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Ionic liquid-doped polyaniline and its redox activities in the zwitterionic biological buffer MOPS

Ke Qu, Xiangqun Zeng*

Department of Chemistry, Oakland University, Rochester,MI 48309, United States

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ABSTRACT

The electropolymerization of aniline in several common imidazolium-based ionic liquids has been accomplished successfully with the potentiodynamic method. Considering the fact that imidazolium-based ionic liquids are acidic, they have been selected as the electrolyte for the electropolymerization of aniline, eliminating the usage of extra inorganic or organic acids. The ionic liquids not only serve as the reaction media, exerting the unique favorable π-π interactions between the imidazolium rings and benzene rings of aniline monomer or the growing polymer, but also act as the dopants to render different properties to the resulting polyaniline. Among the tested imidazolium-based ionic liquids, [BMIM][BF_4], [BMIM][PF_6], [BMIM][NTf_2], [EMIM][ES] and [HMIM][FAP], polyaniline doped by the hydrophilic ionic liquid [BMIM][BF_4] displays the good electrochemical responses in the biologically important MOPS (3-(*N*-Morpholino)-propanesulfonic acid) solution with 2.34×10^{-3} M of sulfuric acid additive. NMR, UV–vis and electrochemical impedance experiments were performed to further characterize the polyaniline/[BMIM][BF_4] composite. In contrast, polyaniline that is doped by the hydrophobic ionic liquid [BMIM][PF_6] is electroactive in the MOPS solution in the absence of the acid additive, with a pH of 5, extending the working pH range of polyaniline, which is typically electroactive in the solutions with the pH values less than 3. It is suggested that the effective hydrogen bonding interactions between BF_4 anion and water facilitate its hydrolysis in the microenvironment of the polymer backbone to provide the acidic protons, which are beneficial to the adjustment of the microenvironments of the polyaniline system and thus renders its observed well-resolved reversible pair of redox peaks in the MOPS solution. PF_6 anion, on the other hand, with its larger size and less basicity, has the weaker interaction with water, thus releasing the protons in a relatively slow manner, which gives some “buffer” capacities and rendering the [BMIM][PF_6]-doped polyaniline electroactive in the pH 5 of MOPS solution without the acid additive.

1. Introduction

Organic conducting polymers, the proven electronic, magnetic and optical materials, have many advantages for the chemical and biosensor development due to their tunable properties through varying their backbone structures [1,2]. Polyaniline, one of the most important family of organic conducting polymers, has received much attention across the scientific communities. Polyaniline materials are easy to synthesize by the chemical or electrochemical means and have good stability and adjustable electric conductivity. They have been used directly as the sensing materials or as the substrate for anchoring the different bio-recognition molecules. Polyaniline can also serve as the mediator for the electron transfer of the redox processes in the relevant biological recognition processes [3]. When the redox states of polyaniline are changed, the counter-ions will transport into the polymer layer to balance the generated charges, which is often the rate-limiting step [4–6]. The investigations showed that the transports of the different ionic species and the solvents into and within the polymer films not only changed the polymer films' structures a lot but also influenced the kinetics and thermodynamics of their redox behaviors [7–9]. So the polymeric structures that affect their electrochemical behaviors strongly depend upon the nature of the supporting electrolytes in which they are being synthesized [10,11]. Polyaniline shows the good electrical conductivity in the solutions with the low pH values, typically less than 3. Since aniline is a base, proton is the best counter-ion to be doped into the polyaniline structures. This might be the reason why the polyaniline formed in the acidic solutions only shows its redox activities in the acidic media. Our lab has been studying the

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* Corresponding author.
E-mail address: zeng@oakland.edu (X. Zeng).

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versatile sensor development, including the conducting polymer-based sensor [12–15]. In 2013, we demonstrated a glycosylated polyaniline sensor [16]. The Polyaniline was functionalized with the mannose for recognizing the lectin Concanavalin A (Con A), in which the polyaniline serves as a solid redox probe for the electrochemical readout. Most significantly, we observed the amine to imine conversion of polyaniline upon the carbohydrate-protein binding, which suggests that polyaniline can not only serve as the solid redox probe for the signal transduction but also as the pH sensitive probe to understand the role of the protons in the carbohydrate-protein recognition events. The development of the functionalized polyaniline as both the solid redox and the pH probe requires the development of polyaniline materials, which can show the good electrochemical and the electronic properties in the biological buffers. But for the biological systems, the neutral or near-neutral environments are preferred. Moreover, doping is necessary for the polyaniline to be electro-active to maintain the overall electro-neutrality through the incorporation of the corresponding counter ions. But many biological buffers are composed of the large ions, for example, the twenty Good's buffer solutions [17], which are zwitterions and renders them more difficult to dope into the polymer matrix due to their large sizes. Thus in this study, we are motivated to further explore and improve the fundamental properties of the polyaniline material itself, particularly its electrochemical responses in the biologically-important buffer containing the bulky zwitterion.

Ionic liquids are composed of bulky organic cations and inorganic/organic anions [18–20] whereas the conducting polymers are solids with the dopants in the rigid organic framework. Dopants can render the resulting polyaniline different properties, so it is reasonably hypothesized that ionic liquids could be utilized as the unique dopants to finely tune the properties of the resulting polyaniline. This hypothesis is supported by many previous researches in the ionic liquid and the conducting polymer systems. For instance, we studied the doping and un-doping processes of the conductive polyvinyl ferrocene (PVF) in different ionic liquids before [21]. In our previous observations, the reconfiguration of the polymer PVF can be effected through its redox cycling in these ionic liquids. Specifically, after conditioning of the PVF polymer in two ionic liquids, [BMIM][BF_4] and [PMIM][OMs], their cyclic voltammetric graphs showed that only the first cycle was different from the subsequent ones, which suggested that these ionic liquids are not only the electrolytes but also interacted with the polymer. The various interactions between PVF and the ionic liquids will significantly facilitate the PVF redox dynamics. Mattes and cowworkers reported in 2002 that polyaniline and polypyrrole, which have been electrochemically cycled in 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate, displayed the enhanced stability and could be used for the development of electrochemical actuators and electrochromic devices [22]. Mu used the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate in the copolymerization of aniline and 2-amino-4-hydroxybenzenesulfonic acid to render the better electrochemical activity and stability to the resultant copolymer [23]. Pringle reported the electrochemical synthesis of polypyrrole in three different ionic liquids as the growth media, which changed the film morphologies, resulting in the enhanced electrochemical activities [24]. Due to the larger size of the organic cations of the ionic liquids, it is expected as well that the porosity of the polymer will change accordingly after their doping, which could be beneficial to the function of polyaniline in biological buffers with larger zwitterions. MOPS (3-(*N*-Morpholino)-propanesulfonic acid, molecular structure with its zwitterion form [25] shown in Fig. 1) solution has been selected to test the above hypothesis. It is also well-known that protonic acids (HCl, H_2SO_4 or $HClO_4$) are often required for the polymerization of aniline monomer. Imidazoline molecule is one of the most important structures in nature [26] and it forms a large family of imidazolium-ring based ionic liquids [27]. With the significance of the role of the proton in the polyaniline formation and taking into consideration the fact that imidazolium-based ionic liquids are acidic in the 2-position [28,29], imidazolium-based ionic liquids could be used as the electrolyte for the electropolymerization of aniline, eliminating the usage of extra inorganic or organic acids [30]. It has also been believed by us that the imidazolium rings could have some favorable π-π interactions with the benzene units either in the aniline monomer or the growing polymer chain (See Figs. 2 and 3 for illustration). These ionic liquids have been proposed to be incorporated into the polyaniline system under the non-permseletive condition during the electrochemical aniline polymerization process (Fig. 3). Permselective condition refers to the doping of only the corresponding counter-ions in the bathing solution into the polymer to keep its electro-neutrality. While the non-permselective condition is the situation that with the doping of these counter-ions, their associated co-ions will be doped into the polymer as well [7,21].

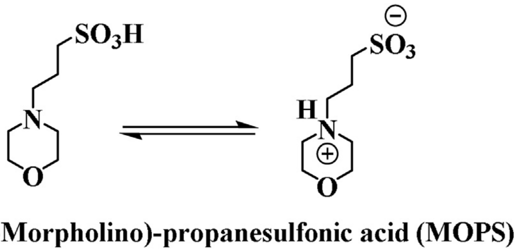

Fig. 1. The zwitterion structure of MOPS.

In this work, electropolymerization of aniline has been achieved in five different imidazolium based ionic liquids, [BMIM][BF_4], [BMIM][PF_6], [BMIM][NTf_2], [EMIM][ES] and [HMIM][FAP] and their electrochemical behaviors have been evaluated in the biologically-important MOPS solution through the cyclic voltammetry and electrochemical impedance spectroscopic techniques. Moreover, NMR, UV–vis spectroscopy and scanning electron microscopy (SEM) experiments were performed to characterize the obtained ionic liquid-doped polyaniline. It has been demonstrated that the electroactive range of polyaniline doped by the imidazolium based ionic liquids moves towards the near-neutral conditions in the biologically-important MOPS solution.

2. Experimental

2.1. Chemicals

1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4], ≥97% (HPLC grade)), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6], ≥97% (HPLC grade)), 3-(*N*-Morpholino)-propanesulfonic acid (MOPS, ≥99.5% (titration)), *N*-methyl-2-pyrrolidinone (≥99.0%) and aniline (≥99.5%) were purchased from Sigma-Aldrich 1-Ethyl-3-methylimidazolium ethylsulfate ([EMIM][ES], 99%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf_2], 99%) and 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide ([BMPip][NTf_2], 99%) were purchased from Io-Li-Tec Inc. 1-Hexyl-3-methylimidazolium tris (pentafluoroethyl)trifluorophosphate ([HMIM][FAP], high purity) was obtained from EMD Millipore. The structures of the ionic liquids used are shown in Fig. 4.

2.2. Experimental methods

Glassy carbon working electrodes (diameter = 2 mm) were purchased from CH Instruments, Inc. and were pretreated by