ELECTROCHEMICAL DETERMINATION OF CADMIUM(II) USING DITHIZONE ASSISTED ION TRANSFER AND ELETROLYTE DROPPING ELECTRODE

Feifei SHU[a1], Shaoai XIE[b] and Jinping JIA[a2,*]

[a] *School of Environmental Science and Engineering, Shanghai Jiao Tong University,*
800 Dongchuang road, Shanghai 200240, P. R. China; e-mail: [1] sophie9901@sjtu.edu.cn,
[2] jpjia@sjtu.edu.cn
[b] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University,*
800 Dongchuang road, Shanghai 200240, P. R. China; e-mail: xieshaoai@sjtu.edu.cn

Received March 30, 2011
Accepted May 5, 2011

The transfer of Cd(II) assisted by dithizone (DzH_2) present in methyl isobutyl ketone (MIBK) at water–MIBK interface was systematically investigated by novel electrolyte dropping electrode (EDE) using cyclic voltammetry (CV) and square wave voltammetry (SWV). The protonation of DzH_2 at polarized liquid–liquid interface was studied. The stoichiometry of resulting metal ligand complex was formulated. Transfer peak current was proportional to the bulk concentration of the Cd(II) varied between 1 μM to 0.1 mM and the maximum value of relative standard deviation was about 3.17%. The presented procedure was successfully applied for determination of Cd(II) in real samples.

Keywords: Electrochemistry; Sensors; Cadmium; Electrolyte dropping electrode; Liquid–liquid interface; Complex formation; Assisted ion transfer.

Because of the toxicity of cadmium to plants and humans, its online determination is increasingly important. Although many methods such as (FAAS)[1], inductively coupled plasma mass spectrometry/optical emission spectrometry (ICP-MS/OES)[2,3], atomic fluorescence spectrometry (AFS)[4], and electrothermal atomic absorption spectrometry (ETAAS)[5,6] provide good sensitivity and selectivity, these methods are limited in their use for online monitoring due to the size, cost, and analysis time.

Electrochemistry, such as stripping voltammetry, plays an important role in the determination of cadmium. However the solid electrode used in electrochemistry is prone to adsorb impurities. Compared with solid electrode, mercury electrode is very reliable. Because of the regular refreshment of electrode surface, possible problems with interfacial blocking by impurities

Collect. Czech. Chem. Commun. 2011, Vol. 76, 10, pp. 1177–1186

doi:10.1135/cccc2011066

are minimized. However, due to its high toxicity the use of mercury has been severely restricted.

Polarography with the electrolyte dropping electrode (EDE) was pioneered by Koryta et al.[7,8] and mercury was substituted by organic solvent such as 1,2-dichloroethane and nitrobenzene. However the stability of EDE is of concern. The flow rate of EDE is controlled by the height of the organic reservoir and the characteristics of glass capillary. Furthermore the ohmic drop in organic solvent is too large when compared with mercury. To solve these problem either advanced cell design or nano- and micro-liquid– liquid interfaces are required. However, these methods are difficult to be applied to real practice since they are complicated and expensive.

In this work an in-house assembled injection-voltammetric system was designed. Novel EDE was acted as working electrode. Because of high ionic conductivity and thermal stability, conventional organic electrolyte tetraphenylborate (TBATPB) was substituted by room temperature ionic liquids (RTILs)[9] hydrophobic 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6). Activated carbon fiber (ACF) was embedded in EDE to decrease the ohmic drop of aqueous phase. Because of the decrease of ohmic drop the conventional three electrode system was successfully applied for investigation of the dithizone assisted transfer of Cd(II) at liquid–liquid interface. This resulted in excellent sensitivity and selectivity for real sample.

EXPERIMENTAL

Instrument

An in-house assembled injection-voltammetric system is depicted in Fig. 1. It consisted of a flow-injection system (KDS 100, KdScientific, Holliston, USA) and electrochemistry workstation (CHI 660A, CHI Instruments, Shanghai, China).

EDE was consisted of a glass capillary, ACF prepared according to the literature[10], and a two-port valve. Springe pump was connected to 2-port valve of EDE with silicone tubing (0.35 mm i.d.) as short as possible to minimize the dead volume. The top of glass capillary was encapsulated in two-port valve. Because the conductivity of the aqueous electrolyte (12 S m^{-1} of 1 M LiCl) was much lower than that of mercury (10^6 S m^{-1})[11], the ACF was embedded in glass capillary to decrease the ohmic drop of aqueous solution.

An electrochemical cell is consisted of an EDE working electrode, a platinum wire counter electrode and Ag|AgCl (3 M KCl) reference electrode (both from CHI Instruments, Shanghai, China).

ICP-OES (Iris Advantage 1000, Oxoid Microbiology, American) was used to perform metal ion analysis. The pH values were measured with a Mettler Toledo LE438 meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China).

Reagents

The stock standard solutions of 1×10^{-2} M Cd, Zn, Cu, Fe, Ca and 1×10^{-3} M Pb were prepared by dissolving appropriated amounts of $CdCl_2$, $ZnCl_2$, $CuCl_2$, $FeCl_3$, $CaCl_2$, $PbCl_2$ (Shanghai Reagent Corporation, China) in ultra-pure water, and then diluted to the required concentration. Organic electrolyte [Bmim]PF_6 was purchased from Henan Lihua Pharmaceutical Co., Ltd. All reagents, including MIBK and DzH_2 (Shanghai Reagent Corporation, China), were of analytical grade. MIBK was saturated with 1 M HCl. The DzH_2 solution was prepared daily by dissolving the appropriate amount of DzH_2 in MIBK. All other chemicals were used without further purification. 18.2 MΩ Ultra-pure water (Maxima ultra pure water system, Elga) was used throughout.

Procedure

Cyclic voltammetry (CV) and square wave voltammetry (SWV) was used to investigate Cd(II) transfer across the water–MIBK interface assisted by DzH_2. Unless otherwise stated the CV waveform parameters were as follows: scan rate 50 mV s^{-1} and quiet time 30 s. The SWV waveform parameters were as follows: amplitude 25 mV, frequency 75 Hz, and increment 8 mV, quiet time 120 s. The CV and SWV were recorded between –1.2 and –0.4 V.

Buffer solution (0.01 M NaAc–HAc) containing 0.01 M LiCl was used as a supporting electrolyte. Unless otherwise stated, the pH of supporting electrolyte was adjusted to 4.5 ± 0.05 with HCl and NaOH. All electrochemical experiments were performed at room temperature (25 ± 3 °C). Scheme 1 described the electrochemical cells used for the experiments presented here.

The sample of Ni-Cd battery was placed in a 500 ml beaker and dissolved in 100 ml aqua regia. The solution was heated on a hot plate for an hour. After cooling to room temperature, the solution was filtered, and transferred into a 500 ml volumetric flask and diluted to the required concentration on a daily basis.

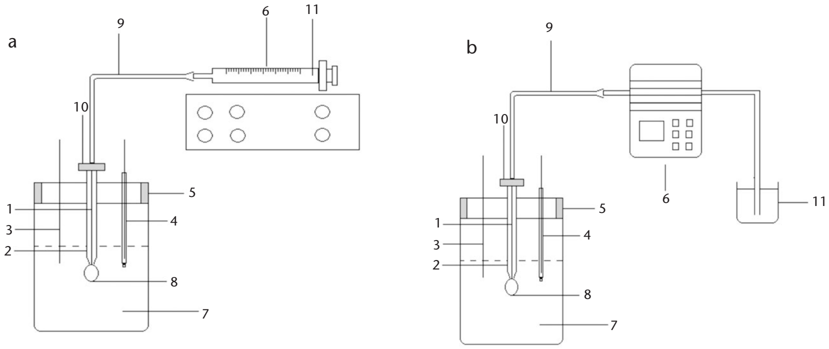
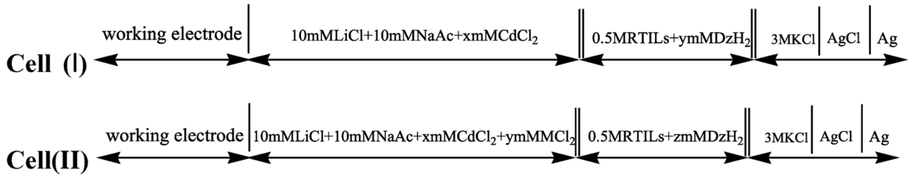


FIG. 1
Schematic diagrams of the electrochemical cell: 1 ACF, 2 burette, 3 Pt wire electrode, 4 Ag|AgCl electrode, 5 lid, 6 springe pump (a)/precise tubing pump (b), 7 organic phase, 8 aqueous electrode, 9 silicone tubing, 10 2-port valve, 11 sample



Scheme 1

Droplet of a sample solution was released upward by springe pump into the organic phase. The liquid–liquid interface was fixed at the tip of the glass capillary. Flow rate of EDE was 0.3 ml min^{-1} and when the volume of droplet increased to certain volume, the flow rate decreased to 0 ml s^{-1}, and the electrochemistry measurement was carried out. Since the density of aqueous phase (1.051 g cm^{-2}) was higher than that of the MIBK (0.80 g cm^{-2}). After measurement the electrochemical cell was taken away and the droplet was dropped down, the next measurement was carried out repeatedly.

For auto-injection and continuous measurement springe pump was replaced by precision engineered pumps (Ismatec, AG, Glattbrugg, Switzerland).

RESULTS AND DISCUSSION

Effect of Experimental Parameters

The effect of scan rate of CV on the diffusion of Cd(II) was investigated. The positive peak current versus the square root of the scan rate were plotted for the ligand and the metal ion excess respectively, giving a straight line with a regression coefficient of 0.9953 and 0.9967. These results indicate that the transfer process is controlled by diffusion. When the ligand is in high excess it is controlled by metal ion diffusion, otherwise controlled by ligand diffusion[12].

The effect of droplet volume on the stripping response of an EDE was analysed. As the volume of droplet increased from 0.002 to 0.01 ml, the peak current increased 12.58%. The volume of droplet continued to increase, the peak current decreased. Maximum sensitivity of stripping response was obtained at 0.01 ml of droplet.

Facilitated Ion Transfer

For a liquid–liquid interface, the potential window is determined by the transfers of cations and anions of supporting electrolytes in both phases. In this work, the potential window was controlled by LiCl and [Bmim]PF_6 in liquid and organic phase, respectively.

In the absence of Cd(II), no peak current is observed and the potential window is from –1.2 to –0.4 V (see Fig. 2a). From Fig. 2b can be seen that Cd(II) could transfer from the water to MIBK without DzH_2 in organic phase, and simple ion transfer potential of Cd(II) is evaluated at –0.916 V. On the contrary from Fig. 2c in the presence of the DzH_2 the transfer potential of the Cd(II) is shifted to more positive potentials at –0.773 V but the transfer peak current is higher. This shift is associated with the complexation reaction at liquid–liquid interface.

From Fig. 2 it is obviously that MIBK saturated with 1 M HCl could extract the metal ion from the aqueous to organic phase. DzH_2 was widely used as a highly selective and sensitive ligand, notably towards heavy metal ions. From Fig. 2c compared with simple ion transfer the peak current of Cd(II) assisted transfer across the water–MIBK interface is sharply enlarged owing to the DzH_2, therefore the DzH_2 is employed to the determination of Cd(II) in further experiments.

Preliminary Study of DzH_2

DzH_2 is insoluble in water below pH 7 but dissolves readily in alkali solution under its deprotonated form dithizonate (DzH^-). In general primary metal dithizonates are derived from the dithizonate anion and have the formula $M(DzH)_z$, and sccondary metal dithizonate are derived from the di-negatively charged and have the formula $M_2/_zDz$[13].

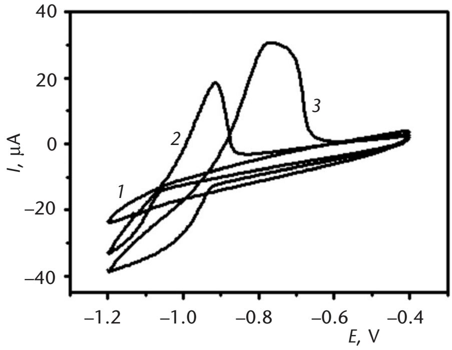


Fig. 2

CV of facilitated Cd(II) transfer across the water–MIBK interface for $x = 0$ mM, $y = 0.2$ mM (*1*); $x = 2$ mM, $y = 0$ mM (*2*) and $x = 2$ mM, $y = 0.2$ mM (*3*)

In order to test the ability of DzH_2 to assist the Cd(II) transfer across the liquid–liquid interface, reliminary studies were carried out. We investigated the form of dithizone in water–MIBK interface.

As described by Reymond et al.[14] an ionic partition diagram could be used to predict qualitatively the influence of the aqueous pH on the nature of the transferring species across the water–MIBK interface. The dependence of the half-peak potential $\Delta\varphi_{1/2}(L_mM^{z+})$ on pH was investigated. From Fig. 3 we can see that the transfer peak current appears from pH 2.08 to 9.28, where a small peak is still obtained by CV. Two independent measurements are shown. A single line in Fig. 3 with the slope of 51 mV per decade confirms that there is one proton involved in the transfer process. The other line is horizontal from pH 2.0 to 4.9 representing the exchange of DzH_2 through the liquid–liquid interface, and the breakpoint of 4.9 is approximate to the pK_a of DzH_2 in 1,2-DCE ($pK_a = 4.47 \pm 0.25$)[15].

Calculation of the Stoichiometry of Metal Ligand Complex

The voltammetric behavior of transfer process was carried out in order to calculate the stoichiometry and charge of metal ion complexes at pH 4.5. According to the literature, Reymond et al.[16] have proposed a model for the calculation of the association constants.

For the case of ligands in excess towards the metal ion, they defined

$$\Delta_o^w \varphi_{1/2}(L_m M^{z+}) = \Delta_o^w \varphi^{o\prime}(M^{z+}) - \frac{RT}{zF}\ln\xi - \frac{RT}{zF}\ln\left(1+\sum_{j=1}^{m}\beta_j^o (c_L^o)^j\right) \tag{1}$$

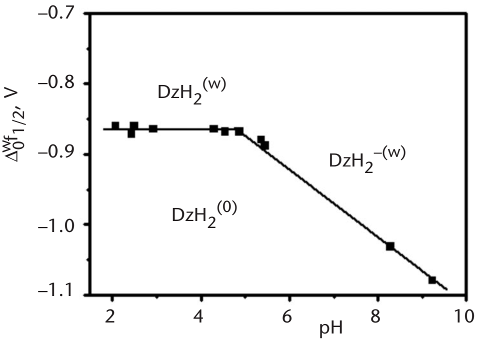


FIG. 3
Dependence of half-wave potential on the pH in the case of DzH_2 excess for x = 0.2 mM, y = 2 mM

where $\Delta\varphi_{1/2}(L_mM^{z+})$ is the half-wave potential of the assisted ion transfer. $\Delta_o^w\varphi^{o'}(M^{z+})$ is the formal potential of simple ion transfer. $\xi = (D_o/D_w)$, where D_w and D_o are the diffusion coefficients of all the species in the aqueous and organic phase, respectively, and which remains unchanged when the organic solution is fixed. c_L^o represents the organic bulk ligand concentration.

Based on the Eq. (*1*) for the case of metal ion in excess, assuming that the association constants for each of the substoichiometric species are smaller than β_m^o [17]. Then Eq. (*1*) becomes

$$\Delta_o^w\varphi_{1/2}(L_mM^{z+}) = \Delta_o^w\varphi^o(M^{z+}) - \frac{RT}{zF}\ln\beta_m^o - \frac{mRT}{zF}\ln c_L^o . \tag{2}$$

Logarithmic analysis of the transfer wave when the Cd(II) concentration is in large excess over the Cd(II) concentration, and the slope is equal to 34 mV per decade. It illustrates that a charge of +2 for the complex can be deduced.

From Eq. (*2*) the dependence of the half-wave potential on the DzH_2 concentration was investigated for the case of an excess concentration of Cd(II), and the slope is equal to 26 mV per decade. This value is in poor agreement with the theoretical value of a metal to lignad ratio of 1:2 for the Cd(II)–DzH_2 complex (see Eq. (*2*), and ligand complex species $Cd(DzH_2)_2^{2+}$ formed in the water–organic interface could be presumed.

Linearity, Reproducibility and Selectivity

The peak current measured by SWV versus the concentration of Cd(II) has been plotted. When the concentration of Cd(II) varied between 1 μM to 0.1 mM in the case of excess ligand (10 mM), the peak current was proportional to the bulk concentration of the Cd(II) in the aqueous phase. The calibration curves exhibit excellent linearity with a correlation of 0.9964.

To investigate the stability of eletrolyte dropping electrode, 0.2 mM Cd(II) containing aqueous was determined continuously 12 times by SWV and RSD is 3.17% (Cd(II) 0.2 mM, DzH_2 10 mM).

Selectively is very important for determination of heavy metal ion. Ligand is the chemical bases for the design of reliable sensor for the particular analyse ions. The interferences from other metal ions were evaluated. The experiments have been carried out for the 0.5 mM Cd(II) and the same concentration of Ca(II), Pb(II), Zn(II), Fe(II) and Cu(II). Just as in Scheme 1 the electrochemical cell (II) was used in this experimental system.

Figure 4 shows voltammograms having forward peaks clearly separated and the recovery of the Cd(II) concentration is 96.48% (0.5 mM $CdCl_2$ + 0.5 mM $CaCl_2$), 120.42% (0.5 mM $CdCl_2$ + 0.5 mM $CuCl_2$), 98.21% (0.5 mM $CdCl_2$ + 0.5 mM $ZnCl_2$), 101.92% (0.5 mM $CdCl_2$ + 0.5 mM $FeCl_3$), 135.10% (0.5 mM $CdCl_2$ + 0.5 mM $PbCl_2$), 102.30% (0.5 mM ($CdCl_2$ + $CaCl_2$, $PbCl_2$, $ZnCl_2$, $FeCl_3$, $CuCl_2$)).

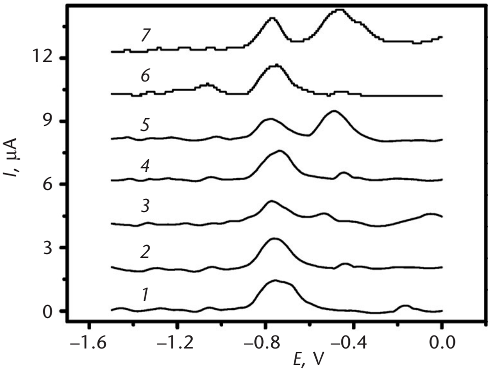


FIG. 4
SWV for 0.5 mM $CdCl_2$ (*1*), 0.5 mM $CdCl_2$ + 0.5 mM $CaCl_2$ (*2*), 0.5 mM $CdCl_2$ + 0.5 mM $CuCl_2$ (*3*), 0.5 mM $CdCl_2$ + 0.5 mM $FeCl_3$ (*4*), 0.5 mM $CdCl_2$ + 0.5 mM $PbCl_2$ (*5*), 0.5 mM $CdCl_2$ + 0.5 mM $ZnCl_2$ (*6*), 0.5 mM ($CdCl_2$ + $CaCl_2$, $PbCl_2$, $ZnCl_2$, $FeCl_3$, $CuCl_2$) (*7*) transfer across water–MIBK interface

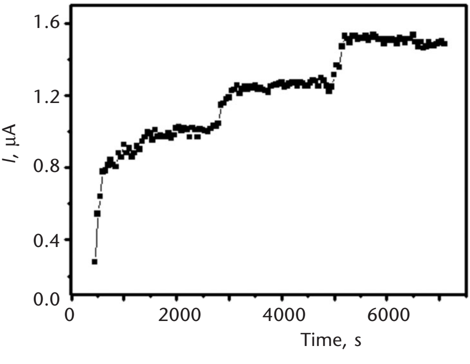


FIG. 5
Dependence of the current peak on the injection time for x = 0.5, 1 and 1.5 mM; y = 10 mM; quiet time 0 s

Continuous Determination

The instrument was equipped with a precision engineered pump. 0.5, 1 and 1.5 mM $CdCl_2$ sample solutions were auto-injected in turn. Without consideration the effect of size of EDE, the flow rate was kept constantly at 0.3 ml min^{-1}. Electrochemical determination was carried out once per minute by SWV, and the transfer peak current was recorded (Fig. 5).

When the Cd(II) concentration is high, the transfer peak current increases accordingly, and 10 min later it reaches the maximum value, after that the peak current keeps mostly unchanged until next sample is injected. The RSD of 0.5, 1 and 1.5 mM Cd(II) are 0.714, 2.16 and 1.26%, respectively and linear coefficient is 0.9914.

Analysis of Real Sample

The novel EDE was applied to real sample. The results are given in Table I. Reliability was checked by comparing the results with data obtained by ICP-OES analysis. 0.2, 0.4 and 0.6 ml sample solutions were added to 10 mM supporting electrolyte. As the results showed, the recovery of spiked sample is good, and there is satisfactory agreement between the results and data obtained by ICP-OES analysis. It is suggested that the proposed procedure is reliable for measurement of the real sample.

TABLE I
Analytical results of Cd(II) in real sample (mean ± s.d., *n* = 3)

Sample	ICP-OES, mg l^{-1}	Found, mg l^{-1}	Recovery, %
1	494.2	523.9 ± 61.6	106.0
2	988.4	1033.2 ± 249	104.5
3	1482.6	1462.8 ± 109.8	98.7

CONCLUSION

A novel electrolyte dropping electrode was designed to investigate the Cd(II) assisted by DzH_2 transfer across the water–MIBK interface. The dependence of the half-peak potential on the DzH_2, Cd (II) concentration was investigated to calculate the stoichimetry of the metal ligand complex. The form of DzH_2 at water–MIBK interface was researched. Cu(II) and Pb(II) have influence on the measurement. The real wastewater sample was determined and the results showed that this novel method was feasible.

RTIL used as organic electrolyte extremely increases the conductively of organic aqueous. Compared with TPATPB, the detection limit is 2 orders of magnitude lower[18,19]. The measurement time for each sample is shorter than 3 min and the electrochemical apparatus of electrolyte dropping electrode is easy to portable and suitable for automatic operation. Compared with sophisticated advanced cell design or nano- and micro-liquid–liquid interfaces, this novel method is simple and efficient. It has prospective application in continuous determination of heavy metal ions in practice.

This work was supported by the Hi-Tech Research and Development (863) Program of China No. 2006AA06Z405.

REFERENCES

1. Walter N. L. D. S., Jorge L. O. C., Rennan G. O. A., Djane S. J., Antonio C. S. C.: *J. Hazard. Mater.* **2006**, *137*, 1357.
2. David E. N., Kenneth R. N., Steven J. E., John A. B., Mary F. B.: *Spectrochim. Acta, Part B* **2004**, *59*, 1377.
3. Tao G-H., Yamada R., Fujikawa Y., Kudo A., Zheng J., Fisher D. A., Koerner R. M.: *Talanta* **2001**, *55*, 765.
4. Reis B. F., Torralba E. R., Buleo J. S., Rubio A. M.: *J. Anal. At. Spectrom.* **2002**, *17*, 537.
5. Burguera J. L., Burguera M., Rondon C., Carrero P., Brunetto M. R., Pena Y. P.: *Talanta* **2000**, *52*, 27.
6. Filgueiras A. V., Lavilla I., Bendicho C.: *Anal. Chim. Acta* **2004**, *508*, 217.
7. Koryta J., Vanýsek P., Březina M.: *J. Electroanal. Chem.* **1976**, *67*, 263.
8. Koryta J., Vanýsek P., Březina M.: *J. Electroanal. Chem.* **1977**, *75*, 211.
9. Wang P., Zakeeruddin S. M., Comte P., Exnar I., Gratzel M.: *J. Am. Chem. Soc.* **2003**, *125*, 1166.
10. Sun T-H., Jia J-P., Fang N-H., Wang Y-L.: *Anal. Chim. Acta* **2005**, *530*, 33.
11. Baars A., Aoki K., Watanabe J.: *J. Electroanal. Chem.* **1999**, *464*, 128.
12. Benvidi A., Lanjwani S. N., Ding Z. F.: *Electrochim. Acta* **2010**, *55*, 2196.
13. Paradkar R. P., Williams R. R.: *Anal. Chem.* **1994**, *66*, 2752.
14. Reymond F., Steyaert G., Carrupt P., Testa B., Girault H. H.: *J. Am. Chem. Soc.* **1996**, *118*, 11951.
15. Ferreira E. S., Garau A., Lippolis V., Pereira C. M., Silva F.: *J. Electroanal. Chem.* **2006**, *587*, 155.
16. Reymond F., Lagger G., Carrupt P. A., Girault H. H.: *J. Electroanal. Chem.* **1998**, *451*, 59.
17. Reymond F., Carrupt P.-A., Girault H. H.: *J. Electroanal. Chem.* **1998**, *449*, 49.
18. Xie S., Jia J., Chen H-J.: *Collect. Czech. Chem. Commun.* **2007**, *72*, 917.
19. Chen K., Xie S., Jia J.: *Acta Chim. Sin.* **2006**, *66*, 532.