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The Electrochemical Analysis of Cadmium in Choline Chloride/Urea Deep Eutectic Solvent Electrolyte at Carbon Nanotubes Modified Electrode

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The electrochemical behavior of Cd at choline chloride/urea electrolyte and multi-wall carbon nanotubes modified electrode was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). A couple of sensitive and quasi-reversible redox peaks of Cd was obtained with -0.75 V of oxidation peak potential (E_{pa}) and -0.91 of reduction peak potential (E_{pc}) ($\Delta E = 0.16$ V) in choline chloride /urea ionic liquids and $0.1 mol \cdot L^{-1}$ HAc-NaAc mixed buffer system (pH 5.4). A sensitive DPV method for the determination of Cd was proposed. The oxidization peak was linearly related to the concentration of Cd in the range of 6.0×10^{-4}–1.5×10^{-2} $\mu g \cdot mL^{-1}$, the detection limit was 6.8×10^{-5} $\mu g \cdot mL^{-1}$. The proposed method is quick, sensitive, reliable and can be used for the determination of Cd in environment and food.

Keywords: Cd; Choline chloride/urea solvent; Electrolyte; Multi-wall carbon nanotubes; Cyclic voltammetry; Differential pulse voltammetry.

1. INTRODUCTION

Cadmium (Cd) is one of the most toxic of metallic elements in environment and biological systems and has stronger transfer activity and biological availability[1-2] than that heavy metals. In particular, Cd can take a very long time to be excreted and be accumulate in soil constantly, and enter into human body through the food chain, resulting in malformation, cancers and mutation effects[3-4]. Therefore, it is always a common concern to develop methods for the determination of Cd in environment and food. At present, different methods have been reported, including AAS[5], ionic association spectrophotometric, ICP-MS, SEC-HPLC-ICP-MS[6], electrochemical analysis(such as anodic stripping voltammetry, potentiometric stripping analysis(PSA), differential pulse voltammetry[7]).

Over the past 20 years, room temperature ionic liquid (RTIL) as a new kind of materials has attracted the concern due to the characteristics[8] of wide electrochemical windows, high conductivity, good thermal and chemical stability, viscosity and structural designother which the traditional materials do not have[9-12] and widely used in the electrochemical field[13].

Ionic liquid modified electrode has been widely used in the electrochemical analysis owing to its unique electrochemical properties, including high ionic conductivity, wide electrochemical windows, low cost and environment-friendly[14]. RTIL is usually combined with some nanotubes materials[15-18] and enzyme[19-20]. For example, Fukushima[21] and Zhao[22] reported a RTIL–carbon nanotubes (CNTs) electrode, and found that RTIL can significantly improve properties of electrode with enhanced conductivity of attached CNTs at room temperature which can improved sensitivity, compatibility and stability[23].

In this paper, we applied a simple and fast way to develop a high sensitive voltammetric analysis method of Cd by using choline chloride/urea deep eutectic solvent electrolyte and abrasively immobilized multi-walled carbon nanotubes (MWCNTs) electrode. The proposed method is very easier, faster and cheaper than that by RTIL/CNTs composite modified electrodes. Furthermore, choline chloride/urea supporting electrolyte can improve the sensitivity of MWCNTs modified electrode effectively.

2. EXPERIMENTAL

2.1 Apparatus and Materials.

Electrochemical measurement was carried out by ZAHNER Zennium IM6 Electrochemical Workstation (ZAHNER-Elektrik GmbH&Co. KG, Kronach, Germany). A three-electrode system including an abrasively immobilized MWCNT graphite working electrode (diameter: 5 mm), a saturated calomel regerence electrode (SCE) and a platinum auxiliary electrode was employed.

Multi-walled carbon nanotubes (MWCNTs, 95%) was purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, China. Cd standard solution(1000 $\mu g\cdot mL^{-1}$, 1% HNO_3) was purchased from National Institute of Metrology[24].

Choline chloride [$Me_3NC_2H_4OH$]Cl, (ChCl) (Sigma-Aldrich, 99.5%) was recrystallized in anhydrous ethanol and dried for 24 h in vacuum at 80 °C. Urea (Sinopharm Chemical Reagent Co, Ltd) was pre-dried under vacuum prior to use.

All the chemicals used were of analytical-reagent grade. Twice-distilled water was used throughout the experiments.

2.2 Experimental methods.

2.2.1 Preparation of choline chloride/urea deep eutectic solvent.

Choline chloride/urea deep eutectic solvent was prepared by stirring the mixture of choline chloride and urea (mole ratio 1:2) at 80 °C until a homogeneous colorless liquid was formed[25] and then stored in vacuum dryer.

2.2.2 Preparation of the abrasively immobilized MWCNTs electrode.

A graphite electrode (5 mm in diameter) was polished to a mirror-like surface with metallographic sand paper and 0.05 μm Al_2O_3 suspension, respectively. After rinsed thoroughly with doubly distilled water between each polishing step, the electrode was subjected successively with 50% nitric acid, ethanol and doubly distilled water in ultrasonic bath and then dried in air. The abrasively immobilized MWCNTs electrode was prepared by gently rubbing the electrode surface on a filter paper supporting two milligrams of MWCNTs for two minutes[26-27]. The prepared electrode was cleaned with distilled water before use.

2.2.3 Preparation of sample solution.

The soil samples were air dried and grounded to pass through a 100-mesh sieve. 2.00 g prepared sample was placed in a teflon beaker and wetted. 10 mL HCl was added and heated at low temperature for 1 h, and then 20 mL HNO_3 was added as 5 mL solution left and heated to near dryness. After that 5 mL HF was added and heated for 10 min. Finally, 5 mL $HClO_4$ was added, heated until no white smoke. The solution and beaker were rinsed with 3 mL pure water and then saved in volumetric flask[28] .

2.2.4 The voltammetric analysis of Cd^{2+}

CV and DPV were performed in the three-electrode cell in 5.0% (v/v) choline chloride/urea ionic liquids, 20.0 μL 100 $\mu g\cdot mL^{-1}$ Cd^{2+} standard solution and 0.1 $mol\cdot L^{-1}$ pH 5.4 HAc-NaAc buffer solution between the potential range of -1.2 V and 0.4 V at a scan rate of 0.05 $V\cdot s^{-1}$. The DPV conditions were pulse width 250 ms, pulse amplitude 20 mV and pulse interval 250 ms[24].

3. RESULTS AND DISCUSSION

3.1 Influence of buffer solution and pH.

The current response of Cd^{2+} was investigated under the addition of 5.0% (v/v) choline chloride/urea deep eutectic solvent electrolyte in different buffer systems, such as 0.1 $mol\cdot L^{-1}$ PBS buffer solution, 0.1 mol·L^{-1} citric acid-sodium citrate buffer solution and 0.1 mol·L^{-1} HAc - NaAc buffer solution, respectively. Where the largest peak current and the best shape of peak in the CV curves of Cd^{2+} were observed in the 0.1 mol·L^{-1} HAc-NaAc buffer system. So, 0.1 mol·L^{-1} HAc-NaAc buffer system was selected in this work.

The DPV curves of Cd^{2+} was measured in 0.1 mol·L^{-1} HAc-NaAc buffer solution at different pH (3.6~6.8), as shown in Figure 1. The oxidation peak was better than others when the pH at 5.4. Therefore, pH 5.4 was chosen for subsequent experiments.

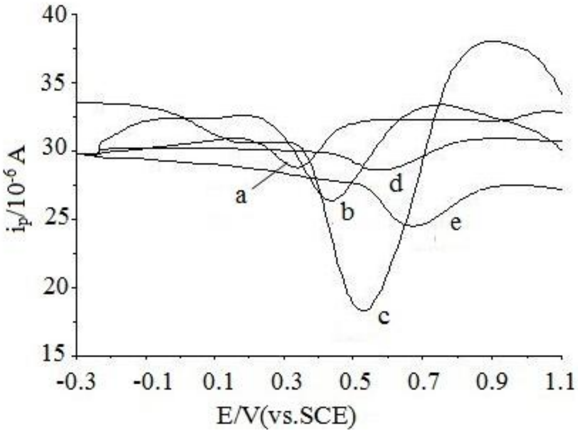

Figure 1. DPV curves of Cd^{2+} in 0.1 mol·L^{-1} HAc-NaAc buffer solution at different pH, (a)pH 3.6, (b)pH 4.3, (c)pH 5.4, (d)pH 6.0, (e)pH 6.8

3.2 Influence of the ionic liquid dosage.

Figure 2 shows that the influence of the ionic liquid dosage of Cd^{2+} on peak current. The current response of Cd^{2+} increases first with the increase of the concentration of choline chloride/urea ionic liquid until it reaches to 5.0% (v/v) and gets the maximum current response at 5.0% (v/v), where decreases as the concentration of choline chloride/urea ionic liquid above 5.0% (v/v). Figure 3 shows that the CV curves of Cd^{2+} was measured at different concentration of choline chloride/urea ionic liquid. When 5.0% (v/v) choline chloride/urea ionic liquid was added, the peak was better than others. So, 5.0% (v/v) choline chloride/urea ionic liquid was selected.

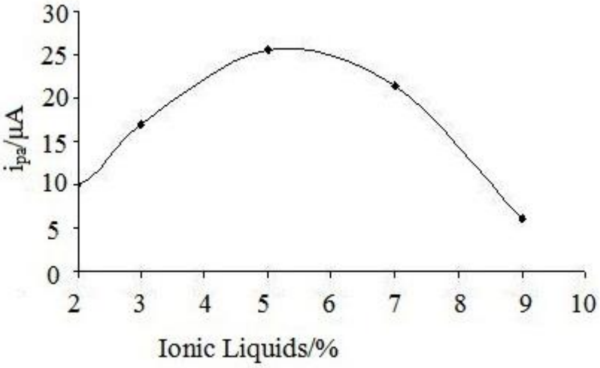

Figure 2. The influence of choline chloride/urea ionic liquid concentration on peak current

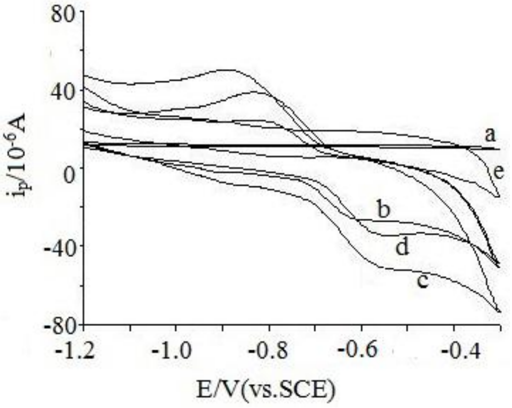

Figure 3. Cyclic voltammetrys of Cd^{2+} at different concentration of choline chloride/urea ionic liquid, (a)0.0% (v/v)choline chloride/urea ionic liquid, (b)3.0% (v/v)choline chloride/urea ionic liquid, (c)5.0% (v/v)choline chloride/urea ionic liquid, (d)7.0% (v/v)choline chloride/urea ionic liquid, (e)9.0% (v/v)choline chloride/urea ionic liquid

3.3 The electrochemical behavior of Cd^{2+}

Figure 4 displays the CV curves of 0.2 μg·mL^{-1} Cd^{2+} at different electrodes. No peak was observed in supporting electrolyte at MWCNT GE (curve a). One peak and the oxidation peak current (i_{pa}) were obtained in 0.1 mol·L^{-1} HAc-NaAc buffer solution (pH 5.4) supporting electrolyte and no reductive peak was observed at MWCNT GE (curve b). A pair of quasi-reversible redox peak was observed in choline chloride/urea ionic liquid and 0.1 mol·L^{-1} HAc-NaAc buffer solution mixed supporting electrolyte at bare GE (curve c) and MWCNT GE (curve d). Oxidation peak current i_{pa} = 16.82 μA and reduction peak i_{pc} = 10.30 μA were observed at bare GE.

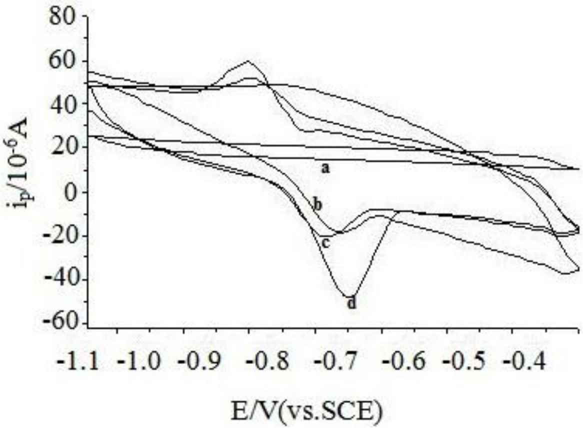

Figure 4. The cycle voltammetric analysis curve of Cd^{2+} at MWCNT GE, (a)supporting electrolyte, (b)0.1 mol·L^{-1} HAc-NaAc buffer solution (pH 5.4) supporting electrolyte, (c)choline chloride/urea ionic liquid/0.1 mol·L^{-1} HAc-NaAc buffer solution mixed supporting electrolyte at bare GE, (d)choline chloride/urea ionic liquid/ 0.1 mol·L^{-1} HAc-NaAc buffer solution mixed supporting electrolyte at MWCNT GE

The oxidation peak potential (E_{pa}) and reduction peak potential (E_{pc}) of Cd were -0.75 V and -0.91 V , respectively, $\triangle E = 0.16$ V at MWCNT GE . The ratio of oxidation peak current (i_{pa}) and reduction peak (i_{pc}) was 1.58. While, the oxidation and reduction peak currents of Cd^{2+} in choline chloride/urea ionic liquid and 0.1 mol·L^{-1} HAc-NaAc buffer solution mixed supporting electrolyte were higher than those in 0.1 mol·L^{-1} HAc-NaAc buffer solution at MWCNT GE, which means that choline chloride/urea ionic liquid can effectively improve the sensibility of MWCNT GE to detect trace Cd.

3.4 Influence of scan rate

Figure 5 shows the influence of scan rate on the CV response of Cd^{2+} in choline chloride/urea ionic liquid and 0.1 mol·L^{-1} HAc-NaAc buffer solution mixed supporting electrolyte. The result shows that oxidation peak potential (E_{pa}) moved positively and reduction peak potential (E_{pc}) almost remained unchanged within the scanning speed range from 0.01 to 0.1 V·s^{-1}, and oxidation peak current (i_{pa}) gradually increased and reductive peak current (i_{pc}) basically remained unchanged. Well-defined oxidation peak was observed as the scanning speed was 0.08 V·s^{-1}. The oxidation peak current (i_{pa}) showed a well linear relationship with the scan rate (υ) in the potential range of 0.01 to 0.07 V·s^{-1}, the regression equation for i_{pa} and υ is $i_{pa} = 49.174\upsilon + 38.804$ ($r = 0.9945$). The results indicate that electrode process in the choline chloride/urea electrolyte and MWCNTs modified electrode system is governed by the surface adsorption-controlled.

The number of electrons transferred (n) was calculated according to the following equation[29]:

$$i_p = \frac{nFQ\upsilon}{4RT}$$

Where i_p represents the anodic or cathodic peak current, Q is the quantity of charge measured from the oxidation or reduction peak area of voltammogram. $Q = nFAT_T$, A is the surface area of the electrode, υ is the scan rate and T_T is the surface coverage of the electroactive quercetin. In this work, the electron transfer number (n) was calculated to be about 2.

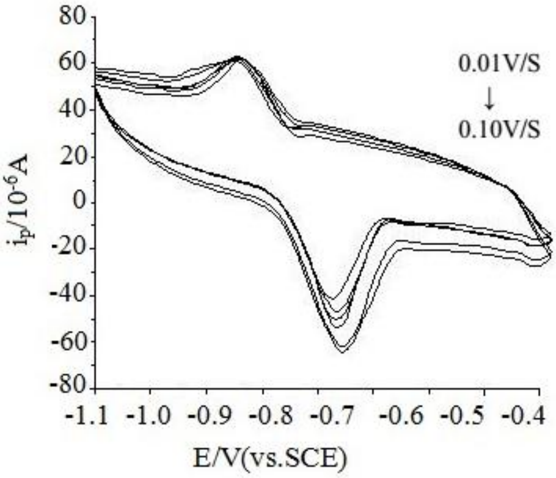

Figure 5. Cyclic voltammograms of Cd^{2+} at different scan rates

3.5 The linear range and detection limit

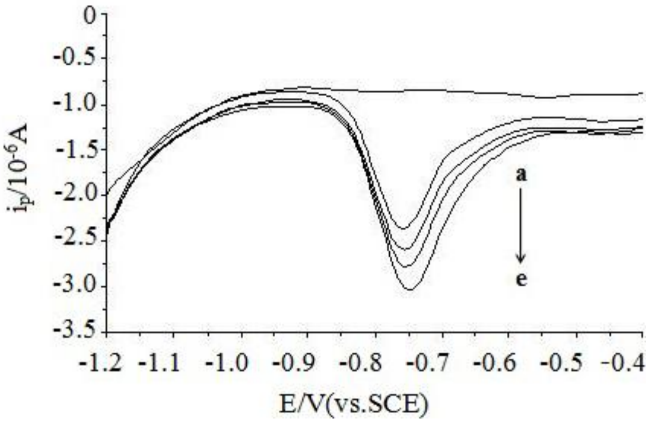

Figure 6. DPV of Cd^{2+} for different concentration, (a)0.0 μg·mL^{-1} Cd^{2+}, (b)6.0×10^{-4} μg·mL^{-1} Cd^{2+}, (c)2.0×10^{-3} μg·mL^{-1} Cd^{2+}, (d)5.5×10^{-3} μg·mL^{-1} Cd^{2+}, (e)1.5×10^{-2}μg·mL^{-1} Cd^{2+}

Well-defined oxidation peak DPV response with a high peak current of Cd^{2+} were observed in the choline chloride/urea deep eutectic solvent electrolyte and MWCNTs modified electrode system as Figure 6 shown. We found that the oxidation peak current value was linearly related to the concentration of Cd^{2+} in the range of 6.0×10^{-4} to 1.5×10^{-2}μg·mL^{-1} and the detection limit was 6.8×10^{-5} μg·mL^{-1}. The regression equation is i_{pa}=0.0894c×10^{4} +1.7900 (r = 0.9981), where, i_{pa} is the oxidation peak current (μA), c is the concentration of Cd^{2+} (μg·mL^{-1}).

3.6 Sample analysis

Cd capsule samples were prepared and 1 mL of prepared solution was taken to constant volume into 10 mL with choline chloride/urea ionic liquid and 0.1 mol·L^{-1} HAc-NaAc mixed buffer solution. Each sample was determined 5 times and spiked recovery experiments was carried out at the same time, the average content were calculated to be 0.416 to 0.475 mg·Kg^{-1}. The relative deviations ranged from 2.7 to 3.4%, the percentage recovery ranged from 92.2 to 97.1%.

Table 1. Samples analysis results

sample	Measured Value / mg·Kg^{-1}	Added / mg·Kg^{-1}	RSD / %	recovery / %	Marked Value* / mg·Kg^{-1}
1	0.416	0.5	3.4	92.2	0.430
2	0.438	0.5	3.1	97.1	0.425
3	0.475	0.5	2.7	95.3	0.466

*Determined by AAS

4. CONCLUSIONS

A new electrochemical analysis method for determination of Cd^{2+}, using choline chloride/urea deep eutectic solvent electrolyte and multi-wall carbon nanotubes modified electrode system has been developed based on the advantages of the ionic liquid with high conductivity, wide electrochemical window. The proposed system has the advantages such as rapid and easy to preparation, low cost over the traditional RTIL/CNTs composite modified electrodes system. The result shows that choline chloride/urea ionic liquid can improve the sensitivity of measurement effectively. We investigated the optimization of determination conditions, and set up a novel, rapid and easy method of determination Cd samples, and the result is satisfactory.

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