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Ionic liquid-carbon composite glucose biosensor

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ABSTRACT

The use of ionic liquids that are solid at room temperature such as *n*-octyl-pyridinium hexafluorophosphate (*n*OPPF$_6$) is shown to be advantageous in the fabrication of new form of biocomposite materials with attractive performance over other types of composites and pastes involving non-conductive binders. The resulting IL/graphite material brings new capabilities for electrochemical devices by combining the advantages of ILs and "bulk" composite electrodes. The electrocatalytic properties of the ILs are not impaired by their association with the graphite powder. The marked electrocatalytic activity towards hydrogen peroxide permits effective amperometric biosensing of glucose in connection with the incorporation of glucose oxidase within the three-dimensional IL/graphite matrix. The accelerated electron transfer is coupled with low background current and improved linearity. The advantages of these IL-based biocomposite devices are illustrated from comparison to conventional mineral oil/graphite biocomposite. The influence of the IL and glucose oxidase (GOx) loading upon the amperometric and voltammetric data, as well as the electrode capacitance and resistance, is examined. The preparation of IL/graphite composites overcomes a major obstacle for creating IL-based biosensing devices and expands the scope of IL-based electrochemical devices.

1. Introduction

Lately, the search for solvents that are less harmful to the environment has been addressed by scientists all over the world. Ionic liquids (ILs) offer themselves as a new class of materials and strong candidates, convincing many scientists as holding a great promise for green chemistry applications (Huddleston et al., 2001; Seddon, 1997; Koch et al., 1998). One definition for room temperature ionic liquids (RTILs) are liquid electrolytes made entirely of ions which have melting points below 100 °C (Buzzeo et al., 2004). The basic structure of any ionic liquid is based on an asymmetric heterocyclic cation such as *N*,*N*-dialkyl substituted imidazolium ions, and a small anion like tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), or bis(trifluoromethylsulfonyl)imide (NTf_2) (Seddon, 1997). The use of the PF_6^- or NTf_2 as the counter ion to an *N*,*N*-dialkyl substituted imidazolium cation causes the resulting structure to be water immiscible (Suarez et al., 1998). The PF_6^- or NTf_2 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 (ionic) conductivity as well as showing thermal stability over the temperature range −25–85 °C (Buzzeo et al., 2004). One important feature of ILs is their very low vapor pressure in ambient conditions (Lee and Chou, 2004).

Carbon paste electrodes made by using ILs as a binder for analytical purposes have been reported in few studies (Liu et al., 2005; Maleki et al., 2006; Safavi et al., 2007; Shul et al., 2006), where they were utilized for analysis of different species such as nitrite, ascorbic acid, uric acid, and dopamine. Due to their thermal stability and high conductivity, it would be advantageous to use ILs to fabricate IL-carbon paste biosensors. However, very high background current limits their use for such application using this configuration. Due to this limitation, researchers have tried to fabricate IL-based biosensors and biosensing schemes using other configurations. A number of studies have shown that biosensors can be operated in RTILs instead of aqueous medium which results in increasing the life time of the biosensor (Xiong et al., 2007; Wang et al., 2007a,b). Modifying the electrode surface with a thin film of an ionic liquid and then immobilizing the enzyme of choice on that film was also shown to be useful in preparing biosensors for several applications (Du et al., 2007; Zhao et al., 2007; Sun et al., 2007). Recently, Wang et al. has shown that it is possible to fabricate an IL-carbon paste biosensor with low background current via mixing the paste

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with paraffin oil "a non-conductive binder" which tends to decrease the background current and hence improve the sensor response. Several heme proteins were evaluated using this paste for the analysis of hydrogen peroxide including myoglobin, hemoglobin, and horseradish peroxidase (Wang et al., 2007a, b). Another type of ionic liquid composite electrode which showed low background current was demonstrated by the use of the ionic liquid "*n*-octyl-pyridinium hexafluorophosphate" that is solid at room temperature (melting point 65 °C) (Maleki et al., 2006). This new composite material showed very improved signal to background current for the detection of different analytes such as ascorbic acid, and NADH. However, one major requirement for the successful operation of this new composite electrode was the need to heat the composite material to the melting point of the IL before using it in order to lower the background current.

This paper reports for the first time the simple preparation of an ionic liquid-carbon composite biosensor using *n*-octyl-pyridinium hexafluorophosphate mixed with graphite powder and glucose oxidase for the detection of glucose without the need for heating to lower the background current. The electrode combines both the ease of fabrication, low background current, and the improved response compared to other traditional glucose oxidase composite and paste electrodes using non-conductive binders.

2. Experimental

2.1. Apparatus

Amperometric, and cyclic voltammetric measurements were performed using a computer controlled μ-Autolab II potentiostat (Ecochemie, The Netherlands) with a three-electrode configuration. The working electrode, the reference electrode (a saturated calomel electrode, SCE, Radiometer, Copenhagen, Denmark), and the counter electrode (a bright platinum wire) were inserted into the 20-mL glass cell (Home made) through holes in its Teflon cover. A magnetic stirrer provided the convective transport during the amperometric measurement. Cyclic voltammetry experiments were carried out under quiescent conditions. SEM images were obtained with the JOEL JSM840F unit with a field emission gun as electron source and an acceleration voltage of 5 kV.

2.2. Chemicals and reagents

All analytical solutions were prepared from double-distilled water. Water was purified by double distillation using an Elix® UV-10 system. All other solvents were used as supplied (analytical or HPLC grade) without prior purification. Potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium ferricyanide, 1-butyl-3-methyl-imidazolium hexafluorophosphate, mineral oil, and synthetic graphite powder consisting of irregularly shaped microparticles 2–20 μm in diameter, were purchased from Aldrich. Glucose oxidase (GOx) (EC 1.1.3.4, Type X-S, Aspergillus Niger, 234,900 U/g), and β-D(+) glucose (97%) were obtained from Sigma (Dorset, England). The ionic liquid *n*-octyl-pyridinium hexafluorophosphate was kindly prepared by the Chemistry Research Laboratory at Oxford University. The procedure of synthesis is explained below. Melting points were recorded on a Gallenkamp Hot Stage apparatus and are uncorrected.

The ionic liquid 1-*n*-octyl-pyridinium hexafluorophosphate was prepared according to a modified version of the procedure described by Safavi (Maleki et al., 2006).

To neat 1-iodooctane (2.00 mL, 11.0 mmol, 1.0 eq.) was added pyridine (0.89 mL, 11.0 mmol, 1.0 eq) and the resulting mixture was stirred at room temperature for 72 h. To the residue was added acetonitrile (MeCN) (0.5 mL) and the resulting solution was washed with diethylether (Et_2O) (3 × 5 mL). The Et_2O washings were discarded and the product dried *in vacuo* at room temperature to give 1-*n*-octyl-pyridinium iodide as clear yellow viscous oil (3.50 g, quant) which was used without further purification.

To a stirred solution of 1-*n*-octyl-pyridinium iodide (1.00 g, 3.10 mmol, 1.0 eq.) in H_2O (1.5 mL) at room temperature was added a solution of ammonium hexafluorophosphate (0.51 g, 3.10 mmol, 1.0 eq) in H_2O (1.5 mL) dropwise. After stirring at room temperature for 2 h, the resulting white precipitate was isolated by filtration and washed with H_2O (3 × 5 mL) followed by Et_2O (2 × 5 mL) and dried *in vacuo* at room temperature for 24 h to give 1-*n*-octyl-pyridinium hexafluorophosphate as a white powder (0.91 g, 87%) with a melting point T_m = 64–65 °C (T_m = 65 °C (Maleki et al., 2006)).

2.3. Electrode fabrication

The required amount of the ionic liquid or mineral oil was mixed using pestle and mortar with the needed amount of graphite for 20 min. Although this IL is a solid powder, it has a sticky nature, and once it is mixed with graphite using pestle and mortar it tends to interact strongly and forms a very solid and mechanically stable composite. The surface of the composite can be polished very well and shows features similar to solid surfaces. Then the required amount of glucose oxidase was added, and the paste was mixed for another 10 min. Exactly 9.4 mm^3 of the resulting paste was then packed firmly into the electrode cavity (2 mm diameter and 3 mm depth) of a glass sleeve. Electrical contact was established via a copper wire. The paste surface was smoothed on a weighing dish and rinsed carefully with double-distilled water prior to each measurement.

2.4. Procedure

Measurements were carried out in a phosphate buffer (0.05 M, pH 7.5) supporting electrolyte medium for amperometric, and cyclic voltammetry measurements. Amperometric detection was made under forced convection, whereas quiescent conditions were used for cyclic voltammetry experiments. In the former 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

3.1. Optimization of the IL-carbon composite ratio

The attractive behavior of the new ionic liquid (*n*-octyl-pyridinium PF_6) towards the fabrication of ionic liquid/graphite/GOx biocomposite electrodes has been illustrated. This was made in connection to amperometric detection of the liberated hydrogen peroxide in comparison to a graphite-based mineral oil electrode with a similar GOx loading. Initial experiments aimed at the optimization of the ionic liquid loadings using ferricyanide as a probe. Fig. 1 displays the effect of different ionic liquid loadings upon cyclic voltammograms in a phosphate buffer solution (A), and in a 5 mM ferricyanide solution (B). Ten percent loading of the ionic liquid shows very large background current as can be seen in Fig. 1A. An increase in background current upon repetitive cycling (data not shown) was also observed at this loading indicating low stability of this composition. On increasing the loading from 10% to 50%, a dramatic decrease in background current was observed along with improved stability upon repetitive cycling. The composites with loadings less than 40% were highly unstable in solution and were showing slow increase in

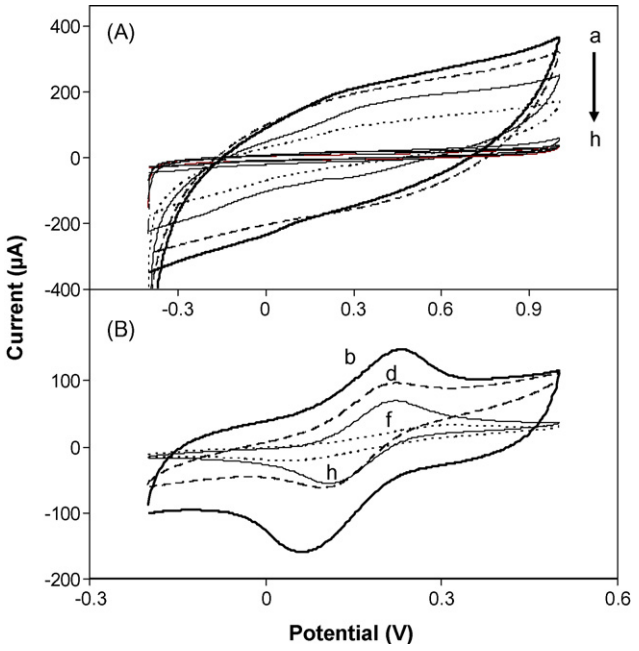

Fig. 1. Cyclic voltammograms for 0.05 phosphate buffer (pH 7.5) (A) and 5 mM potassium ferricyanide (B) using IL/graphite pastes with different ratios: 10/90 (a), 20/80 (b), 30/70 (c), 40/60 (d), 50/50 (e), 60/40 (f), 70/30 (g), and 80/20 (h), respectively. Supporting electrolyte, phosphate buffer (0.05 M, pH 7.5), scan rate 50 mV/s.

background current while in solution. That is why there is a slight difference in background current between blank phosphate buffer and ferricyanice solutions, since in most experiments, the sequence of experiments was first single blank measurement followed by CV in ferricyanide, and finally capacitance measurement in blank phosphate buffer. Loadings of 50% and higher showed nearly the same low background currents and stability. Similar behavior was also observed using 5 mM ferricyanide as shown in Fig. 1B, for 20%, 40%, 60%, and 80% loadings of the ionic liquid. Low loadings show larger background currents with larger peak-to-peak separations as shown for 20%, and 40% loadings. On increasing the loading to 60%, and 80% ionic liquid resulted in a significant decrease in the background currents. As the loading of IL increases, it leads to a better filling between the graphite particles and hence higher mechanical stability. This further leads to lower background currents since less water will be penetrating through the composite. As the background current decreases, the analytical current to background ratio increases. SEM images taken for the 50% *n*-octyl-pyridinium IL were compared with images for another ionic liquid (1-butyl-3-methylimmidazolium hexafluorophosphate) that is liquid at room temperature. SEM images confirm the homogeneity and the well-packing nature of the 50% *n*-octyl-pyridinium paste compared with the other ionic liquid paste using 50% loading and an optimal loading of 30% as shown in Figure S1 (see Supplemental information). It is clear from these images that the 50% *n*-octyl-pyridinium IL paste shows very similar surface morphology to that for the 50% 1-butyl-3-methylimmidazolium IL paste. However, the 50% *n*-octyl-pyridinium IL paste has much better mechanical stability and electrochemical performance compared to that for 50% 1-butyl-3-methylimmidazolium IL paste. Using the optimal composition of 30% 1-butyl-3-methylimmidazolium IL paste leads to the formation of a rough surface with irregular distribution of graphite flakes.

The peak-to-peak separation followed a similar decreasing trend up to 70%, but started to increase afterwards as can be clearly seen for the 80% loading. Further optimization of the composition was performed by measurement of capacitance, resistance, cathodic currents, and peak-to-peak separation using cyclic voltammograms for 5 mM ferricyanide as shown in Fig. 2.

The capacitance of the IL-based electrode decreases greatly above 20% and levels off at 50% as shown in Fig. 2A. This behavior contradicts that for carbon paste electrodes utilizing ionic liquids that are liquid at room temperature such as 1-butyl-3-methylimmidazolium hexafluorophosphate (Figure S2, Supplemental Information) where the capacitance of the IL carbon paste electrode jumps greatly above 40% and levels off at 50%. The exact reason for this is not fully understood. Loadings of ILs above 50% show dramatic increase in resistance, but this is much lower than that for the mineral oil based electrodes. This indicates that the ILs

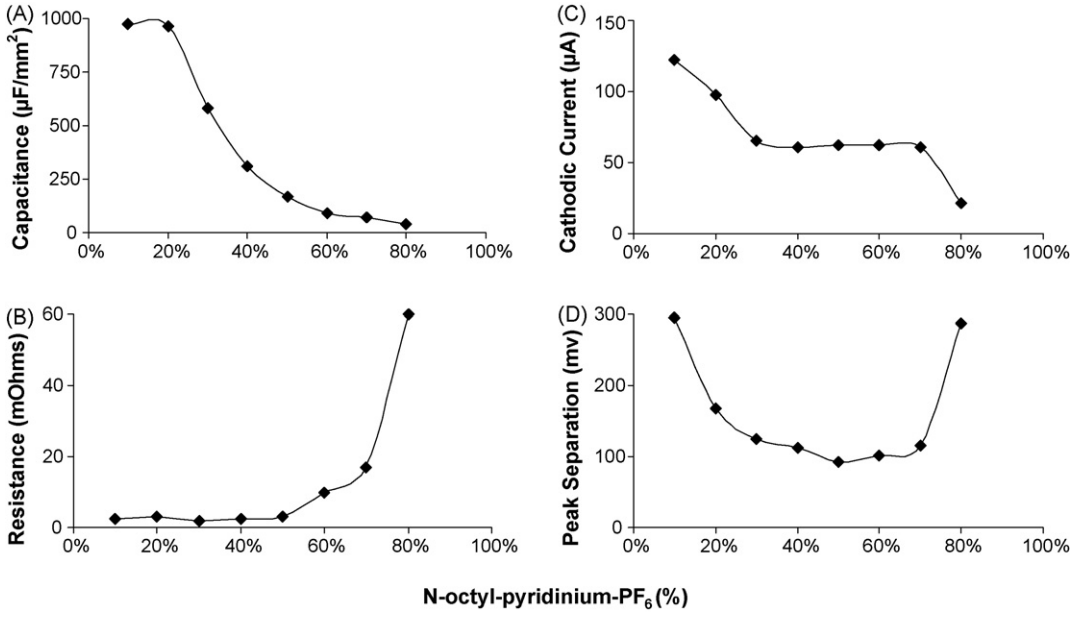

Fig. 2. Effect of ionic liquid loading on electrode capacitance (A), resistance (B), cathodic current (C), and peak-to-peak separation (D) using 5 mM potassium ferricyanide. Other conditions as in Fig. 1.

alone cannot be used to fabricate a good electrode as can be seen in Fig. 2B. The presence of a conductive material such as graphite is therefore important. Cathodic peak currents show high values for loadings below 30%. However, loadings higher than that show nearly identical cathodic peak currents up to 70% loading. For loadings 30–70% IL, the cathodic current was almost the same as shown in Fig. 2C. This is true, because cathodic peak currents were measured from the maximum point of the peak to the point on the tangent of that peak baseline. Going beyond 70%, the cathodic current tends to decrease due to the increase in electrode resistance as can be seen in Fig. 2C. The peak-to-peak separation using ferricyanide redox couple as an example shows that at levels above 70% or below 30% of IL, the peak separation increases. The optimum peak separation was achieved using 50% IL. Based on that, the optimum composition for the subsequent work was 50% IL which gave the highest electron transfer rate as shown in Fig. 2D. Combining the results of Figs. 1 and 2, the 50% loading was chosen as the optimal representative loading and used for subsequent work. However, loadings of 60% and 70% are also possible to use.

3.2. Cyclic voltammetry and hydrodynamic voltammetry for hydrogen peroxide

Fig. 3 displays cyclic voltammograms for 5 mM hydrogen peroxide and blank phosphate buffer solution as recorded at the IL (a and b) and the mineral oil (c and d) based composite electrodes. The IL composite electrode exhibits significant oxidation and reduction currents starting around +0.30 and 0.0 V, respectively. In contrast, no redox activity is observed at the mineral oil surface over most of the potential range. A small gradual increase of the response is observed at higher potentials around +0.85 and −0.35 V. This improved response and potential lowering towards hydrogen peroxide provides a useful avenue for preparing ionic liquid modified composite electrodes and offers great promise for fabricating oxidase-based amperometric biosensors utilizing this unique ionic liquid composite material.

The inset of Fig. 3 compares hydrodynamic voltammograms (HDV) for 5 mM hydrogen peroxide at the IL/graphite (a) and mineral oil/graphite (c) composite electrodes. No redox activity is observed for the conventional mineral oil/graphite electrode using potentials lower than 0.8 V. A small gradual increase of the response is observed at higher potentials. In contrast, the IL/graphite electrode responds favorably at potentials higher than +0.3 V and lower than 0.0 V. The substantial lowering of the detection potential observed for hydrogen peroxide at the IL/graphite composite is coupled to significantly larger current signals. The IL/Graphite composite is believed to increase the electron transfer rates for oxidation and reduction of H_2O_2 and hence lowers both oxidation and reduction over potentials compared to conventional paste electrodes using non-conductive binders. Overall, the data of Fig. 3 indicate that the association of this ionic liquid with the graphite powder strongly improves its electrocatalytic and mechanical properties.

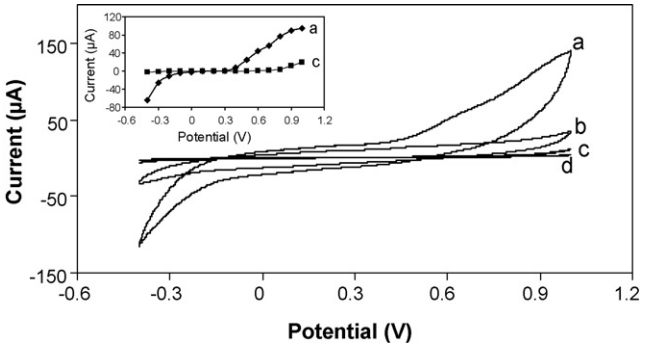

Fig. 3. Cyclic voltammetry for 5 mM hydrogen peroxide (a and c) and phosphate buffer (b and d) at the ionic liquid/graphite (50/50) electrode (a and b) and at the mineral oil/graphite (30/70) electrode (c and d). Other conditions as in Fig. 1. Inset: corresponding hydrodynamic voltammograms for 5 mM hydrogen peroxide for electrodes at (a) and (c).

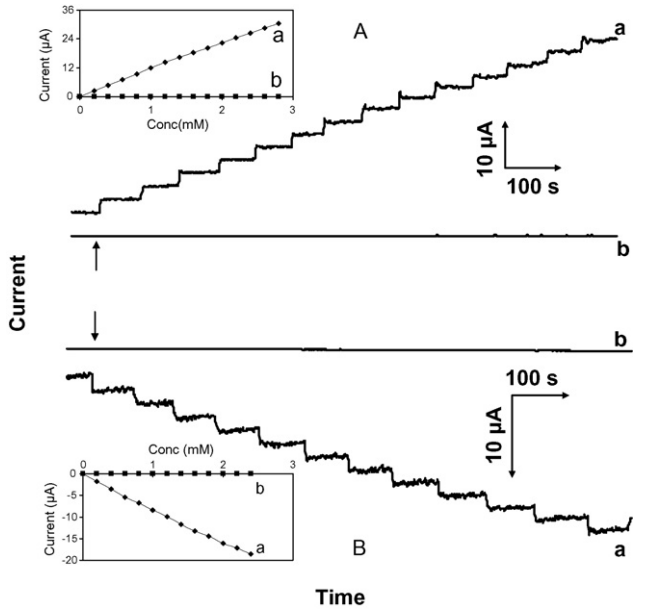

Fig. 4. Current–time recordings for successive 0.2 mM additions of hydrogen peroxide at the ionic liquid/graphite (50/50) electrode (a) and the mineral oil/graphite (30/70) electrode (b) measured at +0.5 V (A) and −0.2 V (B). Other conditions as in Fig. 1.

3.3. Amperometry of hydrogen peroxide

Such electrocatalytic action facilitates low-potential amperometric measurements of hydrogen peroxide. Fig. 4 compares the amperometric response (at +0.50 V (A) and at −0.2 V (B)) of the IL/graphite (a) and mineral oil/graphite (b) electrodes to successive additions of 0.2 mM hydrogen peroxide. As expected from the voltammetric data, the mineral oil/graphite electrode is not responsive to these concentration changes using these low-detection potentials. The IL/graphite electrode, in contrast, responds very rapidly to the changes in the level of hydrogen peroxide, producing steady-state signals within 1–2 s. The hydrogen peroxide enhanced response was coupled with a good linear response up to 2.8 mM at both measured potentials.

3.4. Optimization of glucose oxidase (GOx) loading

The attractive low-potential and amplified detection of hydrogen peroxide makes the IL/graphite composite extremely attractive for amperometric biosensing in connection with oxidase enzymes. The new IL-/graphite-based composites permit convenient and controlled incorporation of the desired enzyme (and its cofactor or mediator), in a manner analogous to other bulk-modified bioelectrodes (Wang et al., 1993; Del Cerro et al., 1997; Pena et al., 2001). The bulk of these biosensors thus serve as a source for the biocatalytic activity. Optimization of the enzyme loading was necessary to improve the measured response and linearity. Fig. 5 compares calibration plots for glucose obtained at electrodes containing different GOx loadings. A low loading of 0.5 mg GOx shows linear response up to 12 mM. Increasing the loading to 1.0 mg resulted in enhancing linearity up to 20 mM. Higher composition loadings show a

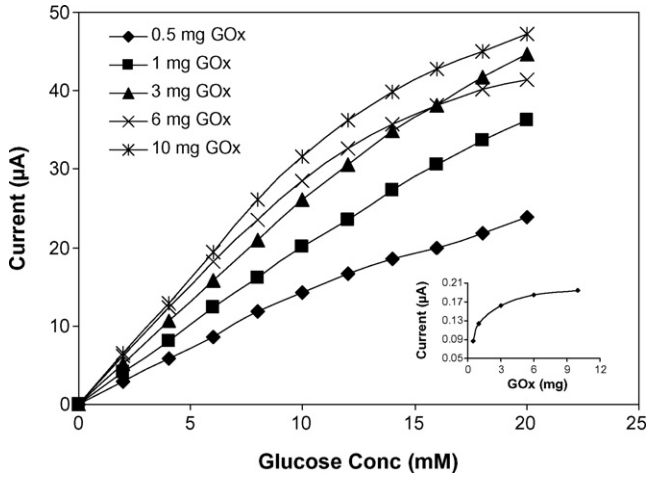

Fig. 5. Calibration plots for glucose using Ionic liquid/graphite/GOx electrodes of different GOx compositions. GOx loadings in a 50/50 ionic liquid/graphite were, 0.5 mg (♦), 1.0 mg (■), 3.0 mg (▲), 6.0 mg (×), and 10.0 mg (*). Inset: amperometric signals due to an addition of 6 mM glucose using different loadings of GOx. Operating potential, +0.9 V; other conditions as in Fig. 1.

decrease in linearity to 16, 10, and 8 mM of glucose corresponding to loadings of 3.0, 6.0, and 10.0 mg, respectively. The sensitivity increases as well with the GOx loading between 0.5 and 6.0 mg and levels off thereafter using a concentration of 6 mM glucose as shown in the inset of Fig. 5.

3.5. Amperometry of glucose

The favorable behavior of the resulting IL-/graphite-/GOx-based biocomposite (in comparison to the mineral oil/graphite/GOx paste) was illustrated in connection with amperometric biosensing of glucose using an optimal loading of 1.0 mg enzyme incorporated within the three-dimensional electrode matrix as shown in Fig. 6. This figure shows a comparison of the amperometric response to successive additions of 2 mM glucose at the IL/graphite/GOx (a) and the mineral oil/graphite/GOx (b) electrodes using an operating potential of +0.9 V, along with the resulting calibration plot (inset). Operating the sensor at high potential such as 0.9 V would be subject to interference from electroactive species such as ascorbic acid which necessitates the use of protective permselective membranes such as nafion. The choice of this potential for glucose detection was based on the corresponding HDV data for

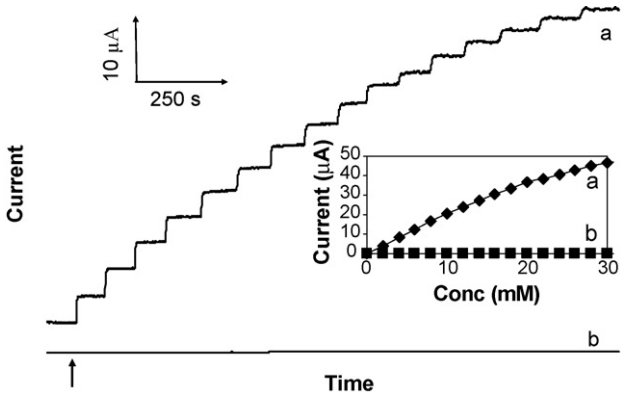

Fig. 6. Current–time recordings for successive 2 mM additions of glucose at the ionic liquid/graphite/GOx (50%/50%/1.0 mg) electrode (a) and the mineral oil/graphite/GOx (30%/70%/1.0 mg) electrode (b) measured at +0.9 V. Other conditions as in Fig. 1.

hydrogen peroxide and to extend the linear range for glucose measurement.

As expected from Figs. 3 and 4, the mineral oil/graphite/GOx electrode is showing negligible response to glucose additions at this potential and enzyme loading. Even with increasing the enzyme loading to 10.0 mg, it only resulted in a small enhancement of response (2–3 folds) (data not shown). Yet, the ionic liquid-based bioelectrode offers substantially larger signals reflecting the electrocatalytic activity of the ionic liquid (a vs. b). Such electrocatalytic action is coupled with a highly linear response (over the entire 2–20 mM range) and a slight curvature thereafter and a fast response time (~5 s). Although the linear range for hydrogen peroxide did not exceed 2.8 mM, it is possible to extend the linear range for glucose. Measurement of glucose is done indirectly through measurement of hydrogen peroxide, but only a small proportion of glucose is converted to hydrogen peroxide by the enzymatic reaction and not all of it. Hence we cannot have an agreement between the linear range for glucose and the linear range for hydrogen peroxide. In addition to that the two operating potentials for hydrogen peroxide and for glucose are different. The resulting calibration plot (shown in inset) indicates that the high sensitivity of the IL/graphite/GOx biosensor is coupled to a wide linear range.

4. Conclusion

The experiments described above indicate that the ionic liquid (*n*-octyl-pyridinium PF_6) "a solid ionic liquid at room temperature" can be used to prepare attractive composite electrodes for amperometric biosensing. The preparation of such IL/graphite composites overcomes a major obstacle for creating IL-based biosensing devices due to its low background current, and ease of fabrication and handling. The resulting composite IL/graphite material brings new capabilities for electrochemical devices by combining the advantages of ionic liquids and bulk composite electrodes. The electrocatalytic properties of the IL towards hydrogen peroxide are not impaired by their association with the graphite powder. Various chemical and biological moieties could be readily incorporated into the bulk of the IL/graphite composite. While most of our data have been obtained with *n*-octyl-pyridinium PF_6, other ILs with melting points above room temperature with different functionalities can be used for fabricating other sensors and biosensors for various applications. The attractive low-potential detection of hydrogen peroxide and NADH (Maleki et al., 2006), along with the minimal surface fouling, makes the IL extremely attractive for fabricating other amperometric biosensors in connection with oxidase or dehydrogenase enzymes for important species such as carbohydrates and alcohols. By providing a useful avenue for preparing renewable IL-based biosensors and IL-modified electrodes, such fabrication scheme expands the scope of IL-based electrochemical devices and holds great promise for routine biosensing applications.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2008.03.015.

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