



A novel all-solid-state ammonium electrode with polyaniline and copolymer of aniline/2,5-dimethoxyaniline as transducers



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ABSTRACT

From the centre outwards, the novel all-solid-state ammonium ion-selective electrode was composed of a silver wire as substrate, covered with conductive polyaniline (PANI), copolymer of aniline/2,5-dimethoxyaniline (CPANI) and ion selective membrane (ISM) layers. PANI was formed in-situ on the Ag wire by the cyclic voltammetry method, scanned from 0 to 0.45 V in 0.1 M aniline hydrochloride solution, and then dipped the electrode in the N,N-Dimethyl formamide (DMF) solution of CPANI and ISM sequentially. The scanning electron microscope (SEM) observation revealed that the PANI formed cross-linked slabs about 0.3–2.5 μm in length and 0.3–0.6 μm in thickness. Under the SEM, CPANI micro particles filled in the cross-linked PANI slabs. Bulk impedance of the transducer was between 100 and 200 Ω , much lower than the poly (vinyl chloride) (PVC) based transducer in the previous work. Fabrication procedures, micro-structure, and the common resolvability of the CPANI and ISM in the DMF were all essential for reducing the cross-boundary resistance. Linear response range of the electrode was 10^{-4} – 10^{-1} M, with a Nernst slope of 54.20–56.59 mV/decade. The potential drifts of each decade were ± 0.5 mV within 400 s. The response time was less than 1 s and the lifetime was three months. The ammonium electrodes were used to test the ammonium in the waste water with pH value from 2.6 to 10.1, and the testing results were in agreement with those obtained by titration method and Nessler's reagent colorimetry method. The ammonium electrode proposed in this paper is suitable for in-situ monitoring NH_4^+ content in the environment in a wide range of pH value.

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1. Introduction

Excess ammonia in the breeding pool may cause massive death of fish and other aquatic organisms due to eutrophication and depletion of the dissolved oxygen [1]. Furthermore, bacteria can convert ammonia into nitrite, which is a potent carcinogen [2]. Therefore, measuring ammonia content in water is important for aquaculture, drinking water and environmental monitoring.

Traditional methods for measuring ammonia content were based on Nessler's reagent colorimetry [3], indophenol [4], o-phthalaldehyde (OPA) and N-acetyl-cysteine (NAC) reagent [5], and titration [6]. Electrochemical methods have attracted great interests in recent years because of its high sensitivity, fast analysis, low detection limit, few reagent requirements, and little cost [7]. Ion selective electrodes (ISEs), which have the specific ion selectivity ionophore, are the most useful indicator electrode now-

adays. They can do microliter sample measurement and in-situ monitoring because of their short response time, well selectivity and sensitivity [8,9]. Most of the currently used commercial ISEs are glass-housed electrodes with liquid internal reference solution [10,11]. ISEs with this structure are difficult to miniaturize, difficult to integrate with other electrodes. Further, concentration of the internal solution is not stable because of diffusion across the membrane [12]. This may cause signal drifting in turn. For these reasons, as well as their physical weakness, glass-electrodes are not suitable for long term in-situ monitoring.

On the other hand, since the first successful preparation of the coated wire electrodes in 1971, by Cattrall and Freiser [13], the all-solid-state ion-selective electrodes have gone through four stages, namely coated wire electrodes [13], neutral ionophore electrodes [14], hydrogel electrodes [15] and conductive polymer electrodes [16]. Electrochemical materials have achieved great progress in recent years, high performance solid ionic conductor has been used to make batteries, and electrodes [17–21], such as poly(3,4-ethylenedioxythiophene) for Ca^{2+} and Pb^{2+} [22,23], poly-

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pyrrole for urea [24], and polyaniline for Ca^{2+} [25]. Subsequently, the conductivity, chemical activity and catalytic activity of inorganic membrane materials have been improved by ion doping technology [26,27], and the organic and inorganic composite membranes have been used for fabricating electrodes [28]. However, even with these developments, the conductor between the substrate and the ISM is still a problem for the all-solid-state ISEs.

In this work, proton doped polyaniline (PANI) and copolymer of 2,5-dimethoxyaniline and aniline (CPANI) were used as solid electrolyte, to develop a novel all-solid-state NH_4^+ -ISE. PANI has perfect conductivity, simple synthesis procedure, good chemical stability, biological toxicity, and good anti-corrosion performance [29–32], the CPANI can be dissolved in the same solvent as the ammonium ionophore and has similar chemical structure but better electrochemical and electronic properties than PANI [33,34]. The design of this ISE consisted of a silver wire coated from inside to outside with conductive polyaniline, soluble polyaniline and ammonium selective membrane.

The electrode was calibrated and used for measuring ammonium content in five different waste liquid samples from Yan Tat Printed Circuit (Shen Zhen) company. Fabrication procedure, calibration results and real performance of this electrode are summarized in this paper.

2. Experimental

2.1. Reagents

Ammonium ionophore I (09877 Fluka), potassium tetrakis (4-chlorophenyl) borate, 2-Nitro phenyloctyl ether, and 0.1 M ammonium ion solution for the ISE were purchased from Fluka. N,N-Dimethyl formamide (DMF), ammonium chloride, and aniline hydrochloride (99%) were obtained from Sigma–Aldrich. Silver wire (99.9%, 0.6 mm in diameter) was obtained from the Precious Materials Company of Changzhou in China. Ammonium-free water was used throughout.

2.2. Preparation of ISEs

2.2.1. Polyaniline coating

The conductive polyaniline (PANI) film was formed by cyclic voltammetry (CV) method, scanning from 0 to 0.45 V at a rate of 50 mV/s for 20 segments in the aniline hydrochloride solution (0.1 M). This process was implemented by a three-electrode system of the CHI760D electrochemical workstation. The working electrode was a silver wire, the reference electrode was a commercial Ag/AgCl, Cl^- electrode, and the auxiliary electrode was a Pt electrode.

The soluble polyaniline layer was prepared by dipping the electrode into the saturated solution of the copolymer of 2,5-dimethoxyaniline and aniline (CPANI) with the molar ratio of 1:5. The copolymer was synthesized with the following procedure: 12 ml 2 M hydrochloric acid was added into a round bottom flask containing 0.9313 g (0.01 mol) aniline and 0.30636 g (0.002 mol) 2,5-dimethoxy-aniline, and stirred in ice bath for 10 min. Then 20 ml of 0.6 M ammonium persulfate solution was added dropwise in about 20 min, with continued stirring in the ice bath for 24 h [35]. The product was collected after washing with ammonium-free water and ethanol in sequence, followed by filtration and natural drying.

2.2.2. Ammonium ISM coating

The membrane solution was made by dissolving ammonium ionophore I, potassium tetrakis (4-chlorophenyl) borate, and 2-Nitro phenyloctyl ether in N,N-Dimethyl formamide (DMF), with the mass fraction of 6.9%, 0.7% and 92.4%, respectively, as suggested by Fluka, and stored under the condition of 2–4 °C. The elec-

trode from the previous step was dipped in the solution for 2 s at room temperature, and then dried in a vacuum desiccator for 2 h at room temperature.

After the above fabricating procedures, the all-solid-state ammonium electrode looks like a silver needle, 0.6 mm in diameter, and 5–10 mm in length. The conductive transducer and ISM are coated on the Ag wire, with a total thickness in microns.

2.3. Apparatus and measurement

2.3.1. SEM observation

The conductive PANI and CPANI layers and the thickness of the electrode were analyzed by FEG650 environment scan electronic telescope of the FEI Company.

2.3.2. Impedance measurements

Impedance measurements were performed with M273 Potentiostat and M5210 Lock-in Amplifier, Princeton Applied Research, USA. The simulating electrodes were made of $10 \times 10 \times 0.1$ mm silver plate coated with different layers used in the real electrode. For measuring the impedance, the simulating electrode was set as the working electrode, matched with a Pt auxiliary electrode and an Ag/AgCl, Cl^- reference electrode. The impedance spectra were recorded in 0.1 M NH_4Cl solution at 25 °C within 10 kHz–10 mHz and $\Delta E = \pm 10$ mV.

2.3.3. Electrode calibrations

All potentiometric measurements were obtained with the CHI760D workstation at room temperature. Calibration solutions were 0.1 M standard NH_4Cl and 10^{-2} – 10^{-7} M diluents made up of stepwise dilution with ammonium-free water. The potential reading were taken for 400 s.

3. Results and discussions

3.1. SEM observation

Proton doped polyaniline (PANI) was introduced because of its high conductivity and stability. Under the SEM, the PANI formed by in-situ electrochemical reaction appeared cross-linked slabs about 0.3–2.5 μm in length and 0.3–0.6 μm in thickness (see Fig. 1a) on the substrate. In this work PANI and the out-layers had never been peeled off from Ag wire, even in the stability test for about 3 months. Scaling-off used to be a problem for similar PANI layers made with potentiostatic and constant current method [36]. It seems that the cyclic voltammetry method is preferable to get a better binding between the PANI layer and the substrate [37].

The CPANI chain with methoxyl became more soluble in Tetra Hydro Furan (THF) and DMF without sacrificing its conductivity [38]. While comparing Fig. 1a with Fig. 1b, it can be seen that the inter slab pores of PANI (in Fig. 1a) were filled up with fine particles (0.2–0.4 μm in diameter) of CPANI (in Fig. 1b). The structure of the PANI/CPANI layer in Fig. 1b was significantly denser than that of the PANI layer in Fig. 1a.

To measure its thickness, the surface of the electrode was damaged by a tweezers. Under the SEM (Fig. 1c), it was clearly seen that the film was mechanical damaged, some fragments broken away from the electrode, and the thickness of the fragment is 400–500 nm.

3.2. Impedance, cross-boundary resistance and cyclic voltammetry studies

In conventional glass-housed ISEs, the internal electrolyte is a conductor for passing the response signal from ISM to the centre metal wire. The solution contacts well with both the ISM and the

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