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

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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 × 10−6 cm2 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 Ru2+ or Os2+ 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
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. 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 MΩ 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 chronopotentiometry. The experiment was carried out in a conventional three-electrode electrochemical cell. The working electrode was a PFIL-modified Pt microelectrode \((d = 20 \mu m)\), 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 be seen (curve ‘b’). 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...
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.

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, $I(t)$ vs the reciprocal of the square root of time, $I^{1/2}$ [Fig. 6(B)], a straight line was found corresponding to the modified Cottrell equation,

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

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

\[
K_p = \frac{C_m}{C_0}
\]  

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.

### 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 \( \mu \text{M} \) 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
The 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.\textsuperscript{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, Fe(CN)\textsubscript{6}^{3−/4−} exhibits surface-enhanced redox waves at the PFIL-modified electrode assembly (Fig. 8). The peak current increased little by little with time, indicating the enrichment behavior of Fe(CN)\textsubscript{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 Ru(NH\textsubscript{3})\textsubscript{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.\textsuperscript{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.
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.

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