

Polyelectrolyte-functionalized ionic liquid for electrochemistry in supporting electrolyte-free aqueous solutions and application in amperometric flow injection analysis†

Yanfei Shen,^a Yuanjian Zhang,^a Xuepeng Qiu,^{‡a} Haiquan Guo,^{‡a} Li Niu^{*a} and Ari Ivaska^b

Received 10th November 2006, Accepted 30th January 2007

First published as an Advance Article on the web 15th March 2007

DOI: 10.1039/b616452h

As a green process, electrochemistry in aqueous solution without a supporting electrolyte has been described based on a simple polyelectrolyte-functionalized ionic liquid (PFIL)-modified electrode. The studied PFIL material combines features of ionic liquids and traditional polyelectrolytes. The ionic liquid part provides a high ionic conductivity and affinity to many different compounds. The polyelectrolyte part has a good stability in aqueous solution and a capability of being immobilized on different substrates. The electrochemical properties of such a PFIL-modified electrode assembly in a supporting electrolyte-free solution have been investigated by using an electrically neutral electroactive species, hydroquinone (HQ) as the model compound. The partition coefficient and diffusion coefficient of HQ in the PFIL film were calculated to be 0.346 and $4.74 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. Electrochemistry in PFIL is similar to electrochemistry in a solution of traditional supporting electrolytes, except that the electrochemical reaction takes place in a thin film on the surface of the electrode. PFILs are easily immobilized on solid substrates, are inexpensive and electrochemically stable. A PFIL-modified electrode assembly is successfully used in the flow analysis of HQ by amperometric detection in solution without a supporting electrolyte. The results indicate a green electrochemical methodology in supporting electrolyte-free solution and a potential application in amperometric detection in a flow system without any supporting electrolyte in the solution, such as the high performance liquid chromatography electrochemical detection (HPLC-ECD) system.

1. Introduction

Ionic liquids (ILs), or more specifically cation–anion pairs that form a stable fluid near room temperature, are playing an increasingly practical role as ‘green’ chemical reaction solvents, electrolytes, and heat-transfer media on scales ranging from the laboratory bench to industrial manufacturing processes. Their advantages include minuscule vapor pressure, high polarity, and relative inertness.^{1,2} In particular, in electrochemistry, they show relatively wide potential windows and high conductivity, and allow studies to be undertaken without any additional supporting electrolyte.^{3–7} Therefore, there is the possibility of using ILs to develop ion-conductive materials. As pioneers, the groups of Murray and also of Wrighton have extensively investigated the solid-state electrochemistry of another class of ILs, namely, undiluted melts of hybrids of lithium electrolytes or redox materials and polyethers.^{8–16} Heller and co-workers have also successfully developed

another kind of semi-solid hydrogel based on the hybrids of polyvinylimidazole or polyvinylpyridine and Ru^{2+} or Os^{2+} complexes.^{17,18} When an electrode surface is modified with these kinds of polymer, the attached layer would function as a supporting electrolyte for electrochemistry in a solution without additional supporting electrolytes. However, studies to use the ionic conductive melts or hydrogels for electrochemistry in aqueous solution without a supporting electrolyte are few in number.^{19,20}

It is common practice that electrochemical experiments should be conducted in the presence of supporting electrolytes. This is due to the recommendation that the ionic strength and conductivity of the solution must be high and constant.^{21–24} In general, supporting electrolytes are usually applied to (i) decrease the *Ohmic* potential drop, (ii) eliminate changes in ionic strength due to electrochemically consumed or generated ionic species, and (iii) eliminate migration as a mode of mass transport.^{22,23} However, within last few years, the general necessity to add an excess of supporting electrolyte has been questioned, and it is desirable to consider even the necessity of using a supporting electrolyte in various cases.^{19,20,25–31} The reasons are numerous, such as: (i) to eliminate the need of an expensive electrolyte, particularly in experiments performed in organic media, which is also highly anticipated for *green chemistry*; (ii) to eliminate the possible interference of any supporting electrolytes in electrochemical synthesis; and (iii) to detect species of interest in gas or non-conductive

^aState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, and Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun 130022, P. R. China. E-mail: lniu@ciac.jl.cn; Fax: +86-431-526 2800.

^bLaboratory of Analytical Chemistry, Process Chemistry Centre, Åbo Akademi University, FI-20500, Åbo-Turku, Finland

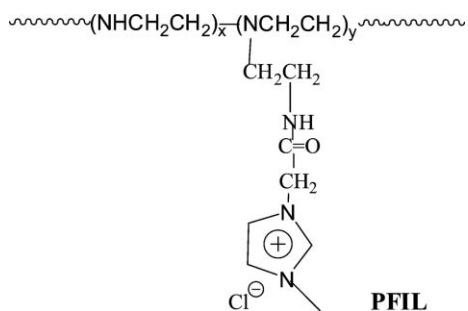
† Electronic supplementary information (ESI) available: Application of HPLC-ECD and FAQ of HPLC-ECD. See DOI: 10.1039/b616452h

‡ In State Key Laboratory of Polymer Physics and Chemistry in CIAC, CAS, P. R. China.

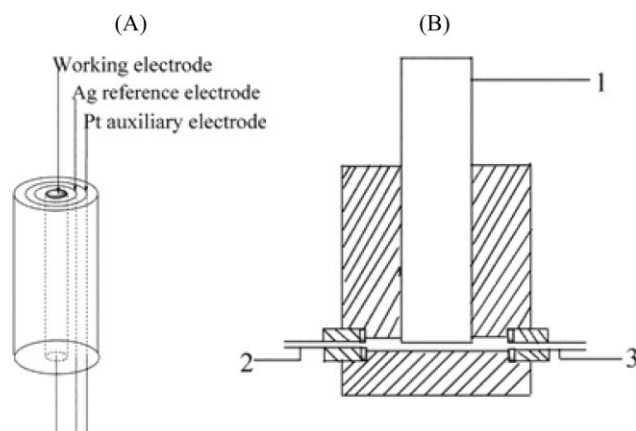
fluids.^{19,20,26–31} Moreover, sometimes the need to use supporting electrolytes for electrochemical detection creates problems. For example, the high performance liquid chromatography electrochemical detection (HPLC-ECD) system has become a powerful tool in chemical, clinical, pharmaceutical and environmental analysis due to its excellent sensitivity and selectivity to electroactive species.^{32–35} However, the supporting electrolytes might precipitate in the HPLC system after long-time use causing, for example, high back-pressure and ghost peaks.³⁶

Some promising methods for electrochemical detection in flow systems have successfully been developed. In these applications, the detection is done with ultramicroelectrodes (UMEs) or their modifications with moist ion-exchange membranes such as Nafion.^{19,26,37–43} Fuchigami and Tajima have developed another novel method to generate *in situ* the supporting electrolyte during the electro-organic synthesis. This procedure not only eliminates the use of expensive supporting electrolytes in organic media, but also makes the product separation very simple.^{30,31}

As part of our ongoing research in developing immobilized ILs,⁴⁴ in this paper, we report a straightforward approach towards electrochemistry in supporting electrolyte-free solutions based on a polyelectrolyte-functionalized ionic liquid (PFIL, as illustrated in Scheme 1) where the imidazolium part functions as the ionic liquid. Our previous results have indicated that the PFIL combines the individual advantages of each functional part in the material: high ionic conductivity, solvation properties originating from the ionic liquid part in the molecule, and good immobilization properties and stability in aqueous solution originating from the polyelectrolyte.⁴⁴ Moreover, when the polyelectrolyte was used for the electrochemical detection of analytes, owing to the high chemical and electrochemical stability, the detection with the PFIL modified on the electrode would not be interfered with by the redox behaviour of polyelectrolyte itself. Therefore, the PFIL is an interesting material to be used for electrochemical measurements in supporting electrolyte-free solutions. Furthermore, two aspects of green chemistry would be involved: one is the elimination of supporting electrolytes for electrochemistry, which are often corrosive and expensive; the other originates from the ionic liquid part of PFIL, such as chemical and thermal stability. The experiments in this work are to develop a simple ion-conductive polyelectrolyte-modified electrode for *electrochemistry in aqueous solutions without any supporting*



Scheme 1 Structure of the polyelectrolyte-functionalized ionic liquid (PFIL) used in this study.



Scheme 2 (A) Illustration of the assembly electrode; (B) the detection cell (cross-section view): (1) electrode assembly; (2) inlet; (3) outlet.

electrolyte. The electrochemical performance of the PFIL-modified electrode assembly [as shown in Scheme 2(A)] in supporting electrolyte-free solution will be studied, and further applied to flow analysis in supporting electrolyte-free aqueous solutions as an example of the potential applications of the developed concept.

2. Experimental

Chemicals and materials

Polyethylenimine (PEI; $M_w = 25\,000$) was obtained from Aldrich. The polyelectrolyte-functionalized ionic liquid (PFIL, Scheme 1) was prepared according to our previous report.⁴⁴ Unless otherwise stated, reagents were of analytical grade and used as received. All aqueous solutions were prepared with double-distilled water from a Millipore system ($>18\text{ M}\Omega\text{ cm}$).

Preparation of electrode assembly and detection cell

The structure of the electrode assembly is shown in Scheme 2(A). The working electrode is a glassy carbon electrode ($d = 3\text{ mm}$), and coaxial Pt and Ag rings are used as counter and quasi-reference electrodes, respectively. The electrodes are a three concentric circle on the same plane. The three parts were encapsulated with epoxy resin and assembled into an integrated electrode.

The detection cell used in this study is schematically shown in Scheme 2(B). The electrode assembly, the inlet and outlet tubes are inserted into their corresponding preset access holes and connected to the cell body with screws. The solutions are pumped through a microinjection pump.

Modification of the electrode assembly with PFIL

The electrode assembly was polished with aqueous slurries of fine alumina powders (1, 0.3 and 0.05 μm) on a polishing cloth. Then this electrode assembly was finally rinsed with double-distilled water in an ultrasonic bath for 5 min. Because the PFIL is a kind of hydrogel, it can form a rather stable film on the electrode surface simply by traditional casting. Typically, *ca.* 15–60 μL of aqueous solution of 3 mg mL^{-1} PFIL was evenly spread onto the surface of the electrode assembly. Then

the electrode assembly was dried overnight in air to form a uniform film. The thickness of the PFIL film was estimated from the volume of PFIL used for modification and the geometry of the electrode. For example, when 30 μL of aqueous solution of 3 mg mL^{-1} PFIL was cast onto the electrode, the film thickness was *ca.* 1.4 μm .

Determination of diffusion coefficient and partition coefficient

The diffusion coefficient and partition coefficient of HQ in the PFIL film was obtained by chronoamperometry. The experiment was carried out in a conventional three-electrode electrochemical cell. The working electrode was a PFIL-modified Pt microelectrode ($d = 20 \mu\text{m}$), the auxiliary electrode was a Pt wire, and the reference electrode was Ag|AgCl (saturated KCl). The thickness of the PFIL film was *ca.* 1.4 μm .

Instruments

All electrochemical experiments were performed using the CHI 660A and CHI 900 electrochemical workstations (CHI Inc., USA).

3. Results and discussion

3.1 Electrochemical performance of the PFIL-modified electrode assembly

3.1.1 Electrochemical microenvironment provided by the PFIL. The electrochemical performance of the PFIL-modified electrode assembly in supporting electrolyte-free solution was investigated by using an electrically neutral electroactive species hydroquinone (HQ) as the model compound. Fig. 1 shows a study where cyclic voltammograms (CVs) of a 20 μM HQ solution have been recorded with different electrode assemblies. As can be seen in curve 'a', in the absence of HQ there are no redox peaks at the PFIL-modified electrode assembly in pure water. Upon addition of HQ to the pure water, a pair of well-defined redox peaks of the HQ can clearly

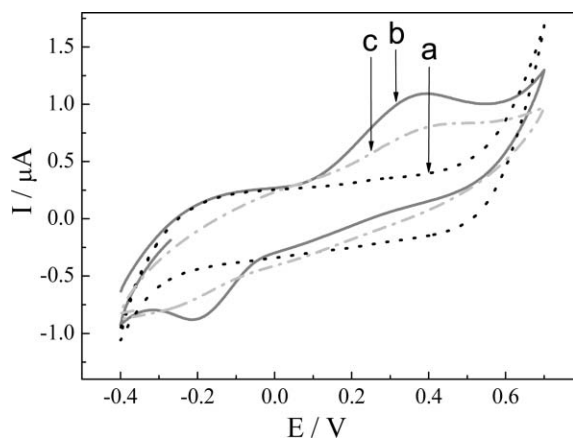


Fig. 1 Cyclic voltammograms (CVs) in supporting electrolyte-free aqueous solutions: (a) pure water at the 1.4 μm thick PFIL-modified electrode assembly, (b) 20 μM HQ at the 1.4 μm thick PFIL-modified electrode assembly, and (c) 20 μM HQ at a bare glassy carbon electrode. Scan rate: 0.1 V s^{-1} .

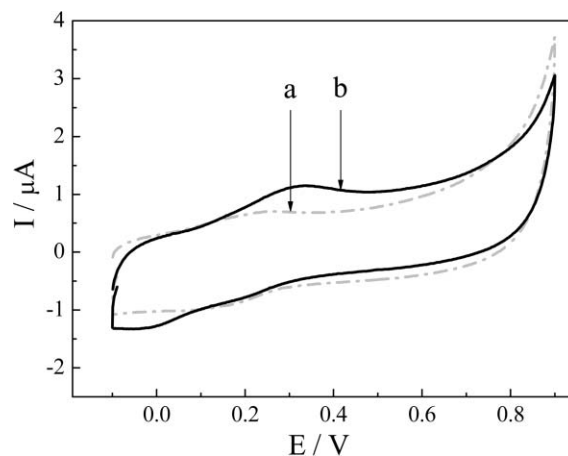


Fig. 2 Cyclic voltammograms (CVs) at a bare glassy carbon electrode in 1 M KCl aqueous solution: (a) without, and (b) with HQ (20 μM). Scan rate: 0.1 V s^{-1} .

be seen (curve 'b').⁴⁵ Those redox peaks can also be found at a bare glassy carbon electrode (curve 'c'), but are much smaller than at the PFIL-modified electrode (curve 'b'). These results indicate that the PFIL film on the modified electrode provides a good electrochemical microenvironment for the redox reaction of HQ.

To further demonstrate the essential role of the PFIL film, two control experiments were also performed. Cyclic voltammograms (CVs) in a traditional manner with a supporting electrolyte were recorded. Fig. 2 shows the CVs at the bare glassy carbon electrode in 1 M KCl aqueous solution. Curve 'a' is recorded in the presence of the supporting electrolyte only and curve 'b' after making the solution 20 μM with respect to HQ. When comparing curve 'b' in Fig. 2 and curve 'b' in Fig. 1, we can conclude that the current recorded at the PFIL-modified electrode is enhanced. This indicates that the PFIL on the electrode assembly not only exhibits the properties of an electrolyte, but also shows a good affinity towards HQ. If HQ, however, is irreversibly absorbed on the PFIL film, similar results would also be obtained. Therefore, we performed an additional experiment where the CVs at the PFIL-modified electrode assembly in HQ solution were recorded. The electrode was briefly rinsed with water and the CVs at the same electrode in pure water were collected. It was found that no redox peaks of HQ were observed, which indicated that although PFIL exhibited a good affinity towards HQ, there was no irreversible absorption in the film. Therefore, these results showed that the PFIL on the electrode assembly offered a suitable electrochemical microenvironment for electrochemical reaction.

3.1.2 Effect of film thickness on the electrochemical performance. The film thickness was expected to influence the electrochemical signal of HQ, because both the ionic conductance of the PFIL film and the diffusion of HQ in the film depend on the film thickness. On the one hand, an increase in the film thickness increases the amount of ionic species in the electrode assembly, thus improving its ionic conductance; on the other hand, the thick film also limits the

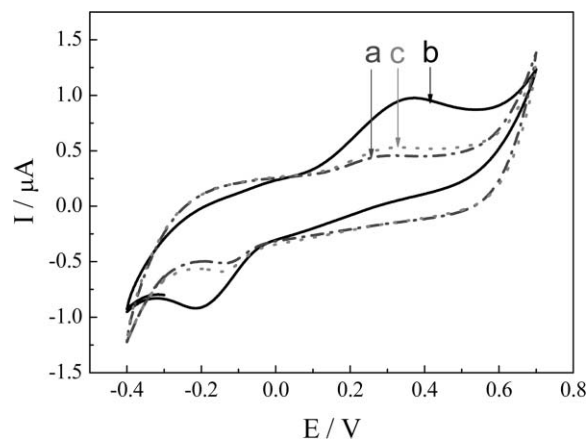


Fig. 3 Cyclic voltammograms for HQ (20 μM) in supporting electrolyte-free solution at an electrode assembly modified with (a) 0.7 μm , (b) 1.4 μm and (c) 2.8 μm PFIL film. Scan rate: 0.1 V s^{-1} .

diffusion of HQ from the solution into the PFIL film matrix and further to the electrode. Therefore, the effect of film thickness was investigated by potential cycling measurements. As shown in Fig. 3 (curve 'a'), a small current peak was obtained on the electrode assembly modified with a *ca.* 0.7 μm PFIL film. When the thickness of the PFIL was increased to *ca.* 1.4 μm , a significant growth in the peak current was observed (curve 'b'). However, when the film thickness was increased to *ca.* 2.8 μm , a decrease in the current peak was observed (curve 'c'), and the control experiments showed that the current did not increase with the incubation times. As a conclusion, the film thickness significantly affected the CVs signal and an optimized film thickness should be adopted for the potential applications. It was also noted that the background currents in Fig. 3(a) and 3(c) were almost the same, which might be due to the fact that in the present experimental conditions there was a balance between film porosity, thickness and ionic conductivity on the influence of the background currents.

3.1.3 Electrochemical dynamics of HQ at the PFIL-modified electrode. To further investigate the electrochemical process of HQ at the PFIL-modified electrode assembly, the relationship between the scan rate and the peak current was studied. Fig. 4 shows the voltammetric scans with different scan rates recorded in 20 μM HQ in supporting electrolyte-free solution at the electrode assembly modified with a *ca.* 1.4 μm PFIL film. As shown in Fig. 4, the peak current was found to be directly proportional to the square root of the scan rate, confirming a diffusion-controlled process. Such a linear relationship may also indicate that there was no significant irreversible adsorption of HQ or its oxidation product, quinone, onto the electrode surface during the potential cycling.

The relationship between the concentration of HQ and the peak current was also studied (Fig. 5). As shown in Fig. 5(B), the peak current is proportional to the concentration of HQ, and the line goes through zero. It indicated that the partition coefficient of HQ was not related to the concentration of HQ in solution. And it again suggested that the electrochemical process was well diffusion-controlled.

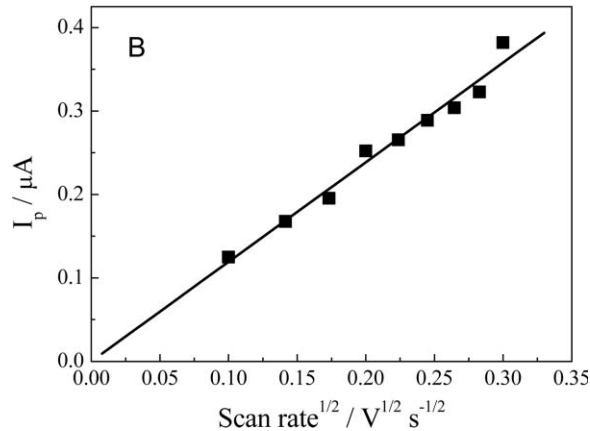
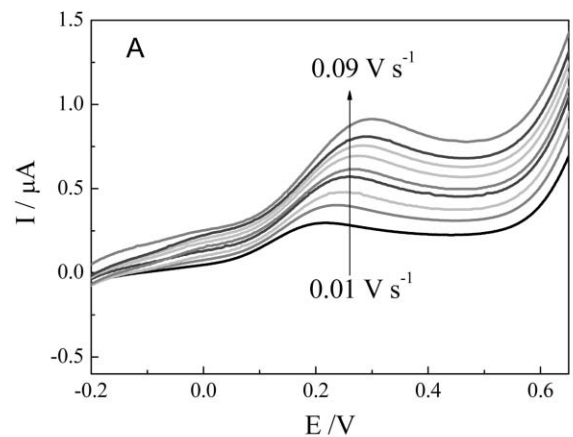


Fig. 4 (A) Linear sweep voltammograms for an aqueous solution of 20 μM HQ without any supporting electrolyte at a 1.4 μm thick PFIL-modified electrode assembly. Scan rate: 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 V s^{-1} . (B) Plot of I_p vs. $v^{1/2}$ for HQ at the PFIL-modified integrated electrode.

The peak potential experiences a positive shifts with the increase in HQ concentration, as shown in Fig. 5(A). The positive shift should originate from the good solubility of the PFIL film to the oxidized product – quinone. The resulting quinone species is enriched in the PFIL film matrix and is hard to diffuse into the solution. It is quite similar to the case where the product is insoluble in the solution. Then, at this time the peak potential should not be constant any more, but shifted to a more positive value for an increase in the concentration of HQ in the body of the solution.

Chronoamperometry was used to determine the diffusion coefficient and the partition coefficient of HQ in PFIL film (Fig. 6). The experiment was performed by holding the potential at 0.1 V for 20 s, and then a step to 0.45 V (which is sufficient for oxidation of HQ) for 5 s [Fig. 6(A)]. By plotting the current, I , vs. the reciprocal of the square root of time, $t^{-1/2}$ [Fig. 6(B)], a straight line was found corresponding to the modified Cottrell equation,⁴⁶

$$I(t) = \frac{nFAD^{1/2}C_m}{\pi^{1/2}t^{1/2}} + \pi nFDC_m r \quad (1)$$

where A is the geometric area of the microelectrode, r is the radius of the microelectrode, D is the diffusion coefficient of

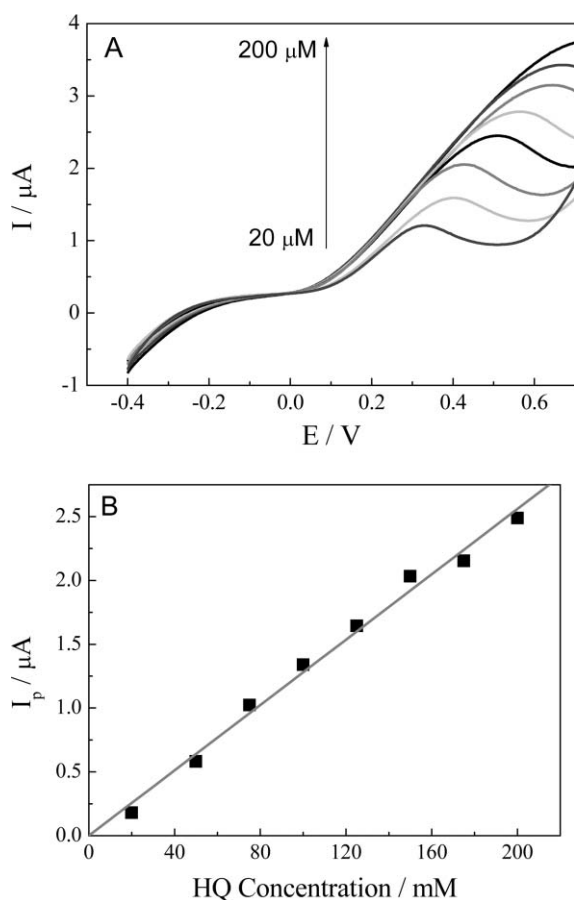


Fig. 5 (A) Linear sweep voltammograms for a supporting electrolyte-free aqueous solution of 20, 50, 75, 100, 125, 150, 175 and 200 μM HQ at a 1.4 μm thick PFIL-modified electrode assembly. (B) Relationship between the current and the concentration of HQ.

HQ in the PFIL film, and C_m is the concentration in the PFIL film. D and C_m values were obtained from the slope and intercept of the linear regression line. The partition coefficient, K_p , is defined as the following way,

$$K_p = \frac{C_m}{C_0} \quad (2)$$

where C_0 is the concentration of HQ in the solution. From this experiment, the following values were obtained: $D = 4.74 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $K_p = 0.346$, which were comparable to the reported values of ions in traditional membranes, such as Nafion film.^{47,48}

Based on all these results, the electrochemical process of HQ at the PFIL-modified electrode assembly is summarized and illustrated in Scheme 3: First, the conductive PFIL film connects the working (WE), counter (CE) and reference (RE) electrodes, giving an electrolytic contact between these electrodes. Second, the good affinity towards HQ and the sufficient diffusion of HQ through the PFIL film to the electrode assembly surface are also crucial factors for the electrochemical process. But it should be pointed out that the thickness of the PFIL film on electrodes should be optimized in order to obtain the high conductivity of the film and effective diffusion of analytes through the film.

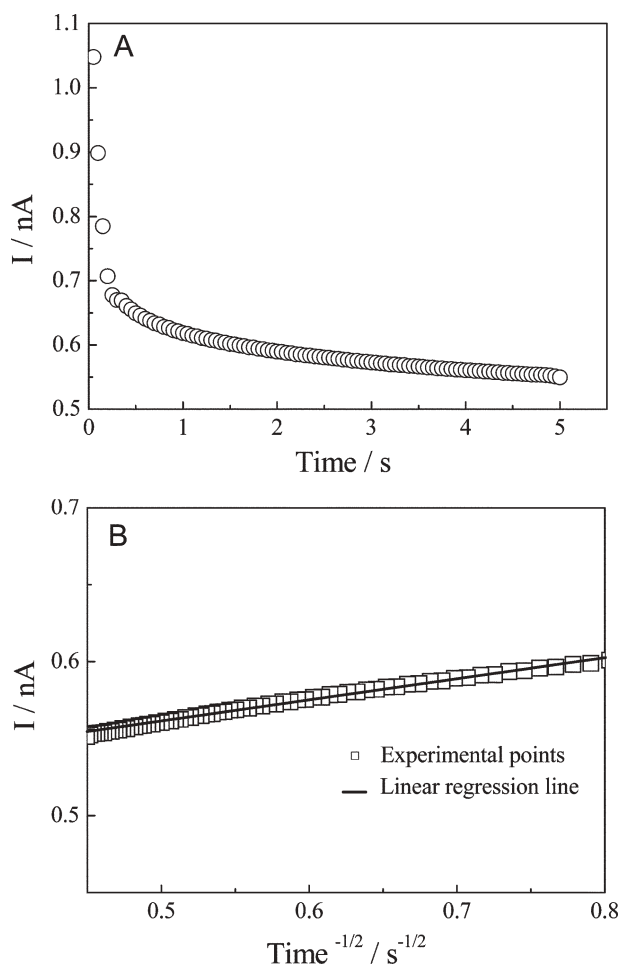
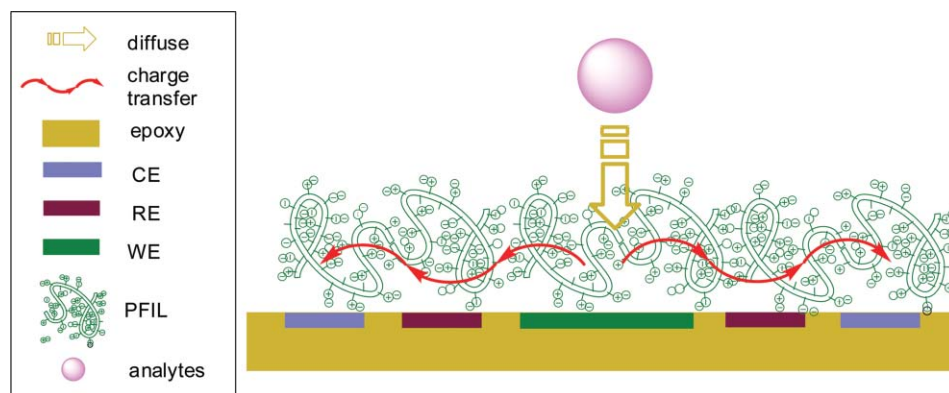


Fig. 6 (A) Chronoamperometry for HQ oxidation at the Pt micro-electrode/PFIL interface in 1 mM HQ solution. The potential was first held at 0.1 V for 20 s, then stepped to 0.45 V for 5 s. (B) The resulting I vs. $t^{-1/2}$ plots.

3.2 Application in amperometric flow analysis

Within the past years, the amperometric detection in supporting electrolyte-free solution in a flow system has received increasing interest.^{49–52} In this work, we will demonstrate how the PFIL-modified electrode assembly can be used in flow injection analysis (FIA) in supporting electrolyte-free solutions.^{37–43} The structure of a detection cell for the flow system was shown in Scheme 2(B).

Fig. 7(A) displays the amperometric responses of the repeated injection of 20 μM HQ in a supporting electrolyte-free solution. The potential of the electrode was held at +0.3 V. The current response remained almost unchanged upon continuous running for several hours. The relative standard deviation was 0.66% ($n = 11$). It should be noted that even after hundreds of repeated cycles; only a small decrease in current response was observed, indicating that the PFIL film on the electrode assembly is rather stable. The response time was determined by the passage of the sample zone over the PFIL-modified electrode assembly.⁵³ As can be seen in Fig. 7, the response time is rather long, even at a few minutes. This is due to the flow cell design where all three electrodes had to be covered by the PFIL film (the



Scheme 3 Illustration of the electrochemical process of the analytes at the PFIL-modified electrode assembly in a supporting electrolyte-free solution.

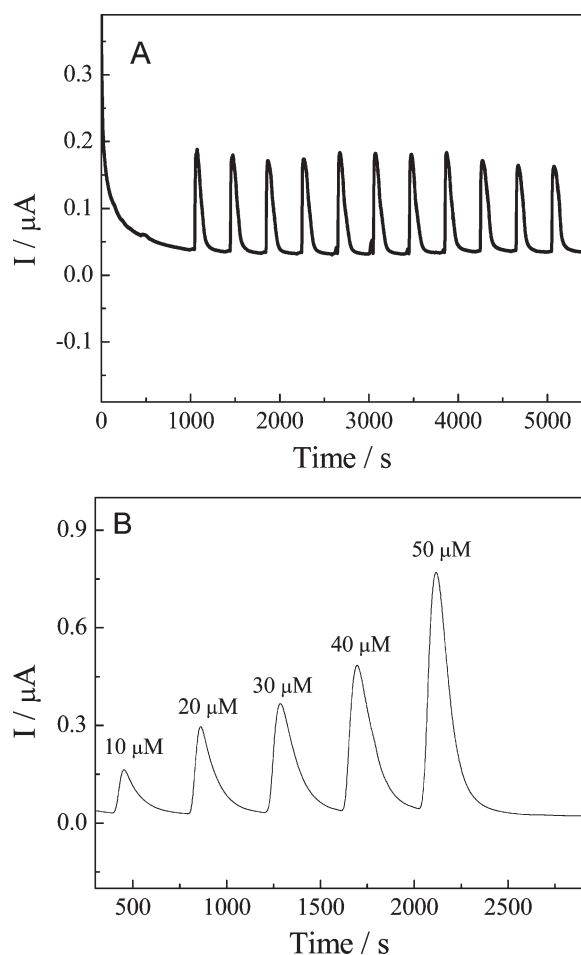


Fig. 7 (A) Amperometric responses of repeated injection of a 20 μM HQ solution. (B) Amperometric response of HQ at different concentrations. The signal was recorded at the 1.4 μm thick PFIL-modified electrode assembly at +0.3 V. Double-distilled water was used as the carrier solution. Flow rate: 1 mL min⁻¹.

diameter of the glassy carbon electrode was 3 mm and the diameter of the electrode assembly was 10 mm). This construction resulted in a rather big dead volume of the cell. For practical assay work, the cell design and flow rate should be optimized.

Fig. 7(B) shows successive injections of HQ at different concentrations. The current is linear with the concentration of HQ. Similar results have been obtained with some other ion-exchange membranes employed in electrochemical flow systems without any added supporting electrolyte.^{37–43} The advantage of our approach is that we do not need any internal electrolyte in the flow cell construction. Another advantage in our system is that the PFIL film has good dissolving properties for many analytes. The FIA results obtained clearly show the good properties of the PFIL-modified electrode in amperometric detection. The same system can certainly also be used in the HPLC-electrochemical detection (HPLC-ECD) system in supporting electrolyte-free solutions.

3.3 Electrochemical behavior with charged analytes

It should be admitted that the PFIL we have demonstrated here is a cationic polyelectrolyte and some special attention should be paid when PFIL is applied to cationic analytes in practical analytical work. For example, $\text{Fe}(\text{CN})_6^{3-/4-}$ exhibits surface-enhanced redox waves at the PFIL-modified electrode assembly (Fig. 8). The peak current increased little with time, indicating the enrichment behavior of $\text{Fe}(\text{CN})_6^{3-/4-}$ at the PFIL-modified electrode assembly [Fig. 8(A)]. And when this electrode was put back into pure water, the current decreased gradually with time [Fig. 8(B)]. Therefore, it is beneficial for the detection of negative analyte species at low-concentration due to significant enrichment of the analyte species in the PFIL film. In contrast, no redox response was found for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ at the PFIL-modified electrode assembly due to electrostatic expulsion [Fig. 8(C)]. Fortunately, the structure of this kind of PFIL can be designed to be a cationic or an anionic polyelectrolyte if necessary.³ The tunable design makes this IL suitable for the detection of most cationic or anionic analytes. Therefore, this PFIL material can be used in electrochemical studies in supporting electrolyte-free solutions.

4. Conclusions

The results presented in this work show how a simple polyelectrolyte-functionalized ionic liquid (PFIL) covering the electrode assembly can be used in electrochemical studies

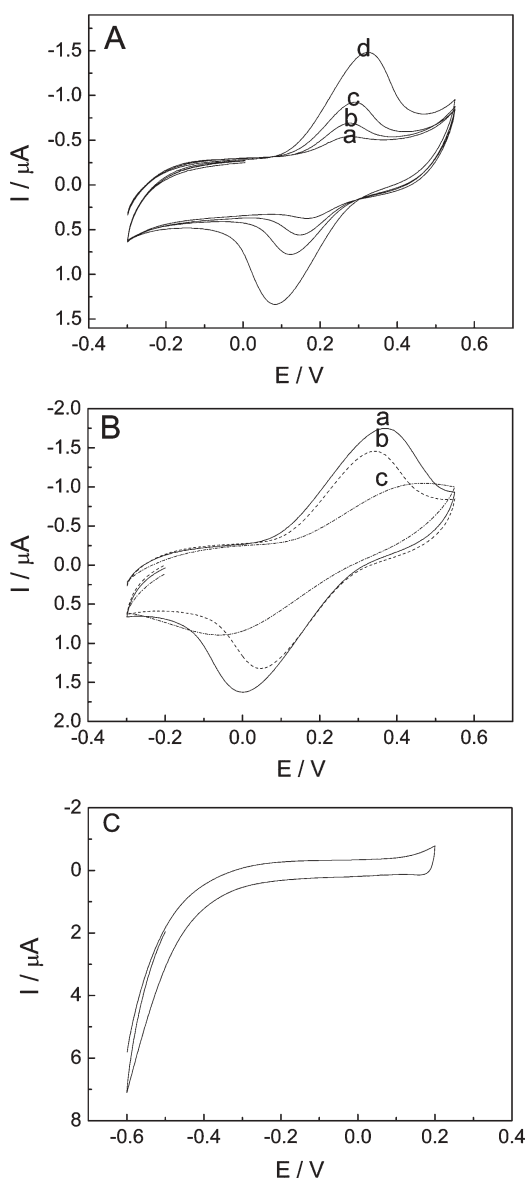


Fig. 8 (A) Cyclic voltammograms (CVs) at the PFIL-modified electrode assembly in 20 μM $\text{K}_3\text{Fe}(\text{CN})_6$ with different immersion times: (a) 0, (b) 4, (c) 7, and (d) 28 min. (B) CVs at the PFIL-modified electrode assembly which has been enriched with $\text{K}_3\text{Fe}(\text{CN})_6$ with different immersion times in H_2O : (a) 0, (b) 10, and (c) 28 min. (C) CV of 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ at the PFIL-modified electrode assembly.

in aqueous solution without a supporting electrolyte. The electrochemical performance of the PFIL-modified electrode assembly in supporting electrolyte-free aqueous solutions was tested with hydroquinone (HQ) as the model compound. The electrochemical reactions take place in the thin PFIL film covering the three electrodes. The analyte has first to enter the PFIL film before any electrochemical reaction can take place. By proper design of the polyelectrolyte, either anionic or cationic species can be excluded in entering the film, and in that way selectivity can also be enhanced. Because the ionically conductive PFIL film covers all of the three electrodes, it is not necessary to have any supporting electrolyte in the carrier solution in amperometric flow injection analysis (FIA)

experiments. The PFIL film can prevent any possible short cuts in amperometric detection, e.g. air bubbles entering the flow system. The same detection concept can also be used in the HPLC-electrochemical detection (HPLC-ECD) system in supporting electrolyte-free solution. The electrochemical system developed in this work can be used in other fields of electrochemistry in supporting electrolyte-free solutions as a green process, such as electrochemical synthesis, and electrolysis in industry. To realize the full potential of such polyelectrolytes grafted with ionic liquid for electrochemistry in supporting electrolyte-free solutions, we are currently investigating the influence of different kinds of ionic liquid polyelectrolytes, such as anionic and cationic ionic liquid polyelectrolytes.

Acknowledgements

The authors would like to thank the referees for their helpful comments on the manuscript. The authors are most grateful to the NSFC, China (No.20475053 and No. 20673109) and to Department of Science and Technology of Jilin Province (No.20050102) for the financial supports. In addition, the joint project between Chinese and Finnish research groups sponsored by NSFC, China and Academy of Finland should also be acknowledged.

References

- 1 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156–164.
- 2 *Ionic Liquids: Industrial Applications for Green Chemistry*, ed. R. D. Rogers and K. R. Seddon, American Chemical Society, Washington, DC, 2002.
- 3 H. Ohno, *Electrochemical Aspects of Ionic Liquids*, Wiley-VCH, Weinheim, 2005.
- 4 J. L. Anderson, D. W. Armstrong and G.-T. Wei, *Anal. Chem.*, 2006, **78**, A2892–2902.
- 5 Y. Gao, N. Li, L. Q. Zheng, X. Y. Zhao, S. H. Zhang, B. X. Han, W. G. Hou and G. Z. Li, *Green Chem.*, 2006, **8**, 43–49.
- 6 J. H. Li, Y. F. Shen, Y. J. Zhang and Y. Liu, *Chem. Commun.*, 2005, 360–362.
- 7 M. C. Kroon, W. Buijs, C. J. Peters and G. J. Witkamp, *Green Chem.*, 2006, **8**, 241–245.
- 8 T. Hatazawa, R. H. Terrill and R. W. Murray, *Anal. Chem.*, 1996, **68**, 597–603.
- 9 T. T. Wooster, M. L. Longmire, H. Zhang, M. Watanabe and R. W. Murray, *Anal. Chem.*, 1992, **64**, 1132–1140.
- 10 L. Geng, R. A. Reed, M. Longmire and R. W. Murray, *J. Phys. Chem.*, 1987, **91**, 2908–2914.
- 11 J. F. Parcher, C. J. Barbour and R. W. Murray, *Anal. Chem.*, 1989, **61**, 584–589.
- 12 J. W. Long, C. S. Velazquez and R. W. Murray, *J. Phys. Chem.*, 1996, **100**, 5492–5499.
- 13 M. Morita, M. L. Longmire and R. W. Murray, *Anal. Chem.*, 1988, **60**, 2770–2775.
- 14 V. Cammarata, D. R. Talham, R. M. Crooks and M. S. Wrighton, *J. Phys. Chem.*, 1990, **94**, 2680–2684.
- 15 T. E. Mallouk, V. Cammarata, J. A. Crayston and M. S. Wrighton, *J. Phys. Chem.*, 1986, **90**, 2150–2156.
- 16 R. Balasubramanian, W. Wang and R. W. Murray, *J. Am. Chem. Soc.*, 2006, **128**, 9994–9995.
- 17 F. Mao, N. Mano and A. Heller, *J. Am. Chem. Soc.*, 2003, **125**, 4951–4957.
- 18 T. J. Ohara, R. Rajagopalan and A. Heller, *Anal. Chem.*, 1993, **65**, 3512–3517.
- 19 F. Opekar and K. Stulik, *Anal. Chim. Acta*, 1999, **385**, 151–162.
- 20 G. Schiavon, G. Zotti, R. Toniolo and G. Bontempelli, *Anal. Chem.*, 1995, **67**, 318–323.

- 21 M. Ciszkowska and Z. Stojek, *Anal. Chem.*, 2000, **72**, 754A–760A.
- 22 A. M. Bond and S. W. Feldberg, *J. Phys. Chem. B*, 1998, **102**, 9966–9974.
- 23 W. Hyk and Z. Stojek, *Anal. Chem.*, 2002, **74**, 4805–4813.
- 24 M. B. Rooney, D. C. Coomber and A. M. Bond, *Anal. Chem.*, 2000, **72**, 3486–3491.
- 25 J. Szymanska, M. J. Palys and B. Van den Bossche, *Anal. Chem.*, 2004, **76**, 5937–5944.
- 26 A. W. E. Hodgson, P. Jacquinet and P. C. Hauser, *Anal. Chem.*, 2000, **72**, 2206–2210.
- 27 N. P. C. Stevens, M. B. Rooney, A. M. Bond and S. W. Feldberg, *J. Phys. Chem. A*, 2001, **105**, 9085–9093.
- 28 P. Jacquinet, A. W. E. Hodgson and P. C. Hauser, *Anal. Chim. Acta*, 2001, **443**, 53–61.
- 29 R. Toniolo, N. Comisso, G. Schiavon and G. Bontempelli, *Anal. Chem.*, 2004, **76**, 2133–2137.
- 30 T. Tajima and T. Fuchigami, *Angew. Chem., Int. Ed.*, 2005, **44**, 4760–4763.
- 31 T. Tajima and T. Fuchigami, *J. Am. Chem. Soc.*, 2005, **127**, 2848–2849.
- 32 Z. Liu, J. Li, S. Dong and E. Wang, *Anal. Chem.*, 1996, **68**, 2432–2436.
- 33 U. Rückert, K. Eggenreich, R. Wintersteiger, M. Wurglics, W. Likussar and A. Michelitsch, *J. Chromatogr., A*, 2004, **1041**, 181–185.
- 34 See ESI† for the application of HPLC-ECD accessed from http://www.esainc.com/applications/esa_applications.htm on 14 September 2006.
- 35 C. Y. Kuo and S.-M. Wu, *J. Chromatogr., A*, 2005, **1088**, 131–135.
- 36 See ESI† for the application of HPLC-ECD accessed from http://www.esainc.com/products/ECD_faqs.htm on 14 September 2006.
- 37 T. W. Kaaret and D. H. Evans, *Anal. Chem.*, 1988, **60**, 657–662.
- 38 D. W. D. Wulf and A. J. Bard, *J. Electrochem. Soc.*, 1988, **135**, 1977–1985.
- 39 X. K. Xing and C. C. Liu, *Electroanalysis*, 1991, **3**, 111–117.
- 40 L. R. Jordan and P. C. Hauser, *Anal. Chem.*, 1997, **69**, 2669–2672.
- 41 C. A. Paddon, G. J. Pritchard, T. Thiemann and F. Marken, *Electrochem. Commun.*, 2002, **4**, 825–831.
- 42 D. Lee, J. C. Hutchison, A. M. Leone, J. M. DeSimone and R. W. Murray, *J. Am. Chem. Soc.*, 2002, **124**, 9310–9317.
- 43 R. Horcajada, M. Okajima, S. Suga and J. Yoshida, *Chem. Commun.*, 2005, 1303–1305.
- 44 Y. F. Shen, Y. J. Zhang, Q. X. Zhang, L. Niu, T. Y. You and A. Ivaska, *Chem. Commun.*, 2005, 4193–4195.
- 45 S. Wang and D. Du, *Sensors*, 2002, **2**, 41–49.
- 46 L. Zhang, C. Hampel and S. Mukerjee, *J. Electrochem. Soc.*, 2005, **152**, A1208–A1216.
- 47 K. L. Huang, T. M. Holsen and J. R. Selman, *Ind. Eng. Chem. Res.*, 2003, **42**, 3620–3625.
- 48 A. Goswami, A. Acharya and A. K. Pandey, *J. Phys. Chem. B*, 2001, **105**, 9196–9201.
- 49 E. F. Sullenberger, S. F. Dressmen and A. C. Michael, *J. Phys. Chem.*, 1994, **98**, 5347–5354.
- 50 R. Toniolo, N. Comisso, G. Bontempelli, G. Schiavon and S. Sitran, *Electroanalysis*, 1998, **10**, 942–947.
- 51 I. Lahdesmaki, A. Lewenstam and A. Ivaska, *Talanta*, 1996, **43**, 125–134.
- 52 I. Lahdesmaki, J. Ruzicka and A. Ivaska, *Analyst*, 2000, **125**, 1889–1895.
- 53 H. Kahlert, J. R. Porksen, I. Isildak, M. Andac, M. Yolcu, J. Behnert and F. Scholz, *Electroanalysis*, 2005, **17**, 1085–1090.