



Review

Ionic liquids in electrocatalysis

Gui-Rong Zhang^a, Bastian J. M. Etzold^{a,b,*}^a Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen 91058, Germany^b Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Technische Universität Darmstadt, Darmstadt 64287, Germany

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ABSTRACT

The performance of an electrocatalyst, which is needed e.g. for key energy conversion reactions such as hydrogen evolution, oxygen reduction or CO₂ reduction, is determined not only by the inherent structure of active sites but also by the properties of the interfacial structures at catalytic surfaces. Ionic liquids (ILs), as a unique class of metal salts with melting point below 100 °C, present themselves as ideal modulators for manipulations of the interfacial structures. Due to their excellent properties such as good chemical stability, high ionic conductivity, wide electrochemical windows and tunable solvent properties the performance of electrocatalysts can be substantially improved through ILs. In the current minireview, we highlight the critical role of the IL phase at the microenvironments created by the IL, the liquid electrolyte, catalytic nanoparticles and/or support materials, by detailing the promotional effect of IL in electrocatalysis as reaction media, binders, and surface modifiers. Updated exemplary applications of IL in electrocatalysis are given and moreover, the latest developments of IL modified electrocatalysts following the “Solid Catalyst with Ionic Liquid Layer (SCILL)” concept are presented.

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1. Introduction

Ionic liquids (ILs), which are usually defined as salts with melting points below 100 °C [1], represent a unique class of fluids combining many highly interesting properties such as good thermal stability, wide range of fluidity, high ionic conductivity, wide electrochemical potential window and low/negligible volatility. Origin of these unique properties stems mainly from the interplay of various interactions between ions (e.g., Coulombic force, hydrogen bond, intermolecular force) [2,3]. Thus, ILs can be strategically designed for specific applications, when the ionic interactions are understood in detail and on a molecular level. Thanks to numerous experimental data concerning the specific properties and applications of ILs being published in the past decade [4–7], and the significant development in the theoretical predication methods [8–12], the application oriented design of IL structures has become more and more feasible. Among their numerous applications highly interesting is the use of ILs in electrocatalysis. In the past decade application of ILs either as reaction media (solvent), binders, or catalyst surface modifiers for some electrocatalytic key energy conversion reactions (Fig. 1) has attracted tremendous research interest. The introduction of the IL phase to electrocatalytic

systems would give birth to a unique local microenvironment created by the solid electrode, liquid electrolyte and other adjacent species. The sensitivity of the electrocatalytic reaction on this local microenvironment can be employed to alter selectivity, activity and stability [13]. The IL phase is supposed to affect the electrocatalytic behavior through changing thermodynamic properties, reaction pathway, mass transportations, surface accessibility and local concentration of reactants at electrode surfaces, while detailed understandings of electrocatalysis involving IL and electrocatalytic systems specifically designed for use in IL are still needed.

Considering that there have been many excellent reviews concerning ILs in surface electrochemistry [3,14], electrified interfaces [2], bioelectrochemistry [15], we will not detail all sides of IL applied in electrochemistry. In the current minireview, we will focus on applications of ILs in electrocatalysis. The purpose is to summarize first how ILs can be employed to affect electrocatalysis and how electrocatalytic properties of ILs can be basis for rationally using IL to achieve performance enhancement and second to highlight some exemplary applications of ILs in the literature which involves any form of electrocatalysis.

2. How ILs would affect electrocatalysis

2.1. As reaction media

ILs have long been realized as alternative reaction media and solvent free electrolyte for electrochemical process [3,16].

* Corresponding author at: Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Darmstadt 64287, Germany. Tel: +49 6151 1629984; Fax: +49 6151 1629982.

E-mail address: etzold@tc1.tu-darmstadt.de (B.J.M. Etzold).

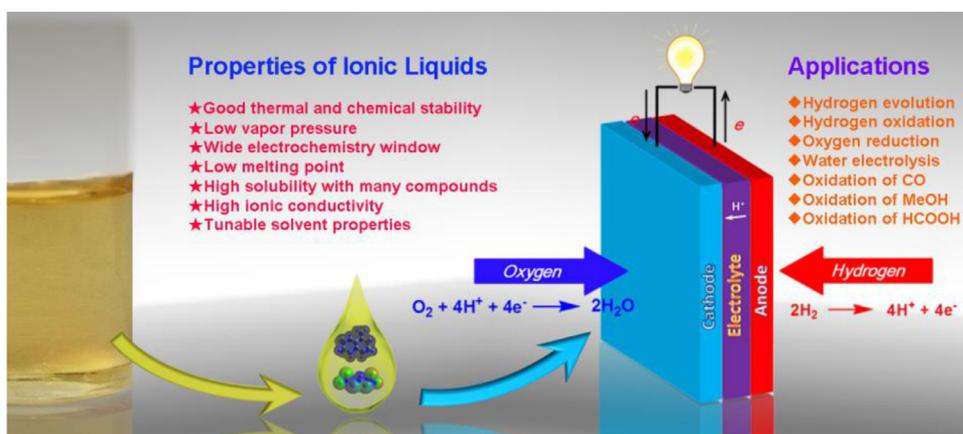


Fig. 1. Scheme illustrating typical properties and applications of ILs in electrocatalysis.

In particular, facile structural manipulation and excellent stability over wide potential/temperature range further make IL a promising electrolyte for electrocatalysis. For instance, IL ([C₄mim][BF₄]) has been used as electrolyte for hydrogen oxidation reaction (HOR) on transition metals such as molybdenum, which were highly active and fairly stable for HOR in IL [17]. The exchange current density is three times higher than that of HOR on platinum [17]. The measurements of activation energies indicate that water could be more easily activated on Mo than on Pt in IL. These results present a prospect of searching low-cost and highly efficient electrocatalysts for HOR in ILs. Electrocatalytic oxidation of hydrogen sulfide at platinum in IL was also studied [18,19]. It is found that the reactants tended to build up at the double layer, reflecting high solubility of the reactant in IL and possible attractive interactions with the IL anions at the electrode [19]. Al Nashef et al. reported that the ILs would facilitate the generation of superoxide ions (O₂^{•-}) which were highly active species for electrooxidation reaction [20]. It is reported that using [C₂mim][NTf₂] and [C₄mpyr][NTf₂] as the reaction media, phenol and 4-tert-butyl-phenol could be efficiently converted to corresponding phenyl triflate molecule [21], while using [C₄mim][BF₄] and [C₄mim][PF₆], benzyl alcohol could be selectively electrooxidized to benzaldehyde on platinum electrode [22]. Besides, IL has also been widely investigated as electrolyte for fuel cell applications, and a number of these studies suggested that fuel cells using protic ILs as electrolyte possessed better stability and performance than conventional inorganic acid electrolyte [23–27]. The promotional effect of IL as electrolyte could originate from the high solubility of reactant gases, weak moisture absorbing properties, and good mass transport properties which are desirable to improve the kinetics of the electrode reactions [27].

2.2. As binders

Due to their good conductivity and suitably viscous, ILs have also been employed as a new kind of binders for replacing conventional non-conductive organic ones in fabricating carbon paste electrode (CPE) for electrocatalytic applications [28]. It is found that IL modified CPE (IL-CPE) gave a very large current response from electroactive substrates. e.g., Maleki et al. prepared an IL-CPE composite electrode based on the use of pyridinium-based ionic liquid. They found that the composite electrode showed surprisingly high electrochemical performance, reflecting by its ability to lower the overpotential of electroactive compounds, and to increase the rate of electron-transfer processes, which is believed to be due to the modification of the microstructure of the electrode surface using ionic liquid as the binder [29]. A metal containing IL of [(C₄H₉)₂-bim]₃[La(NO₃)₆] was used for the fabrication of IL-CPE,

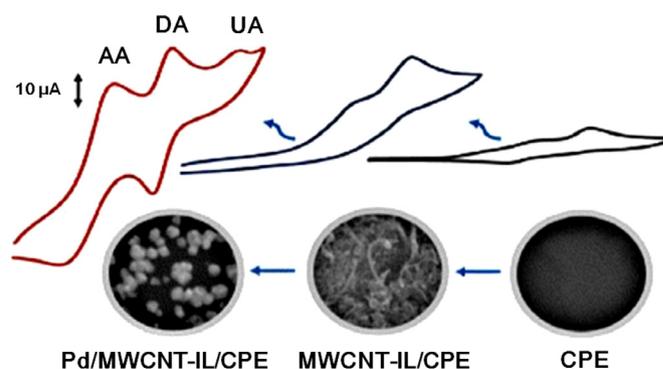


Fig. 2. The CPE was modified with multiwalled carbon nanotubes and an IL. After optimization the electrode was further modified with palladium nanoparticles. The resulting electrode gives three sharp and well separated oxidation peaks for ascorbic acid, dopamine and uric acid (from Ref. [31]).

which showed good electrocatalytic activities toward the reduction of hydrogen peroxide, nitrite, bromate, and trichloroacetic acid [30]. The presence of IL ([C₄mpyr][NTf₂]) in a modified CPE was also reported to improve the electrooxidation rate of ascorbic acid (AA), dopamine (DA) and uric acid (UA), enabling simultaneous determination of these organic molecules with high efficiency and wide linear responses (Fig. 2) [31]. Moreover, it is also well documented that incorporation of ionic liquid into the structure of CPE could improve the electrocatalytic activity of CPE-supported active species such as phosphomolybdic acid [32,33], hemoglobin [34], Pd [35,36], Ag [37], PdAg alloy nanoparticles [38], and Cu(OH)₂ [39]. A survey has been undertaken to clarify the possible reasons for the electrocatalytic activity enhancement by the presence of IL in CPE [40]. It was suggested that different factors, such as the increase in the ionic conduction of the binder, decrease in the resistance of the modified electrode, increase in ion exchange properties of the electrode and the inherent catalytic activity of ILs would be responsible for the considerably improved electrochemical response [40].

2.3. As surface modifiers

Furthermore, ILs show potential for surface modification of carbon materials to improve their compatibility and stability, and introduce more abundant binding sites to anchor metal nanoparticles for electrocatalytic applications. It is reported that IL-modified carbon materials exhibit switchable solubility [41], high charge-transfer activity [42] and high electronic conductivity [43]. In addition, low interfacial tensions of IL resulted in high nucleation rates, allowing formation of very small particles [44].

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