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Design and synthesis of a task-specific ionic liquid as a transducer in potentiometric sensors†

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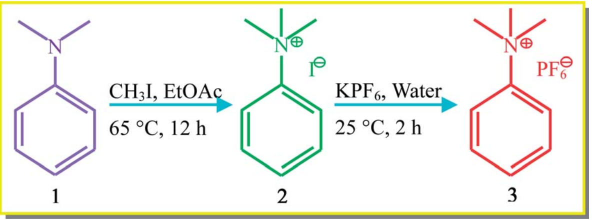
A task-specific ionic liquid called *N*,*N*,*N*-trimethylaniline hexafluorophosphate was synthesized and further employed as an ion-to-electron transducer in potentiometric sensors with excellent performance.

Ionic liquids have attracted extensive attention in the field of chemistry due to their outstanding properties, such as negligible vapor pressure, good thermal stability, wide electrochemical window, excellent designability and intrinsic conductivity.[1] Especially, the designability in which the structures and properties of ionic liquids can be easily tuned by selecting the appropriate combination of organic cations and anions, provides a facile and promising way to prepare multifunctional materials called task-specific ionic liquids (TSILs).[2] During the past decade, various types of TSILs have been designed and synthesized for specific purposes, such as catalysis, synthesis, gas adsorption, analysis, and construction of nanomaterials.[3]

In the field of chemical sensors, potentiometric sensors or ion-selective electrodes (ISEs) are the most frequently used ones due to their intrinsic advantages such as portability, low-energy consumption, and low cost.[4] The development of solid-contact ion-selective electrodes (SC-ISEs) is regarded as the important improvement of ISEs, since these could be truly miniaturized.[5] However, the initial form of SC-ISEs, *i.e.* coated wire electrode (CWE), suffers from the high charge transfer resistance at the interface induced the low potential stability. The introduction of conducting polymers as internal ion-to-electron transducers has significantly improved the potential stability of SC-ISEs in view of they could couple the electronic conductivity of the electrode substrate and the ionic conductivity of the ion-selective membrane.[6] However, the redox side reaction with dissolved oxygen and the unavoidable water layer at the interface between ion-selective membrane and conducting polymers has limited practical applications of these SC-ISEs.[7] Recently, carbon nanomaterials like fullerene, carbon nanotubes, and graphene, are employed as the solid-contact layer to develop high-performance SC-ISEs.[8] These carbon nanomaterials possess excellent conductivity and large double-layer capacitance that are able to convert effectively the ionic signal through the ion-selective membrane into an electronic signal between the metal contact and the sensing member.[9] However, due to the insolubility of these nanomaterials in common solvents, the fabrication of unique nanomaterials-based film is hard and time-consuming. Therefore, new functional materials are still highly desirable for the fabrication of robust SC-ISEs.

In this communication, we firstly synthesized a novel type of aniline-functionalized TSIL called *N*,*N*,*N*-trimethylaniline hexafluorophosphate. This novel TSIL possesses redox, ion conductive and high hydrophobic properties due to the aniline-functionalized cation and hexafluorophosphate anion. On the basis of these excellent properties, this TSIL was employed as a solid-contact layer to construct a novel solid-contact potassium ion-selective electrode (K-ISE) with excellent performance.

Synthesis of TSIL is illustrated in Scheme 1. Firstly, the *N*,*N*-dimethylaniline was dissolved in ethyl acetate (EtOAc). Then,



Scheme 1 Synthesis of TSIL. **1** represents *N*,*N*-dimethylaniline; **2** represents *N*,*N*,*N*-trimethylaniline iodide; **3** represents *N*,*N*,*N*-trimethylaniline hexafluorophosphate.

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methyl iodide (CH_3I) was added into the solution. After keeping the solution at 65 °C for 12 h, a viscous yellow liquid was obtained. The resulted liquid was dried in a vacuum oven at 60 °C for 24 h to obtain the *N*,*N*,*N*-trimethylaniline iodide. Secondly, the *N*,*N*,*N*-trimethylaniline iodide was added into the solution containing potassium hexafluorophosphate (KPF_6), and the solution was stirred for 2 h at 25 °C. After that, the mixed solution was divided into two parts. The upper part of the solution was removed. While the underlying part was collected and washed with deionized water for several times. Finally, the liquid was dried in a vacuum oven at 60 °C for 24 h to obtain the aniline-functionalized TSIL, *i.e.* *N*,*N*,*N*-trimethylaniline hexafluorophosphate.

The redox properties of the synthesized TSIL were studied using cyclic voltammetry (Fig. 1A). It is clear that the aniline-functionalized TSIL shows a complex electrochemistry, which contains three oxidative states, that is very similar to the polyaniline modified electrode.[10] In addition, the background current of the bare GCE in 0.1 M KCl solution is quite low, while the distinct capacitive current is obtained at the TSIL film modified GCE (GCE/TSIL), indicating the large redox capacitance at the TSIL film. Since the solid-contact layer with suitable redox capacitance is one of the conditions required for the potential stability of the solid-contact potentiometric ion sensors,[5] aniline-functionalized TSIL could be used as an effective solid-contact transducer.

To confirm the excellence of TSIL-based transducer, electrochemical impedance spectroscopy, chronopotentiometry, and water layer test were studied in details. Fig. 1B compares the impedance behaviors of the CWE (GCE/K-ISM) and SC-ISE (GCE/TSIL/K-ISM, the fabrication process can be seen in ESI†). It can be seen that the resistance, which is equal to the bulk membrane resistance coupled with the contact resistance between the electrode substrate and the polymeric membrane, decreases from 13.12 MΩ (CWE) to 7.86 MΩ (SC-ISE), indicating the presence of TSIL film between the GCE and polymeric membrane makes the charge transport process much easier. In the region of low frequencies, a large semicircle is observed in the impedance plot of GCE/K-ISM, suggesting the large charge-transfer resistance with a small capacitance at the "blocked" interface (GCE|K-ISM). The negligible low-frequency semicircle in the case of SC-ISE shows that the aniline-functionalized TSIL film significantly increases low-frequency redox capacitance and thus effectively facilitates the ion-to-electron transduction process between the electronically conducting electrode substrate and ionically conducting ion-selective membrane.[5,8]

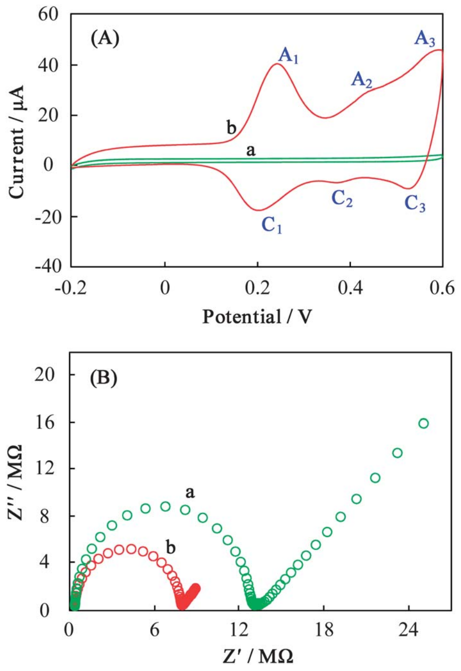

Fig. 1 (A) Cyclic voltammograms of GCE (a) and GCE/TSIL (b) in 0.1 M KCl solution. Scan rate: 100 mV s^{-1}; (B) impedance plots of GCE/K-ISM (a) and GCE/TSIL/K-ISM (b) in 0.1 M KCl solution. Frequency range, 100 kHz to 0.3 Hz; E_{dc}, 0.2 V; ΔE_{ac}, 10 mV.

Reversed chronopotentiometry is used to evaluate the electrical capacity of the solid-contact and the potential stability of the developed electrode. The typical chronopotentiograms recorded for the GCE/K-ISM and GCE/TSIL/K-ISM are illustrated in Fig. S1 (ESI†). The potential jump in the response is used to calculate the total resistance of the electrode. The estimated total resistance for the TSIL-based SC-ISE is 7.91 MΩ that is in good agreement with the resistance of impedance measurement. Furthermore, the potential stability can be derived from the ratio $\Delta E/\Delta t$. The calculated potential drift value of the GCE/TSIL/K-ISM is about 27.6 μV s^{-1}, which is much lower than the value of the CWE (1593 μV s^{-1}), and comparable with those obtained at carbon nanomaterials or conductive polymers-based SC-ISEs.[6,8] The low-frequency capacitance (C_{LF}) of the aniline-functionalized TSIL in the GCE/TSIL/K-ISM was calculated using the equation $\Delta E/\Delta t = i/C_{LF}$. The estimated value is 65.8 μF, which is similar with those of conductive polymers based solid-contact transducers.[6]

In the long-term measurements, the formation of aqueous layer inside the electrodes has been proved to be the main reason of instability because its composition changes due to permeability of the membrane to ions and CO_2, leading to changes in pH. For this purpose, a water layer test was conducted at the GCE/K-ISM and GCE/TSIL/K-ISM (Fig. S2, ESI†). As expected, the response of TSIL-based SC-ISE shows no potential drift, while a substantial potential drift was found at the response of the CWE. This demonstrates that the high hydrophobicity of TSIL film resulted from the hexafluorophosphate anion could significantly eliminate the accumulative water layer inside the electrodes. In addition, the intermediate term stability is calculated with the signal recorded in the third step of the test. The obtained potential drift is 34.6 μV h^{-1} in the 20 h continuous monitoring, revealing that the TSIL-based SC-ISE can be reliably applied in the long term online analysis.

The last outstanding property of the TSIL-based SC-ISE is its insensitivity towards environmental factors, such as light and gas. As illustrated in Fig. S3 (ESI†), no significant potential drift is found when the measurement cell was exposed to different lights, suggesting the aniline-functionalized TSIL transducer has no light sensitivity. The result of gas sensitivity test is shown in Fig. S4 (ESI†). It can be seen that the TSIL-based SC-ISE is

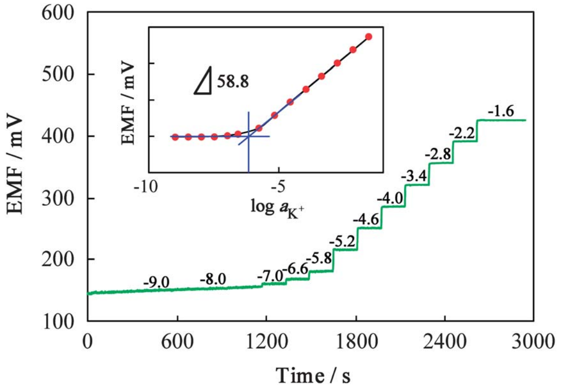

Fig. 2 EMF measurements recorded for increasing the concentration of K$^+$ in the solution. Inset: calibration curve of the GCE/TSIL/K-ISM, conditioned in 0.1 M KCl solution.

insensitive to gas (O_2 and CO_2), confirming the absence of water layer at the TSIL|K-ISM interface. This property was much superior to the conductive polymers-based SC-ISE, since the conductive polymers may react with the O_2 in water layer resulted in the potential drift.[7,8] These demonstrate that aniline-functionalized TSIL film could act as a well-performed transducer in potentiometric sensors.

The potentiometric characterization of the developed SC-ISE was examined by measuring the electromotive force (EMF) value in KCl solution with different concentrations. Fig. 2 displays the dynamic potentiometric response of the electrode recorded as a function of time at increasing the concentration of K$^+$. As shown, the response is much faster (less than 13 s). Such a response time is much shorter than those of electrodes that contain a similar membrane but with liquid contact, indicating the presence of TSIL transducer promotes the response time of the SC-ISE. Furthermore, the response was almost Nernstian displaying a slope of 58.8 mV per decade (standard deviation of the slope is 0.4 mV per decade, $R = 0.9991$) and a linear range from $10^{-5.8}$ to $10^{-1.6}$ M K$^+$ (inset of Fig. 2). The limit of detection calculated as the intersection of the two slope lines was $10^{-6.1}$ M. The selectivity of the electrode was determined using the separated solution method. As summarized in Table S1 (ESI†), the selectivity coefficients were comparable to their liquid-contact electrode counterparts, nevertheless our electrodes are highly sensitive, stable and easy to be prepared.

In conclusion, an aniline-functionalized TSIL was firstly synthesized and further employed to fabricate high-performance potentiometric devices. Due to the high redox capacitance of the TSIL film, the developed potentiometric sensor shows high potential stability. Furthermore, with the high hydrophobic character of TSIL materials, no water film was formed between the ion-selective membrane and the underlying solid-contact layer. This work provides a useful avenue for implementing TSIL as a new generation of ion-to-electron transducer in SC-ISEs, which could expand the scope of TSIL constructed sensing devices and hold great promise for routine sensing applications.

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