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Determination of Ag(I) at a Chemically Modified Electrode Based on 2-Imino-cyclopentane-dithiocarboxylic Acid

Jeong-Sik Yeom, Mi-Sook Won, Sung-Nak Choi, and Yoon-Bo Shim*

Department of Chemistry, College of Natural Science, Pusan National University, Pusan 609-390

Received December 5, 1989

Chemically modified electrodes (CMEs), based on 2-imino-1-cyclopentane-dithiocarboxylic acid (icdc) containing carbon paste, have been characterized using cyclic voltammetric techniques. Ag(I) was chemically deposited on the CMEs, and voltammograms were obtained with the electrode in a separate buffer solution. The CME surface can be regenerated with exposure to acid and reused for deposition. In 10 deposition/measurement/regenerate cycles, the linear response has been reproduced up to 1×10^{-6} M in linear sweep voltammetry and 1×10^{-8} M in differential pulse voltammetry with relative standard deviation of 5.2% and 12.4%, respectively. The sensitivity increased with deposition time and scanning rate, and detection limit was 1×10^{-7} M and 1×10^{-9} M at 20 minutes deposition in the linear sweep voltammetry and differential pulse voltammetry, respectively. The presence of some metal ions does not influence the silver ion response. Satisfactory results were obtained for the analysis of the silver ion for a variety of reference materials without interference of Hg ion at the condition of pH = 5-6.

Introduction

Until now stripping voltammetry have been recognized as

one of the most sensitive electrochemical methods for the determination of trace metals. This utilizes both of the trace organic and inorganic analysis. In general, this method is

based on the preconcentration/stripping of an analyte in the sample solution. There are various electrochemical techniques for preconcentration/stripping of the analytes.^{1,2} Recently a number of investigators have reported new preconcentration procedures for trace metal analyses. The new procedures use chemically modified electrodes (CMEs), on which various ligands are incorporated.^{3,4}

Baldwin and coworkers⁵ recently reported the CMEs coated with dimethylglyoxime for trace determination of Ni(II) ion in a variety of complex samples. They have also reported copper sensitive CMEs containing 2,9-dimethyl-1,10-phenanthroline.⁶ Gehron and Brajer-Toth used modified electrode of quaternized poly(4-vinylpyridine) cross-linked with bathophenanthroline-disulfonic acid for determination of Fe(II).⁷ O'Riordand and Wallace reported the determination of copper ion using poly(pyrrole-N-carbodithioate) modified electrode⁸. Abruna and coworkers⁹ demonstrated the utility of electrodes modified with the Mordant Violet for the determination of Ni(II). This method was based on the coordination of Ni(II) ion in the sample solution by an immobilized layer (*via* ion exchange) of the dye. Wang and coworkers¹⁰ employed a CMEs with an ion exchange resin for determination of Cu(II). Cheek and Nelson¹¹ reported the determination of Ag(I) employing a CME-based amino silanes. Imisides and Wallace¹² reported the deposition and stripping behavior of mercury ions on the electrode modified by poly(pyrrole-N-carbodithioate) moiety and the polymer in its underivatized state. Hoyer and Florence¹³ employed the polymer coated glassy carbon electrode to determine the trace metals in body fluids.

There are several advantages for analytical applications of the CMEs. First, it has a wider adjustable preconcentration range than that of conventional stripping voltammetric techniques, in which one need to apply a constant potential to preconcentrate test ions on the electrode. Second, this method has a high selectivity due to the complexation with specific metal ions. Furthermore, when experimental conditions are optimized, it has a least interference effect from other metal ions present in the sample solution as a result of the selective complexation. For use of CMEs, no potential needs to be applied for deposition in preconcentration. Among these CMEs, carbon paste electrodes (CPEs) offer an advantage that it can be readily prepared and the electrode surface can be easily regenerated.

In this work, we report a preliminary work on electrochemical behaviors of the ammonium salt of 2-amino-1-cyclopentene-1-dithiocarboxylate(acdc) and 2-imino-1-cyclopentene-1-dithiocarboxylate(icdc)¹ in DMSO solvent using glassy carbon electrodes. The icdc is protonated acdc. Electrochemical properties and stripping analysis on acdc compounds have been studied by us previously.¹¹ It is possible to determine the acdc by stripping voltammetry, since its dimerized product adsorbs strongly on glassy carbon electrode.

In our present work, the CMEs have been prepared by making carbon paste mixtures containing appropriate amounts of icdc coated onto graphite particles employing a simple dissolution/evaporation procedure. We have used such modified electrodes to analyze trace metal ions *via* complexation followed by stripping voltammetry. The technique involves complexation of the metal ion with icdc on the modified electrode surface as a sparingly soluble precipi-

tates, followed by electrochemical reduction.

We have chosen Ag(I) ion for initial studies owing to its favorable complexability with dithio group of ligand icdc. To optimize the experimental conditions and to study the mechanism involved following experiments were performed: studying pH dependencies of peak height of currents, the height of peak current as a function of electrode composition (icdc/carbon), the scanning rate, and the effect of deposition as well as complexation time. Interference effects of some metal ions on the electrode surface have been also investigated. Under the optimum conditions determined by these experiments, the calibration curve have been obtained and the detection limit have been also determined by the use of cyclic and differential pulse voltammetry.

Experimental

Solutions were prepared by using triply distilled water and were deoxygenated before use by degassing with pre-purified nitrogen. Pyrrolidine-dithiocarbamate (pdc) was obtained from Fluca Co.. Other chemicals and solvents used in this work were spectroscopic or reagent grade and were used without further purification.

Preparation of 2-amino-1-cyclopentene-1-dithiocarboxylate(acdc). Acdc was prepared by following a modified procedure¹⁰ of Takeshima *et al.*. The ammonium salt of acdc was prepared by stirring a mixture of cyclopentanone (25 g), carbon disulfide (30 g) and 28% ammonia water (300 ml) below 0°C for 8 hours. The yellow crude product was collected, washed with ether and dried over calcium chloride in vacuo; yield 18 g. The ammonium salt is not stable at room temperature, loses ammonia on standing.

Preparation of 2-imino-1-cyclopentene-1-dithiocarboxylic acid(icdc). Icdc was prepared by dissolving acdc (2.3 g) in the water of about 50 ml and slowly neutralizing with 2 N-acetic acid under ice-cooling. The yellow crystals were collected, washed with cold water and dried in vacuo. This compound was dissolved in ethanol until saturation, and then an equal volume of water was added to the filtered solution. The shiny yellow crystals were collected, washed with cold water and dried over calcium chloride in vacuum; yield 1.5 g, m.p. 98°C (decomposition).

Preparation of dimer, di(2-imino-cyclopentylidene-mercaptomethyl disulfide). 0.01 M-icdc solution was added dropwise with stirring to Ca. 50 ml solution of 0.01 M sodium hydroxide containing acdc (3 g). The yellow product was collected by filtration, washed with water and dried in vacuum at room temperature.

Preparation of complex, Ag(icdc). Ca. 50 ml AgNO₃ (0.3 g) solution was added dropwise with stirring to Ca. 50 ml solution of icdc (0.29 g) containing same mole sodium hydroxide. the stirring was continued for 15 minutes. The yellowish-red precipitate was collected by filtration, washed with cold water and dried in vacuum at room temperature. The product was insoluble in water and was not recrystallized. Yield 75%, Anal. Calcd. for Ag(icdc): C; 27.05%, H; 3.00%, N; 6.19%. Found: C; 26.87%, H; 4.50%, N; 6.02%.

Electrode. Icdc-coated graphite powders (10%-90%) were prepared by dissolving weighed amount of icdc in 96% ethanol, adding the required amount of reagent grade graphite powder, and stirring the slurry formed until essentially

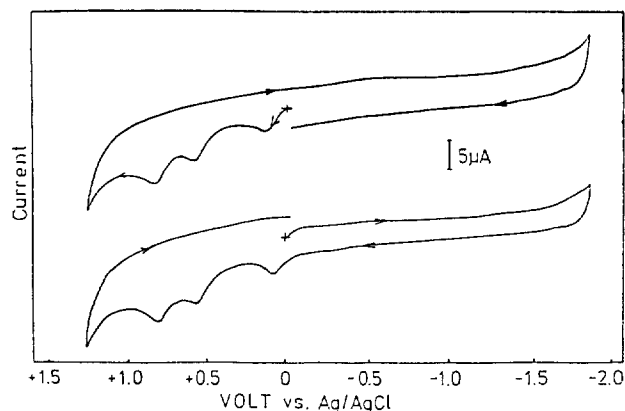


Figure 1. Cyclic voltammograms of 1×10^{-3} M acdc (0.1 M NaClO_4 /DMSO) taken for the anodic and cathodic scan at a glassy carbon electrode, separately.

all the ethanol had evaporated. Modified carbon pastes were prepared by thorough mixing of 5 g of coated graphite powder and 3 ml of Nujol oil (Sigma Co.) in a mortar. Unmodified carbon paste was prepared by a similar fashion from uncoated graphite powder. Electrode body was made of 1 ml polyethylene syringes (5 mm diameter), the tips of which had been cut off. This body was filled with approximately 2 cm of paste. Electrical contact to the paste was established by passing a thin copper wire through the piston. Fresh electrode surfaces were obtained by squeezing out a small amount of paste, scraping with paper until the surface show a shiny appearance. Fresh surfaces were subsequently conditioned by exposure to 1 M nitric acid for 5 seconds, and then to distilled water. Before the experiments, this conditioning cycle was repeated 3 times.

Instrumentals. Conventional *dc* polarograms and cathodic stripping voltammograms were recorded with a Yanaco P-8 type polarograph, cyclic voltammetry and differential pulse voltammetry were undertaken by the use of Potentiostat/Galvanostat Model 273 and 174A of EG&G PAR. The working electrodes were a carbon paste electrode containing icdc and a glassy carbon electrode (Yanaco GC-2 type, 3 mm diameter). The auxiliary electrode was a platinum wire. The reference electrodes were an aqueous saturated calomel electrode and a Ag/AgCl electrode (0.1 M LiCl in DMSO) in nonaqueous. All test solutions were thoroughly degassed with nitrogen gas and a continuous stream of nitrogen was passed over the solution while measurements were being taken. Test solutions were thermostated at $25 \pm 0.1^\circ\text{C}$.

Analytical procedure. Chemical deposition of silver ion was carried out in a 100 ml pyrex beaker containing about 50 ml test ion species (test solution). During deposition, the solution was stirred with a magnetic bar (about 600 rpm). For the voltammetric measurements, the CMEs were transferred to 0.1 M- KNO_3 solution (blank solution). The scan range was from +0.2 V to -0.7 V, the scanning rate was 60 mV/sec in optimum condition.

Results and Discussion

Electrochemical Behavior of Ligand and Metal Complex on Electrode Surface. Before its use for the analytical determination, the redox mechanism of acdc was studied by cyclic voltammetry in DMSO solution (0.1 M NaClO_4). A typical cyclic voltammogram of acdc ligand obtained exhibited three oxidation peaks at +0.11 V, +0.55 V and +0.88 V *vs.* Ag/AgCl is shown in Figure 1. The radical cations formed from the first oxidation step rapidly go to its dimer. The second peak indicates the 5-membered ring formation of dimer and third one represents an oxidation process of amine within ligand acdc as reported in acetone solution¹¹.

We also investigated the redox mechanism of dimer of acdc prepared with iodimetry by cyclic voltammetry. The dimer has two oxidation peaks at +0.55 V and +0.80 V *vs.* Ag/AgCl. It does not appear at +0.11 V (the first peak) since the dimer is a species after radical formation. This result also indicates that electrochemical behavior of acdc in DMSO is similar to one in acetone solution¹¹. These reaction steps and peak potentials are summarized in Table 1.

The acid form of acdc(icdc) was used to make carbon paste electrode, since the redox peaks of acdc did not appear at potential range between 0.0 V to -1.0 V *vs.* Ag/AgCl. Figure 2 shows the icdc modified electrode can be used as a working electrode to determine Ag(I). The working electrode was first immersed for 2 minutes in pH = 7 buffer solution spiked with 1×10^{-5} M Ag(I) solution and then it was rinsed thoroughly with water and transferred to a blank solution. Scanning range was from +0.40 V to -0.75 V *vs.* SCE. Only the cyclic voltammogram of (d) obtained using icdc-containing electrode exhibited one reduction peak and one oxidation peak at -0.42 V and +0.20 V *vs.* SCE, respectively. The height of these peaks gradually increases as the concentration of silver ion and the time of complexation increases.

As shown in Figure 3, during the first anodic scan, no ox-

Table 1. The Redox Potentials (*vs.* Ag/AgCl) of Acdc and Dimer on the Glassy Carbon Electrode in DMSO and Acetone

Reaction	DMSO		Acetone	
	Acdc E_{pa}	Dimer E_{pa}	Acdc E_{pa}	Dimer E_{pa}
$\text{NH}_2\text{C}_5\text{H}_6\text{CS}_2 \xrightleftharpoons[\text{-e}]{\text{+e}} \text{NH}_2\text{C}_5\text{H}_6\text{CS}_2^{\cdot+}$	+0.11V		+0.17V	
$2\text{NH}_2\text{C}_5\text{H}_6\text{CS}_2^{\cdot+} \longrightarrow (\text{NH}_2\text{C}_5\text{H}_6\text{CS}_2)_2$				
$(\text{NH}_2\text{C}_5\text{H}_6\text{CS}_2)_2 \xrightarrow{-2e} (\text{NH}_2\text{C}_5\text{H}_6)_2\text{C}_2\text{S}_3 + \text{S}$	+0.55V	+0.55V	+0.74V	+0.75V
$(\text{NH}_2\text{C}_5\text{H}_6)_2\text{C}_2\text{S}_3 \xrightarrow{-2e} (\text{NHC}_5\text{H}_6)_2\text{C}_2\text{S}_3 + 2\text{H}^+$	+0.80V	+0.80V	+0.98V	+1.03V

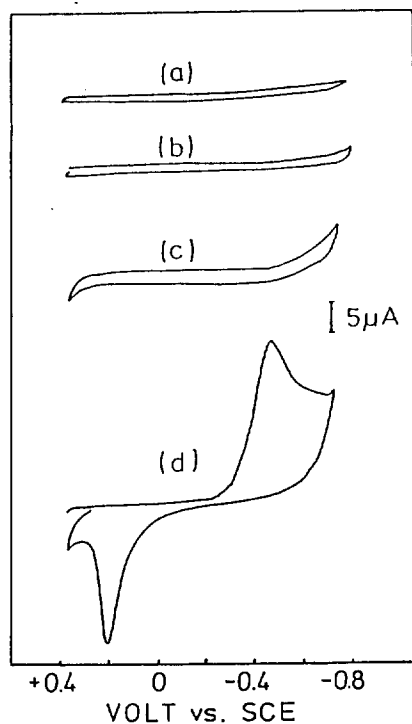


Figure 2. Cyclic voltammograms taken at a unmodified carbon paste electrode (a) in 0.1M KNO_3 aqueous solution (b) with 1 min immersion in $1 \times 10^{-5}\text{M}$ Ag(I) solution, (c) and (d) taken at a modified carbon paste electrode in same solution of (a) and (b).

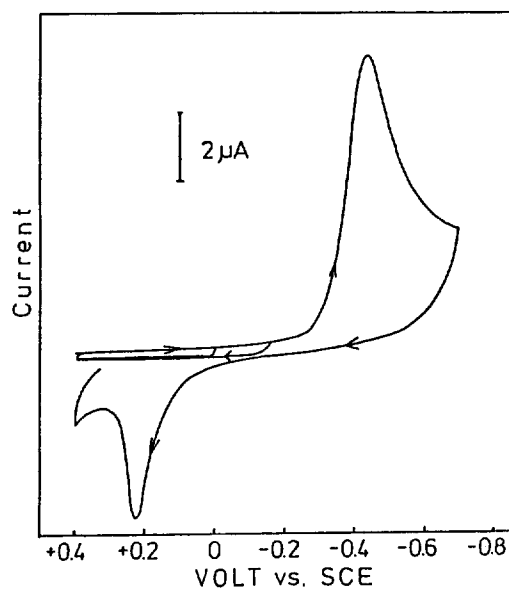


Figure 3. Cyclic voltammogram of $1 \times 10^{-5}\text{M}$ Ag(I) with modified carbon paste electrode in 0.1M KNO_3 aqueous solution.

oxidation peak appears. However after a cathodic scan up to negative potential an oxidation peak start to appears at +0.22 V. This says that the reduction peak at -0.42 V is related to silver ion included in the complex, and especially the oxidation peak at +0.22 V vs. SCE is arisen from the oxidation of free silver ion dissociated from the reduction of complex. Since, the oxidation peak only appears after the cathodic scan has passed to the position of -0.42 V vs. SCE. The similar behavior of silver ion had been reported for other

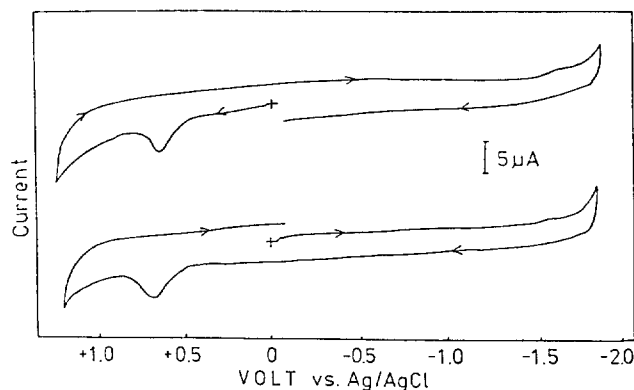


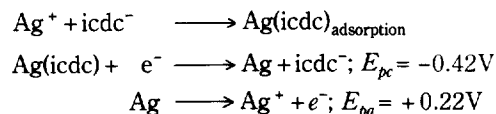
Figure 4. Cyclic voltammograms of $1 \times 10^{-3}\text{M}$ $\text{Ag(icdc)}/\text{DMSO}/0.1\text{M}$ NaClO_4 at a glassy carbon electrode.

silver complex¹². Therefore, silver-icdc complexation seems to occur at the electrode surface and the reduction peak at -0.42 V is due to reduction of complex; $\text{Ag(icdc)} + e^- \rightarrow \text{Ag} + \text{icdc}^-$. The variation of reduction potential was observed when different solvents were used.

Figure 4 shows a typical cyclic voltammogram of Ag(icdc) complex in DMSO solution at glassy carbon electrode. The Ag(icdc) complex exhibits one oxidation peak at +0.7 V vs. Ag/AgCl . In comparison with cyclic voltammogram of Figure 1, oxidation peaks of dithio group disappear and oxidation peak of amine are shifted. These results indicate that Ag(I) is strongly bonded to the dithio group of ligand icdc.

In addition, redox behaviors of pyrrolidine dithio carbamate(pdc) were investigated by cyclic voltammetry in DMSO. The pdc exhibits one oxidation peak at +0.24 V vs. Ag/AgCl . This oxidation peak of pdc has been reported to be arisen from the formation of radical species, followed by rapid dimerization¹³. This says that redox mechanism of pdc is quite similar to that of acdc. When carbon paste electrode containing pdc is used as a working electrode, the reduction peak of silver ion also appears at -0.42 V vs. SCE. This fact also supports that silver is bonded to dithio group.

The carbon paste electrode containing icdc is treated with Ag(I) in the solution to form Ag(icdc) complex on the surface of electrode, and then this electrode is transferred to blank solution for use. We suggest the following electrode surface reaction to take place;



The analytical condition for silver determination was tested by the use of cathodic stripping voltammetry. The CPEs prepared at various composition of icdc and graphite powder (10%–90%) were first immersed for two minutes in 0.1 M KNO_3 aqueous solution spiked with $1 \times 10^{-5}\text{M}$ Ag ion, then rinsed thoroughly with distilled water, and transferred to similar blank solution, before performing cathodic stripping voltammetry (Figure 5). In all cases, silver ion responses could be obtained. Before preparation of the CPEs, oxygen must be completely removed from the graphite powder because the reduction peak of oxygen molecule appears around -0.6 V vs. SCE, which overlapped onto the analytical peaks of Ag(I) ion if the peak of -0.42 V is used.

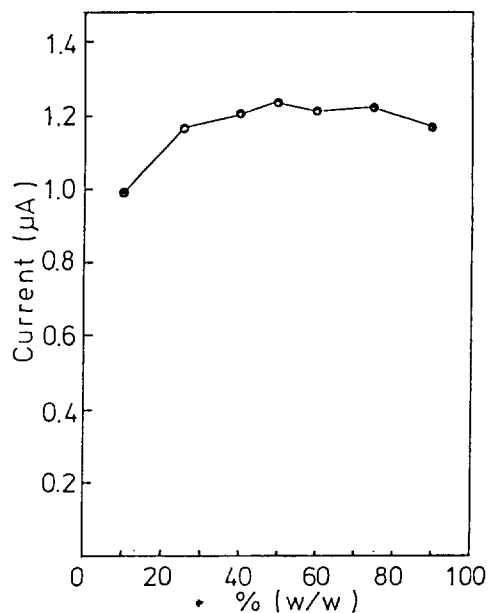


Figure 5. Effect of peak height vs. electrode composition (icdc/carbon) w/w%.

Table 2. The Peak Current and Peak Potential of Ag with Carbon Paste Electrode According to the Change of pH

pH	E_{pc} (volt vs. SCE)	I_{pc} (μ A)
3.4	-0.38	0.302
5.0	-0.40	0.615
6.0	-0.42	1.205
7.0	-0.42	2.601
8.25	-0.44	2.500
9.0	-	-

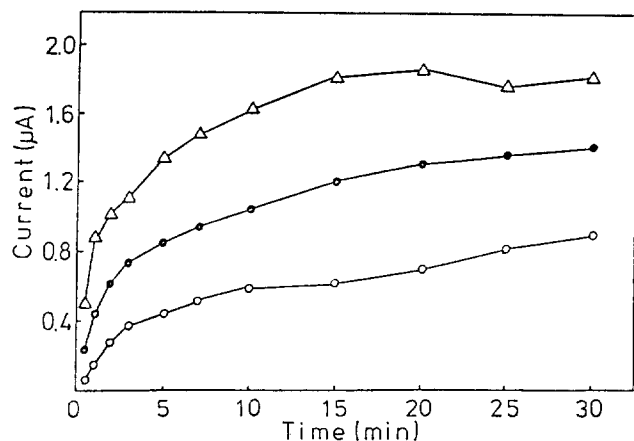


Figure 6. Effect of peak height vs. deposition time of Ag at different bulk concentrations (1×10^{-6} M(○), 5×10^{-6} M(●), 1×10^{-5} M(Δ)).

When the electrode of 90% graphite composition was used, the redox peak was not reproducible presumably due to the high resistance of CMEs. The remaining electrodes exhibited well-behaved peaks. However, the height of peak currents increased as the icdc percentage employed in this case increase until the graphite composition is 50%. Thus

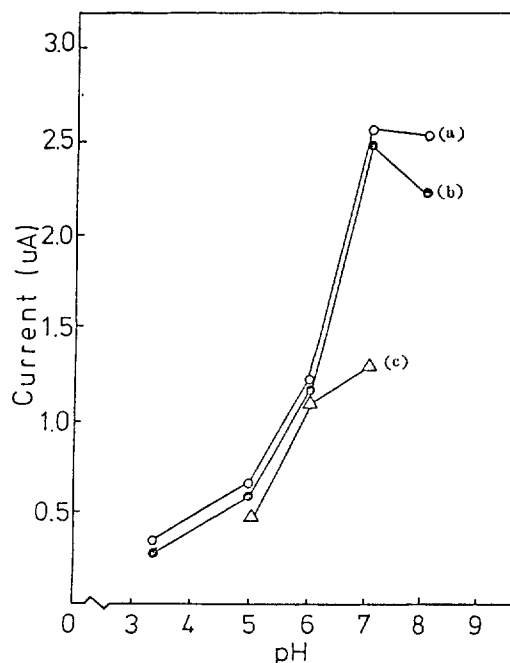


Figure 7. Interference of all other metals for pH. (a) 1×10^{-4} M Ag(I) only, (b) 1×10^{-4} M Ag(I) + 1×10^{-4} M all other metals (Mn^{2+} , Ni^{2+} , Cd^{2+} , VO^{2+} , Cu^{2+} , Co^{2+} , Pb^{2+} and Cr^{3+}). (c) 1×10^{-4} M Ag(I) + 1×10^{-4} M Hg^{2+} .

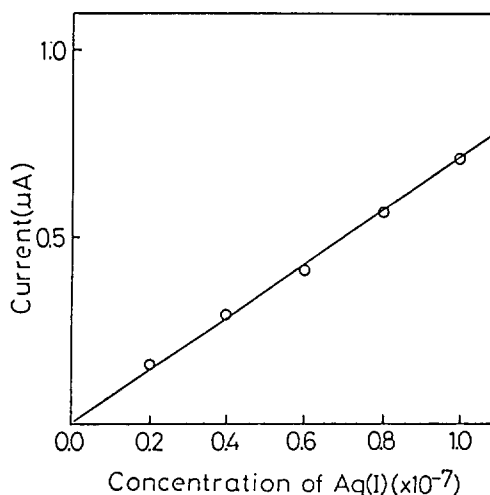


Figure 8. A calibration curve for the determination of Ag(I) with CMEs using differential pulse method.

50% icdc electrode were used in all subsequent works. The reduction peaks of Ag(icdc) were obtained with the CPEs immersed in buffer solutions (0.2 M acetate and NH_4NO_3/NH_4OH) of pH = 3.4, 5.0, 6.0, 7.0, 8.2 and 9.0 (Table 2). In the range of pH = 3.4–8.2, chemical deposition occurs under identical condition. In the pH = 7–8, the signal amplitudes obtained were rather insensitive to the variation of pH. Therefore, in all subsequent works, a pH condition of 7.0–8.0 were employed.

The effect of deposition time on the peak height in the bulk concentrations was studied (Figure 6). In 1×10^{-6} M and 5×10^{-6} M Ag(I) solution, the height of reduction peak gradually increased as the time of deposition increased. If the concentration of Ag(I) solution was 1×10^{-5} M and deposition

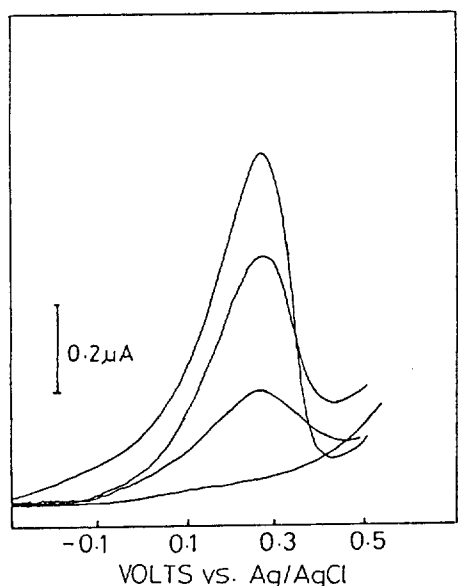


Figure 9. Differential pulse voltammograms obtained with the CMEs. Deposition was carried out by a 20 minutes immersion in (a) 0.4×10^{-7} M, (b) 0.8×10^{-7} M, (c) 1.2×10^{-7} M Ag(I) solution.

time was greater than 20 minutes, the peak height decrease due to the saturation of active site of electrode surface. The height of reduction and oxidation peaks also increased as the scan rate increased. All works were done at 60 mV/sec scan rate to obtain better defined peaks.

Using differential pulse voltammetry, we have obtained a calibration curve as shown in Figure 8 at a icdc modified electrode from solution containing 2×10^{-8} M– 1×10^{-7} M Ag(I) concentrations. Figure 9 shows the differential pulse voltammograms taken at different Ag(I) ion concentrations. The oxidation peak of Ag(I), +0.22 V vs. Ag/AgCl, was used for the calibration curve since this peak was more sensitive to the concentration of Ag(I) solution in differential pulse voltammetry. There was a good linearity between Ag(I) ion concentration and peak height with 12.4% relative deviation. The detection limit was 1×10^{-9} M.

Linear sweep voltammetry also performed at the same optimum condition. In this case, the linearity up to 1×10^{-6} M with 5.2% relative deviation. The detection limit was found to be 1×10^{-7} M with 20 minutes deposition time.

Advantage of this study lies in the added dimension of the selectivity, which is provided by the chemical requirements

of the modifier-analyte interaction. Thus, interference due to simple overlap of stripping peaks or to the involvement of silver ion in intermetallic compound formation are likely to occur in buffers (acetate/ NH_4OH - NH_4NO_3). The deposition time selected was 20 minutes and scanning rate was 60 mV/sec.

Other metallic species tested were Mn(II), Ni(II), Cd(II), VO(II), Cu(II), Co(II), Pb(II), Hg(II) and Cr(III) ions of 1×10^{-4} M (Figure 7). At pH = 7.0, the other metal ions except Hg(II), did not influence the silver response. At the pH > 8.0, the peak height of the silver ion decreased due to the complexation of Ni(II) or Cu(II) (Figure 7-b). However, at pH = 5.0–6.0 region, Hg(II) did not influence the silver response (Figure 7-c).

Acknowledgement. This work was financially supported by 1986 Grant for Korean Science and Engineering Foundation.

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