SHORT COMMUNICATIONS

*Chronopotentiometry at Varying Current Density with the Use of Current Controlled Dropping Mercury Electrode**

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The authors have previously introduced a new method for obtaining the polarogram at the dropping mercury electrode with controlled current[1], whose phenomena were mathematically revised by Senda et al.[2] In connection with this study, potential-time curves have been investigated and many interesting phenomena were observed with several electrode reactions. From the stand point of analytical chemistry, it is expected that, with proper control of current, the wave of a more cathodically reducible substance is recorded alone on the chronopotentiogram (potential-time curve), independently, in the presence of large quantities of less cathodically reducible substances. For instance, with a solution of cadmium in hydrochloric acid, a very negative potential corresponding to that of hydrogen deposition is expected at the beginning of the drop growth and then it moves to a positive potential of the cadmium ion—cadmium amalgam system with the decrease in current density due to the increase in surface area, so that a chronopotentiogram of inversed shape to that in the ordinary chronopotentiometry is recorded even in the presence of less cathodically reducible substances e.g. the lead ions. Apparently this characteristic is more effective than any other voltammetric methods hitherto used in trace analysis. Therefore a preliminary report is presented here.

The chronopotentiogram was recorded by the x-y recorder made by Shimadzu Mfg. Co. (Pen speed: 0.8 sec./25 cm.,

1) M. Ishibashi and T. Fujinaga, *J. Electrochem. Soc. Japan (Denki-kagaku)*, **24**, 375, 525 (1956); *Anal. Chim. Acta*, **18**, 112 (1958).

2) M. Senda, T. Kambara and Y. Takemori, *J. Phys. Chem.*, **61**, 965 (1957).

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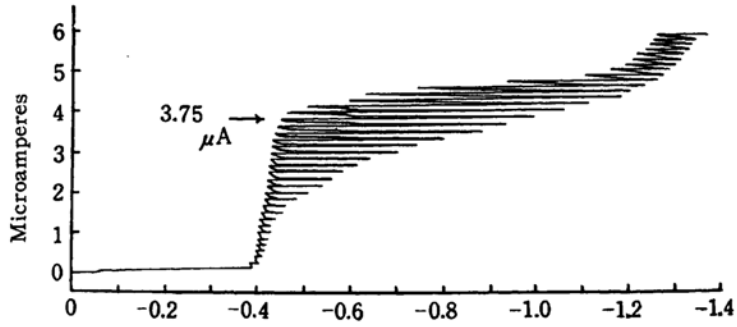

Fig. 1. Current scanning polarogram.
(4×10^{-5}M-Cd^{2+}, 1×10^{-3}M-Pb^{2+}, 0.01%-Polyacrylamide and 0.1 N-HCl)

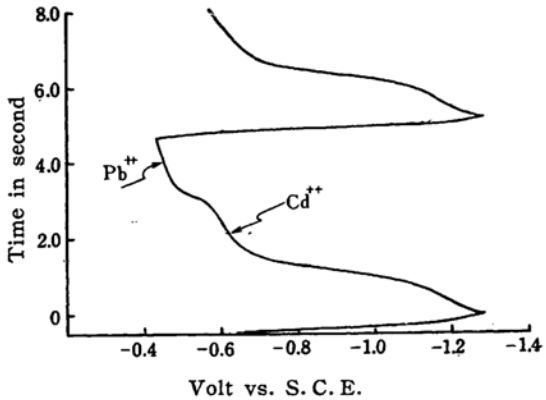

Fig. 2. Chronopotentiogram.
(Solution: same as Fig. 1, t=5.26 sec. at i=3.75 μA)

maximum sensitivity: 10 mV./25 cm. and maximum chart speed: 2.0 sec./35 cm.), to which were attached a pre-amplifier of increasing the input impedance for the x-axis and a voltage scanner of changeable velocity for the y-axis. The controlled current was supplied from a DC source composed of a high voltage and a high resistance used in a previous paper[1].

Fig. 1 shows a current scanning polarogram of cadmium ions in the presence of 25 times as many lead ions. Fig. 2 is the corresponding chronopotentiogram for cadmium wave at the current of 3.75 microamperes.

Besides the use of the ordinary dropping mercury electrode for the change of current density, combination of the dropping mercury electrode with extremely slow drop rate (ca. 60 sec./drop) and the potentiometer-recorder for ordinary chronopotentiometry was investigated. Also an ordinary chronopotentiometry with stationary electrode but with decreasing current scan was studied. These methods show a similar effect to that of the present method described above. Therefore these three methods, all employing varying current density, would give potential values for analytical instrumentation. The detailed discussion will be presented later.

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