Electrochemistry Communications 73 (2016) 5–9

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Platinum/poly(*N*-ferrocenylmethyl-*N*-allylimidazolium bromide) quasi-reference electrode for electrochemistry in non-aqueous and ionic liquid solutions

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ARTICLE INFO

Article history:
Received 7 September 2016
Received in revised form 11 October 2016
Accepted 11 October 2016
Available online 14 October 2016

Keywords:
Redox polymer
Electrochemistry
Quasi-reference electrode
Polymer ionic liquid
Non-aqueous solutions

ABSTRACT

A platinum wire coated with partially oxidized poly(*N*-ferrocenyl-*N*-allylimidazolium bromide) is proposed as a quasi-reference electrode (QRE) for use in non-aqueous and ionic liquid solutions. The electrode was fabricated by the electrochemical polymerization of *N*-ferrocenylmethyl-*N*-allylimidazolium bromide on a Pt wire. The stability of the QRE was investigated by cyclic voltammetry in acetonitrile and ionic liquid solutions. The QRE exhibits better performance in terms of stability than conventional metal wire based quasi-reference electrodes (Ag, Pt). Furthermore, unlike the classical reference electrodes (SCE or Ag|AgCl), the proposed QRE prevents contamination of the test solution.

1. Introduction

Electrochemical investigations in non-aqueous solutions require stable reference electrodes, which are not easy to obtain. Compared with classical organic solvents, ionic liquids (ILs) have some interesting physico-chemical properties (low vapor pressure, large electrochemical window and high electrical conductivity) that make them very attractive for diverse applications, including synthesis [1,2], electrocatalysis [3,4], electropolymerization [5], and capacitors [6]. Electrochemistry in ionic liquids has been widely investigated because ILs act as both solvent and supporting electrolyte [7]. Indeed, ionic liquids have been successfully used in molecular electrochemistry and electrochemical grafting, exhibiting different properties to classical solvents [8–11].

One of the drawbacks frequently encountered in this environment is related to the selection of an appropriate reference electrode (RE). Because of the unique physico-chemical requirements, the choice of REs for electrochemical measurements in ionic liquids and molten salts is very restricted. Currently, saturated calomel electrodes (SCE) and Ag|AgCl are widely used as REs in non-aqueous solutions. However, these electrodes generate an undesirable liquid junction between the aqueous phase inside the electrode and the non-aqueous phase from the bulk solution, as well as causing water to diffuse from the RE to the solution, resulting in undesirable contamination. An ideal reference electrode should be stable over time, i.e. the reference potential does not drift or shows minimal drift (ideally <10 mV per day) [12]. The RE commonly reported in the literature for use in ionic liquids is based on a metal/metal ion system ($Ag|Ag^+$). This RE was fabricated by immersing Ag wire in an ionic liquid solution containing a silver salt [13–15]. Despite the moderate stability of these REs, the presence of a small amount of water inside the electrode may cause the formation of silver nanoparticles in a solution containing Ag^+ and the ionic liquid anion ($TFSI^-$). In addition, these types of electrodes can cause undesirable electrochemical signals due to the diffusion of Ag^+ from the RE into the test solution. To overcome this problem, quasi-reference electrodes (QREs) based on metallic wires (silver or platinum) have been proposed [16]. In this case, an internal reference such as ferrocene is frequently employed to calibrate the reference electrode against the commonly used reference system. However, the latter exhibits a potential drift with time during a series of electrochemical measurements due to the formation of metal oxide. Recently Kötz et al. proposed activated carbon as a convenient QRE for use in non-aqueous media [17,18]. Solid state QREs based on metallic wire coated with polymers have also been proposed for electrochemical investigations in non-aqueous media [19–22].

In this report, poly(*N*-ferrocenylmethyl-*N*-allylimidazolium bromide), poly(FcIL), was deposited on a platinum wire by electrochemical reduction of its corresponding monomer. The polymer film was

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http://dx.doi.org/10.1016/j.elecom.2016.10.007
1388-2481/

characterized by electrochemical methods. Next, the Pt coated with partially oxidized poly(FcIL) was used as a quasi-reference electrode. The stability of the proposed QRE was investigated in acetonitrile and ionic liquid solutions.

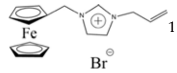
2. Experimental section

2.1. Chemicals

Iodomethane, *N*-ethylimidazole, imidazol, and allylbromide were supplied by Sigma-Aldrich and were used as received. Supporting electrolytes: tetrabutylammonium perchlorate (TBAP), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), TBABr, TBACl, TBAOH, $TBAClO_4$, $TBAHSO_4$, $TBACF_3SO_4$, and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), with purity >99% were supplied by Sigma-Aldrich and were used as received. (Ferrocenemethyl)trimethylammonium iodide and ferrocene were purchased from Alfa-Aesar. Acetonitrile and chloroform were supplied by VWR chemicals at the highest purity available.

2.2. Synthesis of N-ferrocenylmethyl-N-allylimidazolium bromide

N-ferrocenylmethylimidazole was prepared according to the previously published procedure [5]. Next, allylbromide (0.91 ml, 10.5 mmol) was added to a solution containing (1.2 g, 4.5 mmol) of *N*-ferrocenylmethylimidazole in chloroform under stirring. The mixture was refluxed for 2 h then the solvent and unreacted starting materials were evaporated under reduced pressure. The yield of this reaction was 87%.



^{1}H NMR (400 MHz, DMSO) δ (ppm): 4.22 (m, 7H), 4.45 (t, $J = 1.6$ Hz, 2H), 4.83 (m, 2H), 5.26 (s, 2H), 5.33–5.36 (m, 2H), 6.04 (m, 1H), 7.71 (s, 1H), 7.81(s, 1H), 9.23 (s, 1H). ^{13}C NMR (400 MHz, DMSO) δ (ppm): 135.9, 132.6, 123, 121.1, 69.38, 69.27, 51.08, 48.8.

2.3. Electrochemical measurements

For the fabrication of the quasi-reference electrode, a platinum wire was used as the working electrode; an Ag|AgCl electrode and a stainless steel mesh were used as the reference and counter electrode, respectively. The electrochemical polymerization was performed in acetonitrile solution. A glassy carbon electrode was used as the working electrode to test the electrochemical performance and the stability of the reference electrode. The electrochemical tests were performed using a CHI920C potentiostat (CH Instruments, Austin, Texas).

3. Results and discussion

3.1. Electrochemical polymerization

Poly(vinylferrocene) modified electrodes have been prepared by several polymerization methods, including electrochemical ones. Indeed, Leech et al. reported that the electrochemical reduction of vinylferrocene monomer provides a stable and compact electroactive polymer film [23]. This procedure was followed to polymerize *N*-ferrocenylmethyl-*N*-allylimidazolium bromide monomer on a platinum electrode.

The electrochemical polymerization was carried out with a three-electrode setup using a Pt wire as the working electrode, a stainless steel mesh as the counter electrode and Ag|AgCl as the reference electrode. Platinum wire was immersed in a solution containing 5 mM of *N*-ferrocenylmethyl-*N*-allylimidazolium bromide and 0.1 M of $TBAPF_6$ in acetonitrile (MeCN). The solution was deoxygenated by argon flow for 30 min. Successive cyclic voltammetry (20 cycles) over the potential range from 0.8 to −2.8 V vs Ag|AgCl was performed, as shown in Fig. 1a. During the first scan, a reversible redox signal attributed to the ferrocenyl group linked to the vinyl monomer was observed at 0.55 V. Scanning to negative potential shows a reduction current starting from −1.8 V, which is assigned to the reduction of the allyl group. At this potential, the allyl group was reduced to form a radical anion which can become attached to the electrode surface [24]. Upon continuous cycling the reduction current decreased due to the formation of an electronically insulating film, indicating that the polymer had been formed. After a few cycles the current saturated and the film thickness reached its limit. A yellow film was observed on the platinum wire, indicating the formation of a polymer film. The modified wire was characterized by SEM which shows the presence of a dense and homogeneous polymer film coating the Pt wire (inset Fig. 1a). In the literature, poly(vinylferrocene) has been produced under the same conditions, showing similar behavior, and the film was found to be stable and free of large pinholes [23]. After the polymerization, the modified electrode was rinsed carefully with acetonitrile.

To check for the presence of polymer on the electrode, the latter was characterized by cyclic voltammetry in MeCN solution containing 0.1 M $TBAPF_6$. The redox signal of the immobilized ferrocenyl groups was observed at 0.45 V as illustrated in Fig. 1b. The peak-to-peak separation was found to be around 30 mV and the current intensity was slightly

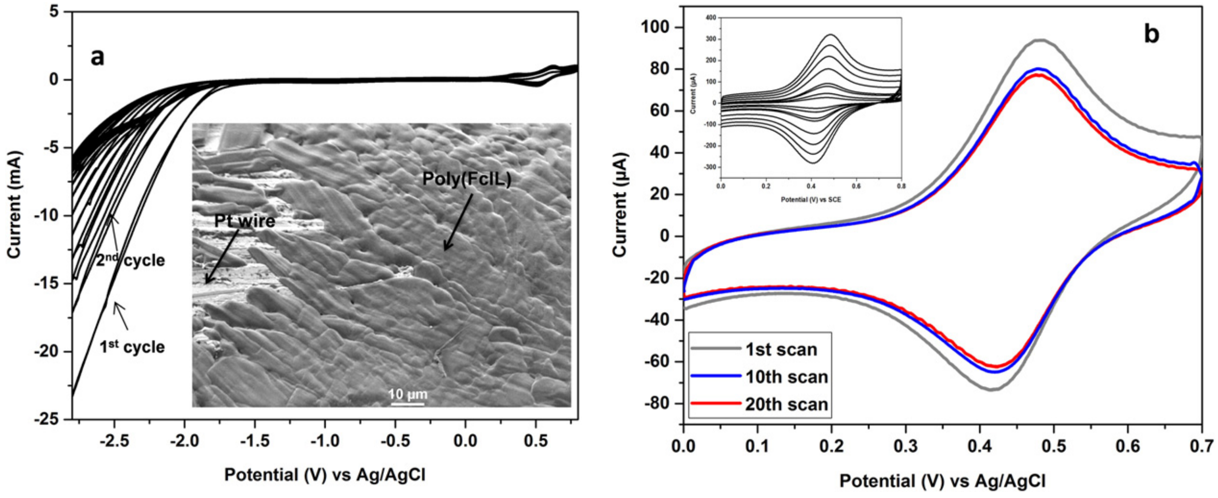


Fig. 1. (a) Cyclic voltammetry at Pt wire in an acetonitrile solution containing 5 mM of *N*-ferrocenylmethyl-*N*-allylimidazolium bromide monomer and 0.1 M $TBAPF_6$, inset represents the SEM image of Pt/Poly(FcIL); (b) cyclic voltammetry of polymer-coated Pt wire in MeCN containing 0.1 M $TBAPF_6$, 1st scan (gray), 10th scan (blue) and 20th scan (red). Inset: variation of the CVs as function of the scan rate.