A Glassy Carbon Electrode Modified with *N*-(2-Hydroxybenzyl)chitosan for Voltammetric Determinations of Cu^{2+} and Pb^{2+}

Yoshiaki KURAUCHI, Eiichi TSURUMORI, and Kazuya OHGA*
Department of Environmental Chemistry and Engineering, Faculty of Engineering,
Oita University, Dannoharu, Oita 870-11
(Received November 24, 1988)

Synopsis. A glassy carbon electrode was chemically modified with *N*-(2-hydroxybenzyl)chitosan which could act as an agent to preconcentrate Cu^{2+} and Pb^{2+}. The modified electrode was stable for 30 d and its calibration curves for the voltammetric determination of these ions are linear in the concentration range of $(1—10)\times10^{-7}$ mol dm^{-3}. The usage limitation of this electrode has also been discussed.

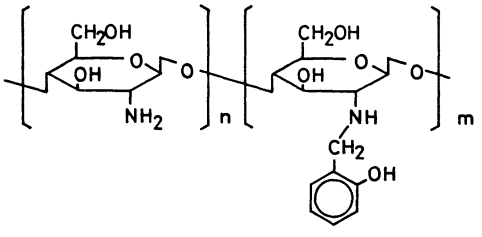
High metal-chelating ability is one of the most attractive functions of chitosan which is obtained by deacetylation of chitin, a naturally occurring polysaccharide.[1] The chelating ability arises primarily from the amino group of the 2-amino-2-deoxy-D-glucose (glucosamine) unit and is enhanced by chemical modification of the amino group. For example, the capacity of *N*-(2-hydroxybenzyl)chitosan (HBC) to adsorb Cu^{2+} is 47 times as much as that of chitosan itself.[2]

Recently much attention has been drawn to the voltammetric determination of metal ions using electrodes modified with preconcentrating agents or media. The agents frequently used to preconcentrate transition metal ions are chelating compounds, including 2,9-dimethyl-1,10-phenanthroline[3] and cross-linked polystyrene with bis(carboxymethyl)amino groups.[4] Chitosan and its derivatives with high chelating abilities are therefore anticipated to act as efficient agents for transition metal ions. In this research, we prepared a glassy carbon (GC) electrode modified with HBC and examined its applicability to the determination of trace amounts of Cu^{2+} and Pb^{2+}.

Experimental

Reagents. Chitosan (100% deacetylation) was kindly donated by Katokichi Co., Kagawa, Japan. Commercial salicylaldehyde and dicyclohexylcarbodiimide (DCC) were distilled under reduced pressure just before use. Water was purified by reverse osmosis (Millipore Milli RO15) and deionization. All other chemicals were of reagent grade or better and used without further purification.

Modification of a GC Electrode. *N*-Salicylidenechitosan was formed from chitosan and salicylaldehyde[5] and reduced with $NaBH_3CN$ to give a HBC gel.[2] The molar quantity of salicylaldehyde used was half that of the glucosamine unit. A GC electrode (Tokai Carbon GC-30S, 6 mm diameter) covered with a Teflon tube was polished with alumina (FUJIMI FM-No. 4, 0.5 μm) and then oxidized with H_2SO_4 according to the procedure reported by Wingard and Gurecka.[6] After being washed with water and dried at 120 °C for 2 h, the oxidized surface was coated with 20 mm^3 of 2% aqueous acetic acid–methanol (7:3) containing 0.08 mg of HBC and was dried again at room temperature for 5 h and further at 120 °C for 12 h. The dried electrode having a thin HBC film was immersed in 20 cm^3 of DMF–acetonitrile (1 : 1) containing 2 g of DCC for 5 h at room temperature. The HBC-modified electrode (HME) thus obtained was washed successively with DMF, 2% aqueous acetic acid, and water and was stored in 0.05 M (1 M=1 mol dm^{-3}) aqueous KNO_3.



HBC

Cyclic Voltammetry. After being soaked in 0.05 M aqueous KNO_3 containing a metal ion to be analyzed for a prescribed period, the HME was rinsed briefly with water and then subjected to a cyclic voltammetry in 0.05 M KNO_3 which had previously been deaerated with N_2 and thermostated at (25.0±0.5) °C. The cyclic voltammetry was carried out with a Hokuto Denko HB 104 function generator, a Hokuto Denko HA 301 potentiostat, and a Yokogawa 3086 X-Y recorder. The HME was used as a working electrode, and reference and counter electrodes were Ag/AgCl and Pt, respectively.

Results and Discussion

The IR spectrum of HBC showed no absorption band at 1640 cm^{-1} which is assigned to the C=N stretching vibration of *N*-salicylidenechitosan, while the band assigned to the aromatic C-H bending vibration (760 cm^{-1}) still remained. These suggest that the reduction reaction took place sufficiently. The presence of the remaining amino groups was confirmed by observation of a band at 1600 cm^{-1}. The treatment with DCC during the modification of the GC electrode with HBC was carried out with the intention of forming amide bonds from the amino groups and the carboxylato groups on the oxidized electrode surface (Fig. 1), and resulted in formation of a thin HBC film adhering firmly to the electrode surface.

Figure 2 shows typical cyclic voltammograms

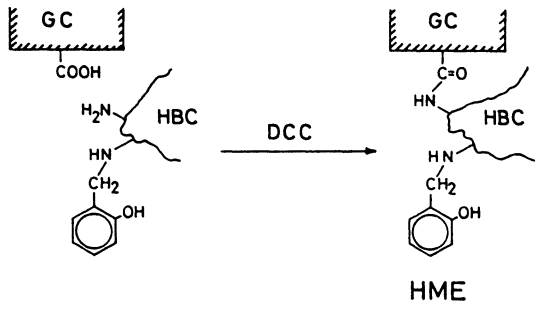


Fig. 1. Modification of a GC electrode with HBC.

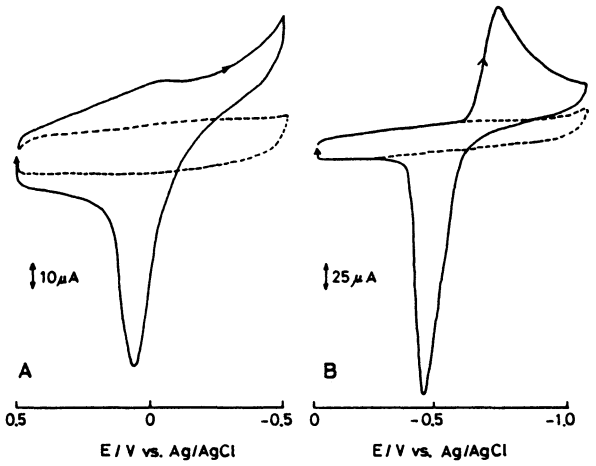


Fig. 2. Cyclic voltammetric *I–E* curves after soaking in 1.0×10^{-5} M Cu^{2+} (A) and 1.0×10^{-5} M Pb^{2+} (B) solutions: scan rate, 100 $mV\,s^{-1}$; soaking time, 60 min; electrolyte, 0.05 M KNO_3. Dashed lines represent the curves before soaking.

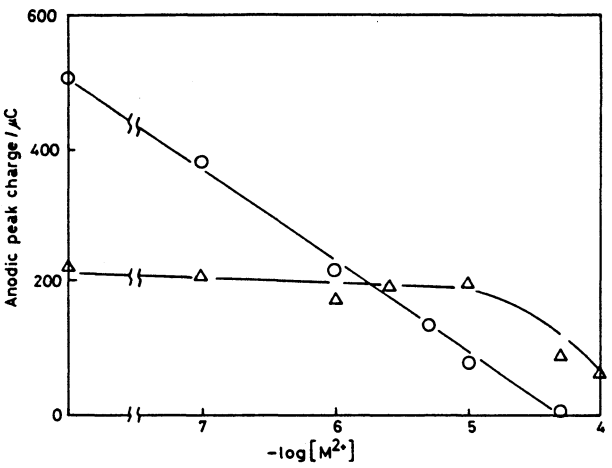


Fig. 3. Anodic-peak-charge changes for 1.0×10^{-5} M Pb^{2+} by the addition of Cu^{2+} (○) and for 1.0×10^{-5} M Cu^{2+} by the addition of Pb^{2+} (△). The left edge of the abscissa implies the absence of the coexisting divalent cation. Other conditions are as in Fig. 2.

obtained with the modified electrode HME which was soaked in 1.0×10^{-5} M Cu^{2+} and Pb^{2+} solutions for 60 min. Large anodic waves were observed at +0.04 V for Cu^{2+} and −0.45 V for Pb^{2+}. The anodic peak charge of Pb^{2+} (273 μC) calculated from the peak area is about twice as large as that of Cu^{2+} (132 μC). At lower metal-ion concentrations, 10^{-7} M, the uptake was slower and hence a longer soaking time was required to obtain such well-defined anodic peaks. The accumulated Cu^{2+} and Pb^{2+} were completely removed by dipping in 0.1 M EDTA for 10 min.

The anodic peak charge of the 1.0×10^{-5} M Pb^{2+} sample was reproducible to ±4% for 10 accumulation/measurement/renewal cycles. The ability of the HME to accumulate Cu^{2+} or Pb^{2+} lowered only slightly with repeated runs. The peak charge of 1.0×10^{-5} M Pb^{2+} was 90% of its initial value even after the cycle was repeated about 100 times for 30 d. In addition, the calibration curves of peak charge vs. concentration for Cu^{2+} and Pb^{2+} were both linear in the concentration range of $(1—10)\times10^{-7}$ M (soaking time, 120 min; correlation coefficient, 0.990 for Cu^{2+} and 0.999 for Pb^{2+}). These results suggest that the HME is available for the voltammetric determination of trace amounts of Cu^{2+} and Pb^{2+}.

On the other hand, when no DCC treatment was applied, the HBC film peeled off after three cycles and the accumulation ability disappeared nearly completely. Further, when chitosan itself was used in place of HBC, the electrode obtained showed a Pb^{2+} peak charge only one fifth of that of the HME, though having a stable film.

In the case of the other metal ions, Cd^{2+}, UO_2^{2+}, Co^{2+}, and Ni^{2+}, no redox waves were observed when the HME was soaked for 60 min in a 1.0×10^{-5} M solution of each metal ion. The selectivity of the HME toward Cu^{2+} agrees with the fact that HBC has a high ability to adsorb Cu^{2+},[2] though the reason why the peak charge of Pb^{2+} is larger than that of Cu^{2+} is not yet clear.

As shown in Fig. 3, the anodic peak charge of Pb^{2+} ($[Pb^{2+}]=1.0\times10^{-5}$) was reduced enormously by the presence of Cu^{2+} and to nearly zero when the Cu^{2+} concentration increased up to 5×10^{-5} M. The peak charge of Cu^{2+}, in contrast, was not so much affected by the addition of Pb^{2+} of concentrations below 1×10^{-5} M ($<[Pb^{2+}]/[Cu^{2+}]=1$). Such a more significant reduction of the Pb^{2+} peak charge may be explained in terms of the weaker coordination ability of hydroxyl and amino groups to Pb^{2+} than to Cu^{2+}.[7] Thus, in the Pb^{2+} determination, it is necessary to previously remove other metal cations which can strongly form complexes with HBC, if present.

References

1) R. A. A. Muzzarelli and O. Tubertini, *Talanta*, **16**, 1571 (1969).
2) L. D. Hall and M. Yalpani, *Carbohydr. Res.*, **83**, C5 (1980).
3) S. V. Prabhu and R. P. Baldwin, *Anal. Chem.*, **59**, 1074 (1987).
4) N. Egashira, M. Kudo, and F. Hori, *Chem. Lett.*, **1986**, 1045.
5) S. Hirano, N. Matsuda, O. Miura, and H. Iwaki, *Carbohydr. Res.*, **71**, 339 (1979).
6) L. B. Wingard, Jr. and J. L. Gurecka, Jr., *J. Mol. Catal.*, **9**, 209 (1980).
7) D. Hopgood and D. L. Leussing, *J. Am. Chem. Soc.*, **91**, 3740 (1969).