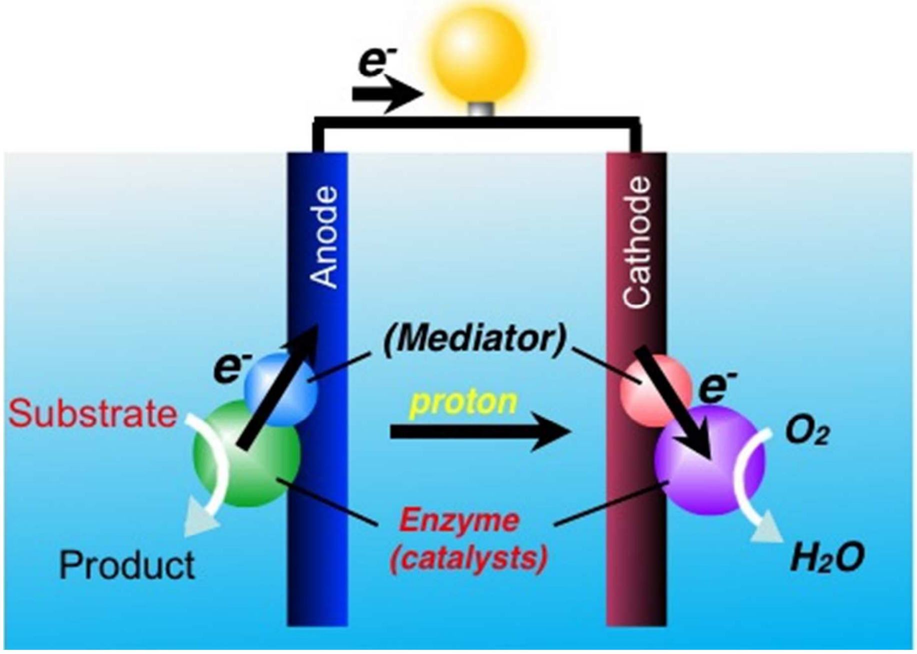

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Table 1. Inclusive list of acronyms/abbreviations used for the ILs mentioned in this review

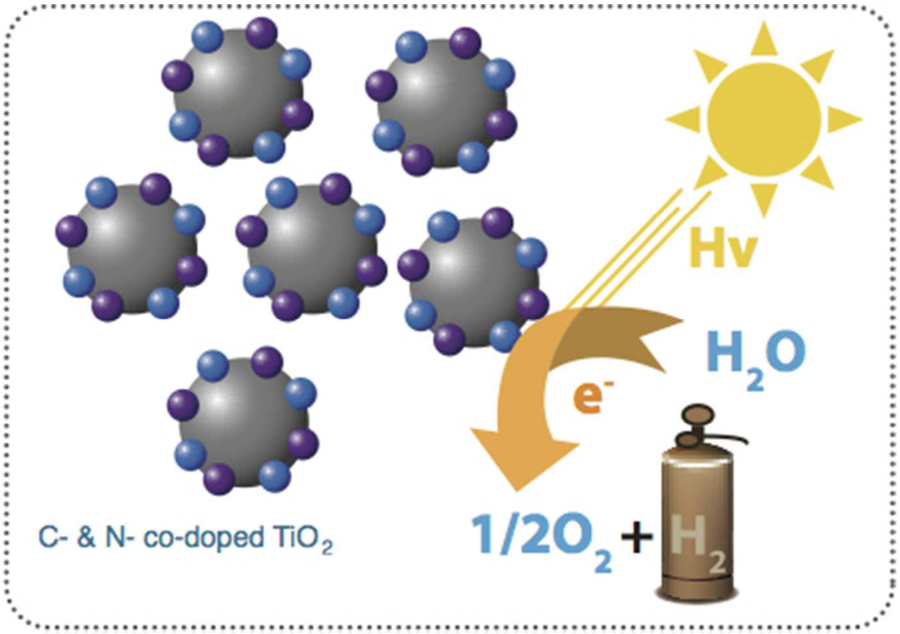
Acronyms/Abbreviation	**Ionic Liquid**
[EMI][TFSI]	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide)
[BMI][TFSI]	1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide)
[MTBD][BETI]	7-methyl-1,5,7-triaza-bicyclo [4.4.0]dec-5-ene-bis(pentafluoroethanesulfonyl)imide
[BMP][DCA]	N-butyl-3-methylpyrrolidinium cyanamide
[C$_4$mim][Br]	1-butyl-3-methylimidazolium bromide
(3-MBP[[DCA]	3-methyl-1-butyl pyridinum dicyanamide
[C$_{16}$mim][Br]	1-hexadecyl-3-methylimidazolium bromide
[BMP][TF$_2$N]	1-buthyl-pyrrolidinium bis (trifluoromethanesufonyl)imide
[C$_4$mim][PF$_6$]	1-butyl-3-methylimidazolium hexaflurophosphate
[C$_4$mim][CH$_3$CO$_2$]	1-butyl-3-methylimidazolium acetate
[C$_2$mimCl]	1-ethyl-3-methylimidazolium chloride
[C$_4$mim][BF$_4$]	1-butyl-3-methylimidazolium tetrafluoroborate
[Cmim][HSO$_4$]	3-carboxymethyl-1-methylimidazolium bisulfate
[C$_4$C$_1$Py][TF$_2$N]	1-butyl-3-methylpyridinium bis(trifluoromethanesulfonyl)imide
[C$_8$mim][PF$_6$]	1-octyl-3-methylimidazolium hexafluorophosphate
[VEI][NO$_3$]	1-vinyl-3-ethylimidazolium nitrate
[C$_2$mim][DCA]	1-ethyl-3-methylimidazolium dicayanide
[Ch Sac]	choline saccharinate
[C$_4$mpyr][DCA]	N-butyl-N-methylpyrrolidinium dicyanide
[Ch] [dhp]	choline dihydrogen phosphate
[C$_4$mim][dhp]	1-butyl-3-methylimidazolium dihydrogen phosphate
[Ch][dbp]	choline dibutyl phosphate
[C$_4$mim][CH$_3$CO$_2$]	1-butyl-3-methylimmidazolium acetate
[C$_4$mim][MeSO$_4$]	1-butyl-3-methyl imidazolium methanesulfonate
[Ch][Lac]	1-butyl-3-methylimidazolium lactate
(Hy[Ch][dhp])	hydrated choline dihydrogen phosphate
[Dimim][MeO][H]PO$_2$	1,3-dimethyl imidazolium-methylphosphonate

Table 2. Summary of materials for use in electrochemical energy conversion devices produced in IL media. The used ILs and their functional roles are also indicated.

Materials obtained	ILs used	Role of the IL
IL-Pt/CNT	[EMI][TFSI], [BMI][TFSI]	Reaction media
N-doped graphene	EAN-based IL +10% (v/v) H_2O	Exfoliating agent & in-situ dopant
(IL-Ni-Pt)/C	[MTBD][BETI]	Advanced Solvent, surface modifier
Pt-loaded carbon aerogels	[C$_4$mim][BF$_4$]	Stabilizer
IL-functionalized MWCNTS-Au	1-(3-Aminopropyl)-3-methylimidazolium bromide	Surface modifier
N-doped Pt/C	[BMP][DCA]	N- and/or C – precursor
Core-shell Au-Pt bimetallic	[C$_4$mim][Br]	Solvent and morphology directing
N-doped hollow C spheres	[3-MBP][DCA]	C precursor
S- & N-co-doped porous C	[BMP][TF$_2$N]	N, S, & C precursor
PtAg/RGO	[C$_{16}$mim][Br]	Surface capping, structure-directing
IL-CNTS/Pt	1-(3-Aminopropyl)-3-methylimidazolium bromide (NH$_2$–IL)	Surface functionalizing
Pt/GnP	[C$_4$mim][PF$_6$],[C$_4$mim][CH$_3$CO$_2$]	Structure-directing
PtRu	[C$_4$mim][BF$_4$]	Stabilizer
Pt/C	[C$_4$mim][BF$_4$]	Advanced Solvent
Pd nanoparticles	[C$_4$mim][Br], [C$_4$mim][Cl]	Morphology/structure directing
Pt-WC/TiO_2	[C$_4$mim][BF$_4$]	Structure and morphology directing
CuPt-/IL-graphene	[C$_8$mim][PF$_6$]	Increase conductivity
PIL/Pt hybrids	[BviM][Br]	Monomer
Pt/XC-72@C-N	[VEIM][NO$_3$], [C$_2$mim][DCA]	Dopant
ILs/Graphene supported Pt	[C$_4$mim][BF$_4$], [C$_4$mim][PF$_6$]	Surface functionalizing
Pt-Ru/C	[C$_4$mim][BF$_4$], [C$_4$mim][PF$_6$]	Advanced solvent
Pd/C	[C$_4$mim][BF$_4$]	Advanced solvent
Dy_2O_3	Eutectic choline chlorine/urea (1:2, molar ratio)	Electrolyte for electrodeposition
MnO_x (x=1.5-2)	EAN (Ethyl Ammonium Nitrate)- based IL	Electrolyte for electrodeposition
Phosphate surface-modified MnOx	Phosphate buffer ionic liquid	Surface modification
B - & F- doped graphitic carbon carbides	[C$_4$mim][BF$_4$]	Texture & chemistry modifier
TiO_2/RGO	[C$_4$mim][PF$_6$]	Advanced Solvent
N - & - C –co-doped TiO_2	[C$_2$mim][Cl]	N - & C precursor
Mesoporous TiO_2	[C$_4$mim][PF$_6$], [C$_4$mim][BF$_4$]	Templating
CeO_2-TiO_2	[C$_{16}$mim][Br]	As template
TiO_2/RGO	[C$_4$mim][PF$_6$]	Reducing agent
Anatase TiO_2	[C$_4$mim][BF$_4$]	Templating agent
TiO_2 films	[Cmim][HSO$_4$]	Structure directing agent
ZnO	[C$_4$C$_1$Py][TF$_2$N]	Reaction media, functional surface modifier
Cytochrome C Protein	[C$_4$mim][MeSO$_4$], [C$_4$mim][CH$_3$CO$_2$], [Ch][dbp], [C$_4$mim][dhp], [ch][dhp], [C$_4$mpyr][DCA], [Ch][Sac], [Ch][Lac]	Advanced solvent & Extracting agent
Oxidized Cellobiose	[Ch] [dbp],	
Metallo Protein	(Hy[Ch][dhp])	
Fructose dehydrogenase mobilized on Au or C	(Hy[Ch][dhp])	
Cellobios dehydrogenase mobilized on Au or C	(Hy[Ch][dhp])	
Dissolved cellulose	[C$_2$mim][MeO]][R][PO$_2$], R= H, Me, MeO	
Extracted cellulose and Xylan from from wehat bran	[C$_1$mim][MeO][PO$_2$]	

ToC text

Ionic liquids as eco-friendly and designer reaction media open new avenues in the field of electrochemical energy conversion devices.



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Broader context

The advent of ionic liquids (ILs) as eco-friendly and designer reaction media has opened new avenues in the field of energy storage and conversion devices. ILs offers many distinct advantages, such as negligible vapour pressure, good thermal stability, wide liquidus range, broad electrochemical window, and high synthetic flexibility. These peculiar properties endow ILs as designer reaction media in production and processing of highly engineered and tailored products via acting as advanced solvents, precursors, charge-compensating groups, structure directing/inducing agents. ILs-assisted synthesis help to obtain task-oriented specific materials with non-typical features, suitable for variety of specific applications. The synthesis and processing of energy conversion materials is one of the most rapidly growing application of ILs. Herein, a critical assess of the current status quo of the application of ILs in the fabrication and processing of materials for use in fuel cells, photo-electrochemical water splitting, dye sensitized solar cells (DSSC), and bio-fuels is made. This review also critically highlights crucial issues that should be addressed and provides perspectives for the future research directions in the field.