

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/aca

Sensitive and stable amperometric measurements at ionic liquid–carbon paste microelectrodes

Mustafa Musameh^{a,*}, Joseph Wang^{b,c,**}

^a Department of Biology and Chemistry, American University of Sharjah, Sharjah, P.O. Box 26666, United Arab Emirates

^b Department of Chemical & Materials Engineering, The Biodesign Institute, Arizona State University, Tempe, AZ 85287, USA

^c Department of Chemistry and Biochemistry, The Biodesign Institute, Arizona State University, Tempe, AZ 85287, USA

ARTICLE INFO

Article history:

Received 2 August 2007

Received in revised form

5 November 2007

Accepted 7 November 2007

Published on line 17 November 2007

Keywords:

Ionic liquids

Carbon paste

Mineral oil

Surface fouling

ABSTRACT

Ionic liquids (ILs) were utilized in preparing carbon paste electrodes with improved sensitivity, linearity, and stability. In order to overcome the large capacitance encountered with these pastes which affects the measured signal, microelectrodes were used to minimize the background current and improve the signal to background response. A number of ILs were tested including those having the same anions, such as butyl, hexyl, and octyl hexafluorophosphate (PF₆), and those having the same cation, including hexyl-imide, trifluorophosphate (PF₃) and PF₆. Based on the structure of each ILs, different responses were obtained. Several probes were utilized for those studies including hydrogen peroxide, acetaminophen, and ascorbic acid. The butyl-methyl-imidazolium (BMI)-PF₆ displayed the highest response among other ILs with similar anions and the smallest peak separation. The optimum ILs loading in terms of electrode resistance, capacitance, and peak separation was 30–40%. Improved resistance to surface fouling was observed at the ILs–carbon paste electrode compared to that using mineral oil when tested for NADH detection. Very good linearity up to 1 mM hydrazine (correlation coefficient 0.996) was obtained using the ILs–carbon paste electrode.

© 2007 Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids (ILs) are a class of materials which have attracted many scientists as holding a great promise for green chemistry applications [1–3]. Room temperature ionic liquids are liquid electrolytes composed entirely of ions. The basic structure of any ionic liquid is based on a heterocyclic cation such as *N,N*-dialkyl substituted imidazolium ions, and an anion like BF₄[−] or PF₆[−] [2]. The use of the PF₆[−] as the counter ion to an *N,N*-dialkyl substituted imidazolium cation causes the resulting structure to be water immiscible [4]. The PF₆[−] based ILs have been shown to be electrochemically stable with a wide

potential window of over 5 V. Because they are mainly made up of ions, they reveal excellent electrical conductivity over the temperature range −25 to 85 °C. They also exhibit a high boiling temperature and hence a low vapor pressure in ambient conditions [5]. In addition, ILs have been shown to be suitable media for supporting biocatalytic processes [6,7]. The use of ionic liquids as electrolytes for many electrochemical and analytical applications has been discussed in several papers [5,8,9]. It has been shown that the unique properties of ILs compare favorably with other traditional types of solvents. ILs droplet and film deposits have been used to modify electrochemical reactivity. It has been shown that ILs have very

* Corresponding author. Tel.: +971 6 515 2440.

** Corresponding author. Tel.: +1 480 727 0399.

E-mail addresses: mmusameh@aus.edu (M. Musameh), joseph.wang@asu.edu (J. Wang).

0003-2670/\$ – see front matter © 2007 Elsevier B.V. All rights reserved.

doi:10.1016/j.aca.2007.11.012

specific selectivity effects upon the partitioning for certain ions [10].

Preparation of carbon paste electrodes where ILs are used as a binder has been reported in several studies [11–14]. However, one major concern was the high background current which limits the analytical utility of these IL-based pastes. One approach to minimize the background current and to increase the analytical signal-to-background ratio is made via decreasing the electrode active surface area and increasing mass transport rates by utilizing microelectrodes.

In this study we further investigate the use of ILs as a pasting liquid towards fabrication of ILs–carbon paste microelectrodes. Important model compounds were used in this investigation such as hydrogen peroxide, ascorbic acid (AA), acetaminophen, NADH, and hydrazine; all having important applications in the medical, industrial, and environmental fields. A comparison between several ionic liquids is made to explore the effect of structure on properties of each. The length of carbon chain on the imidazolium cation greatly affects their conductivity due to the change in other physical properties such as viscosity. Also the presence of different anions seems to affect the conductivities of those ILs as well. One of the most important requirements for making a good carbon paste electrode is stability and conductivity. ILs have shown to be very stable and highly conductive material which can be used as a pasting material. We investigated the electrocatalytic properties and electroconductivity of these pastes compared to conventional carbon paste electrodes based on a non-conductive binder. ILs paste electrodes show very sensitive and stable response compared to pastes made of non-conductive binder. The enhanced antifouling effect of the ILs paste electrodes is another feature to be added to this attractive class of material.

2. Experimental

2.1. Apparatus

Amperometric experiments were performed with a Bioanalytical Systems (BAS) CV-27 voltammograph, in connection with a BAS X-Y recorder. Cyclic voltammograms were recorded with the Autolab PGSTAT10 Electrochemical Analyzer (Eco Chemie BV, Utrecht, Netherlands). The working electrode, the Ag/AgCl reference electrode (Model CHI111, CH Instruments, Austin, TX), and platinum wire counter electrode were inserted into the 20-mL cell (BAS, Model VC-2) through holes in its Teflon cover. A magnetic stirrer provided the convective transport during the amperometric measurement. The flow injection system consisted of a carrier solution reservoir, an injection valve with 250 μ L loop, interconnecting PTFE tubing, and a peristaltic pump (FIALab, Alitea US, Medina, WA).

2.2. Chemicals and reagents

All solutions were prepared from double-distilled water. NADH (β -nicotinamide adenine dinucleotide, reduced form), potassium dihydrogen phosphate, and dipotassium hydrogen phosphate, were purchased from Sigma. Hydrogen peroxide (30 wt.%), hydrazine, ascorbic acid,

acetaminophen, and mineral oil were purchased from Aldrich (Milwaukee, WI). Graphite powder (grade #38) was received from FisherScientific (Fair-Lawn, NJ). Ionic liquids 1-butyl-3-methyl-imidazolium hexapfluorophosphate (BMI-PF₆), 1-hexyl-3-methyl-imidazolium hexafluorophosphate (HMI-PF₆), and 1-octyl-3-methyl-imidazolium hexapfluorophosphate (OMI-PF₆), were obtained from Fisher (Acros). 1-Hexyl-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate (HMI-PF₃), and 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide (HMI-Imide) were purchased from Merck (Germany).

2.3. Electrode fabrication

The required amount of ionic liquid or mineral oil was mixed using pestle and mortar with the needed amount of graphite for 10 min (30–40% IL and 70–60% graphite was the optimum composition). The paste was then packed at the end of a pipette tip (diameter 350 μ m) to a depth of 3 mm. Electrical contact was achieved via a copper wire.

2.4. Procedure

Measurements were carried out in a phosphate buffer (0.05 M, pH 7.4) supporting electrolyte medium for amperometric and cyclic voltammetry measurements. Amperometric detection was proceeded under forced convection for batch, flow conditions for FIA, and quiescent conditions for 50 mV s⁻¹ cyclic voltammetry experiments. The desired working potential was applied, and transient currents were allowed to decay to a steady-state value. All measurements were performed at room temperature.

3. Results and discussion

Initial experiments compared an ordinary IL-based paste macroelectrode (2 mm id) to the microelectrode housing (350 μ m id). The later offers a five-fold increase in the analytical signal-to-background current ratio (not shown). Therefore, the microelectrode configuration was utilized throughout the study.

The use of ILs (rather than using mineral oil) for fabricating CPEs greatly promotes catalytic activity towards important analytes with a sluggish redox process [11–14]. Fig. 1 shows typical cyclic voltammograms for hydrogen peroxide (A), ascorbic acid (B), and acetaminophen (C) at the mineral oil based electrode (a) and the IL-based (b) carbon paste electrodes. At the conventional electrode the redox activity is observed only above 0.8 V using hydrogen peroxide. The overvoltage for the oxidation process is greatly lowered at the IL surfaces, with oxidation starting around 0.3 V. The oxidation for the IL-based electrode is about 50 times larger than that for the mineral oil counterpart. Similar lowering of overvoltages and signal amplification are observed for the oxidation of ascorbic acid and acetaminophen (Fig. 1 (B) and (C)). The anodic peak potentials for AA, and acetaminophen at the IL surface are 0.3 and 0.5 V, respectively, compared to 0.7 and 0.65 V at the mineral oil paste. The ILs-based electrode displays a quasi-reversible cyclic voltammogram for acetaminophen,

Download English Version:

<https://daneshyari.com/en/article/1170116>

Download Persian Version:

<https://daneshyari.com/article/1170116>

[Daneshyari.com](https://daneshyari.com)