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Electrochemical Preparation of a Chelating Polymer-modified Electrode for Selective Incorporation of Ag(I)

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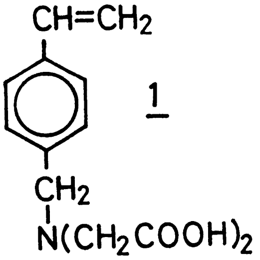
The electrode modified with styrene-divinylbenzene copolymer containing -$N(CH_2CO_2H)_2$ has been prepared electrochemically on a glassy carbon rod, and applied to the selective incorporation of Ag(I) from aqueous solutions.

Recently many polymer-modified electrodes with anionic or cationic domain have been prepared and examined for the incorporation of counter ions into the polymer films.1) Some reports2) have dealt with their applicabilities to analytical chemistry by use of the condensation effect of ion species into the polymer films. However the selective incorporations of ion species can not be expected in principle so long as the incorporations are attributed simply to ion exchange. Karayama et al.3) reported the incorporation of Ag(I) into a chemically modified electrode containing some chelating compounds. Such an electrode suffers two defects; low stability of the electrode and low coverage of the functional group on the electrode. In order to overcome these disadvantages, the polymer-modified electrode which has a chelate effect must be used. We therefore prepared a chelating polymer-modified electrode by electrochemical means and examined applicabilities of the electrode to the trace analysis of Ag(I).



The polymer thin film was prepared on a glassy carbon rod (disc diameter: 6 mm) by the electrochemically reductive copolymerization of 1 4) and divinylbenzene at the controlled potential of -2.66 V vs. SCE.5) The electrolyte solution contained 1×10^{-3} M (M = mol dm^{-3}) 1, 1×10^{-4} M divinylbenzene, and 0.1 M tetra-n-butylammonium perchlorate (TBAP) in dimethylformamide (DMF). The charge passed during the electrolysis was always 4.2 C, resulting in deposition of the film with a constant thickness.6) After being soaked into 1×10^{-2} M KOH solution for 30 min, the electrode was washed with water and immersed into 1×10^{-4} M $AgNO_3$ solution for an hour to incorporate Ag(I).7) The electrode was washed with water and then subjected to cyclic voltammetry in 0.1 M KNO_3 solution. The obtained voltammograms are shown in Fig. 1. The anodic peak area in the first scan was larger than that of the bare glassy carbon electrode by a factor of about 30, and was found to be linear with the bulk concentration of Ag(I) in the range from 10^{-7} to 10^{-6} M. The sensitivity of the electrode is superior to that of an ion-selective electrode which is commercially available.

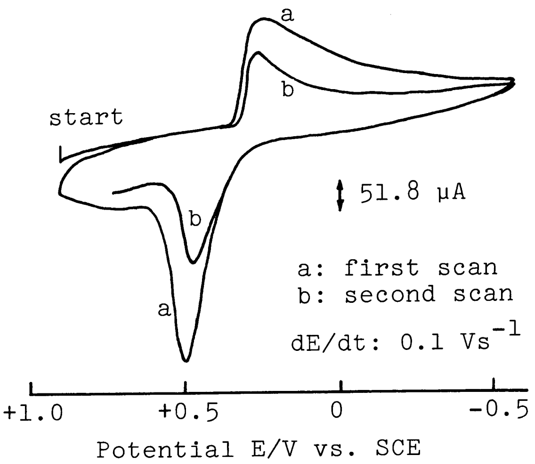


Fig. 1. Cyclic voltammogram of Ag(I) in 0.1 M KNO_3 aqueous solution.

Table 1. Incorporation of metal ions into the polymer-modified electrode

Metal ions$^{a)}$	Quantity of incorporation/μC$^{b)}$
Ag(I)	305
Pb(Ⅱ)	108
Cu(Ⅱ)	118
Mn(Ⅱ)	27
Cd(Ⅱ), Zn(Ⅱ), Ni(Ⅱ) Cr(Ⅲ), Eu(Ⅲ), Fe(Ⅲ)	none

a) The concentration of the metal ions was 10^{-4} M.

b) The values were determined from the anodic peak area of cyclic voltammogram obtained in the first scan.

A series of metal ions (1 x 10^{-4} M) were incorporated as represented in Table 1. The order of the incorporation was different from that of the commercial chelating resins which have the same structure as the film of the electrode.$^{8)}$ The electrode was found to be selective toward Ag(I) since even Pb(Ⅱ) and Cu(Ⅱ) were incorporated less than Ag(I) by the factor of 1/3 and the other metal ions except for Mn(Ⅱ) were not incorpotated. This electrode therefore can be applied to a trace analysis of Ag(I). However the incorporation of Ag(I) decreased with the addition of an alkaline metal ion (AM^+); the incorporation in the 1 x 10^{-4} M Ag(I) solution containing 5 x 10^{-3} M AM^+ decreased to 1/2 of that in the absence of AM^+. Attention should be given to the presence of AM^+. The repetition of the potential sweep caused a gradual suppression of voltammetric waves and the waves disappeared after 30 min-sweeps. This result indicates that Ag(I) was completely leached out from the film to allow repeated use as the ion-selective electrode.

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4) 1 was synthesized in the way reported by L. W. Morris et al.$^{9)}$
5) The potential was determined from the cathodic peak potentials for 1 and divinylbenzene, -2.66 and -2.64 V vs. SCE.
6) The film thickness was estimated to be of ca. 1 x 10^4 layers from the charge of 4.2 C. The details for the structure and composition of the film are now under investigation.
7) The quantity of the incorporation became constant in an hour.
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