

Electronic Supplementary Information

Design and Synthesis of a Task-Specific Ionic Liquid as Transducer in Potentiometric Sensors

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Chemicals and reagents

N,N-dimethylaniline, methyl iodide, ethyl acetate and potassium hexafluorophosphate were obtained from Sinopham Chemical Reagent Co., Ltd (Shanghai, China). Valinomycin (M_w 1111.32), poly(vinyl chloride) (PVC) (M_w ~43,000), 2-nitrophenyl octyl ether (*o*-NPOE) (M_w 251.32), potassium tetrakis(4-chlorophenyl)borate (KTPClPB) (M_w 496.11), tetrahydrofuran (THF), and potassium chloride (KCl) were purchased from Sigma. All other chemicals were of analytical grade and used without further purification. Millipore-Q (18.2 M Ω ·cm) water was used for all solutions.

Synthesis of aniline-functionalized TSIL

In a typical synthesis procedure, 12 g of N,N-dimethylaniline was dissolved into 50 mL of ethyl acetate (EtOAc). Then, 15 g of methyl iodide (CH₃I) was gradually added into the solution when the temperature of the mixed solution was kept below 35 °C. After kept 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, 20 g of N,N,N-trimethylaniline iodide was added into the solution containing 15 g of potassium hexafluorophosphate (KPF₆), and the solution was stirred for 2 h at 25 °C. After that, the mixed solution was divided into two parts. The underlying part was collected and washed with deionized water for several times. Finally, the resulted liquid was dried in a vacuum oven at 60 °C for 24 h to obtain the aniline-functionalized TSIL N,N,N-trimethylaniline hexafluorophosphate.

Preparation of GCE/TSIL

Glassy carbon electrode (GCE, 3 mm diameter) was polished with 1, 0.3, and 0.05 μ m alumina powder sequentially and then washed ultrasonically in water and ethanol for a few minutes, respectively. The cleaned GCE was dried with nitrogen steam for the next modification. The TSIL solution was prepared by dissolving 40 mg TSIL into 1 mL acetone. Then, the TSIL film modified electrode (GCE/TSIL) was fabricated by casting 20 μ L of TSIL solution onto the electrode surface and dried under room temperature. The thickness of TSIL film was measured as ~45 μ m.

Fabrication of potassium ion-selective electrode (K-ISE)

The composition of the potassium ion-selective membrane (K-ISM) cocktail used in this

study was ca. 1% (w/w) valinomycin ($\sim 9.00 \text{ mmol kg}^{-1}$), 0.2% (w/w) KTpCIPB ($\sim 4.03 \text{ mmol kg}^{-1}$), 65.8% (w/w) *o*-NPOE ($\sim 2.62 \text{ mol kg}^{-1}$), and 33% (w/w) PVC ($\sim 7.67 \text{ mmol kg}^{-1}$) dissolved in THF. The dry fraction of the membrane cocktail was ca. 15% (w/w).¹

The SC-ISE (GCE/TSIL/K-ISM) was prepared by drop-casting 100 μL of the above THF solution onto the GCE/TSIL surface. The thickness of the ion-selective membrane was $\sim 30 \mu\text{m}$. For comparison, the traditional coated wire electrode (CWE, namely GCE/K-ISM) was fabricated by drop-casting 100 μL of the above solution onto the GCE. The solvent was evaporated overnight at room temperature. All the prepared K-ISEs were conditioned in 0.01 M KCl solution for at least one day before further measurements and also between the measurements.

Electrochemical impedance spectroscopy (EIS), Cyclic voltammetry (CV), Chronopotentiometry

EIS measurements were performed using a Solartron Analytical model 1260 Impedance-Gain-Phase Analyzer in combination with a model 1287 Electrochemical Interface (Solartron Analytical, Farnborough, UK) with the Zview and Zplot software. All tests were conducted at an open circuit, and a sinemodulated AC potential with the amplitude of 10 mV applied for impedance measurements. The tested frequency range was from 0.3 Hz to 100 kHz.

CV and chronopotentiometry were carried out on a CHI 440 electrochemical workstation (CH Instruments, USA). All the electrochemical experiments were performed in a one-compartment electrochemical cell. A conventional three-electrode system, consisting of the prepared electrodes (GCE, GCE/TSIL, GCE/K-ISM and GCE/TSIL/K-ISM) as the working electrode, a saturated Ag/AgCl electrode as a reference electrode, and a platinum wire as an auxiliary electrode, was employed. CV curves were recorded at the scan rate of 100 mV s^{-1} in 0.1 M KCl solution. For the chronopotentiometry, constant current of $\pm 1 \text{ nA}$ was applied on the K-ISEs, while the potential of the electrodes was measured in 0.1 M KCl solution (Figure S1).

Potentiometry

Potentiometry were carried out using a PalmSens (Palm Instrument BV, Houten) that consists of a portable potentiostat interfaced with a palmtop PC. All the potentiometric

measurements were carried out with a two-electrode system which comprises a saturated Ag/AgCl reference electrode and the prepared working electrodes.

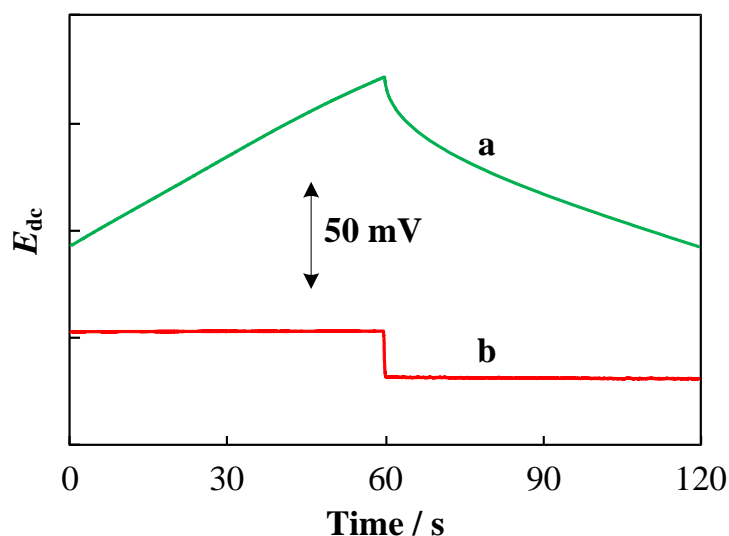


Figure S1 Chronopotentiograms for GCE/K-ISM (a) and GCE/TSIL/K-ISM (b) recorded in 0.1 M KCl solution. The applied current is +1 nA for 60 s and -1 nA for 60 s.

Water layer test

The water layer test was carried out as follows: firstly, the prepared ISEs (GCE/K-ISM and GCE/TSIL/K-ISM) were initially conditioned in 0.1 M KCl for 24 h, and their response was then alternately measured in 0.01 M KCl, 0.01 M NaCl, and again in 0.01 M KCl. Results were shown in Figure S2.

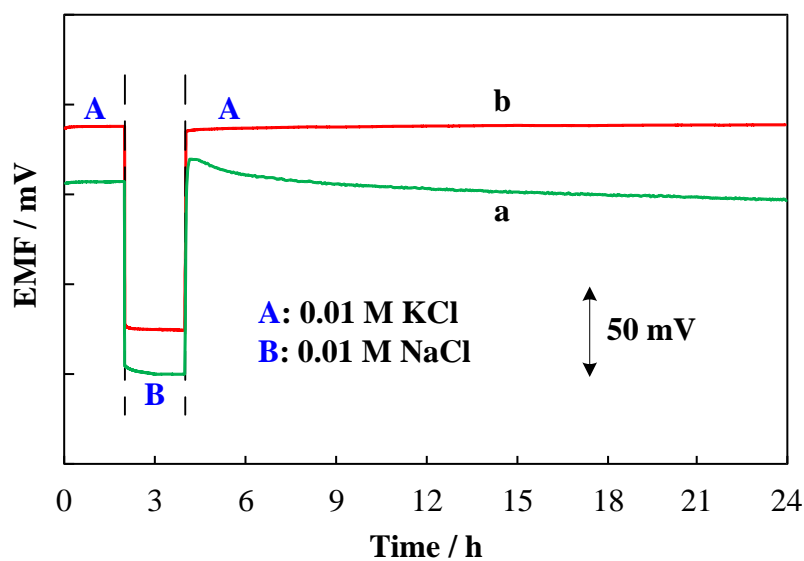


Figure S2 Water layer test for the GCE/K-ISM (a) and GCE/TSIL/K-ISM (b), the measurements were switched between 0.01 M KCl solution and 0.01 M NaCl solution.

Interference test

For the test of light sensitivity, the whole electrochemical cell was kept in the dark until the electrode was exposed either to room light or to UV light or to infrared light for 300 s, followed each time by a return to the dark. Electrode potential response was recorded in 0.01 M KCl solution. Figure S3 shows the typical response of the GCE/TSIL/K-ISM under different lights. The O₂ and CO₂ sensitivity was evaluated by measuring the potential in 0.01 M KCl solution first purged with N₂ for 600 s, then CO₂ for 600 s, lastly O₂ for 600 s. Result is illustrated in Figure S4.

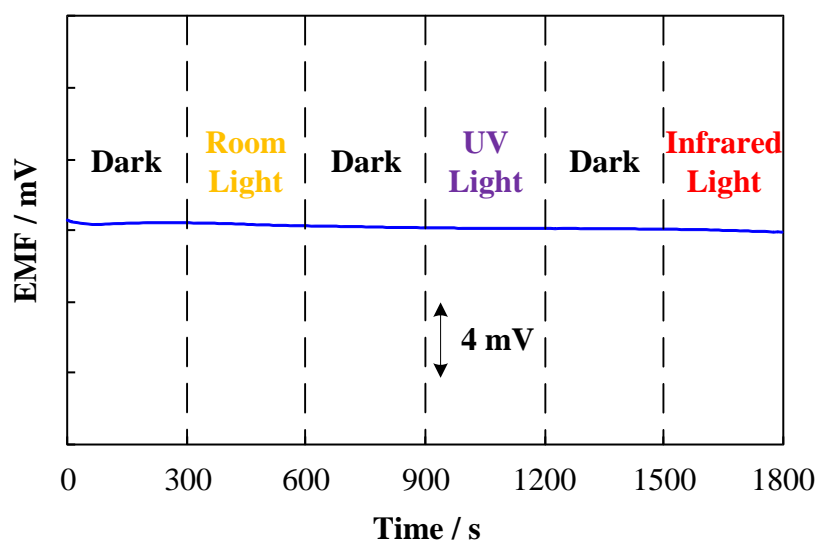


Figure S3 Effect of light on potential stability of the GCE/TSIL/K-ISM in 0.01 M KCl solution.

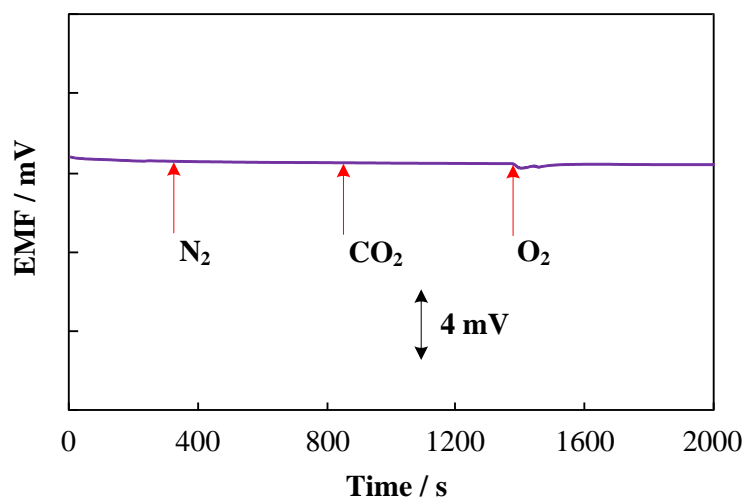


Figure S4 Effect of O₂ and CO₂ on potential stability of the GCE/TSIL/K-ISM in 0.01 M KCl solution.

Selectivity of GCE/TSIL/K-ISM

The selectivity of the electrode was determined using the separated solution method.² For this test, the GCE/TSIL/K-ISM was firstly conditioned in the solution containing 0.1 M interfering ion and then the potentiometric response of this interfering ion at the developed electrode was obtained.

Table S1 Selectivity coefficients ($\log K^{\text{pot}}_{ij}$) of the GCE/TSIL/K-ISM

Interference (M)	Slope (mV/decade)	Selectivity coefficient ($\log K^{\text{pot}}_{K-M}$)
Li ⁺	45.7 ± 0.8	-3.6 ± 0.2
Na ⁺	52.1 ± 0.9	-4.4 ± 0.3
NH ₄ ⁺	43.6 ± 1.1	-2.1 ± 0.4
Mg ²⁺	36.2 ± 1.4	-4.7 ± 0.2
Ca ²⁺	39.5 ± 1.3	-3.5 ± 0.3

Notes and references

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- 2 E. Bakker, E. Pretsch, P. Bühlmann, *Anal. Chem.*, 2000, **72**, 1127; C. Wardak, *J. Hazard. Mater.*, 2011, **186**, 1131.