Polarography with a dropping carbon electrode

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Abstract

Fluid carbon electrodes for polarography were studied. A mixture of dioctyl phthalate and diiodomethane was found to be suitable to prepare a dropping carbon electrode. With this dropping electrode, anodic polarography of ferrocenecarboxylate in aqueous solution was performed at room temperature.

Key words: Polarography; Liquid electrodes; Dropping electrodes; Carbon paste electrodes

1. Introduction

Polarography at dropping mercury electrodes possesses several advantages over voltammetry at stationary solid electrodes. One of them is its good reproducibility derived from the automatically renewable smooth electrode surface. Mercury has been the only liquid electrode material available for polarography, but nowadays its use is very restricted because of its toxicity.

Many attempts have been made to find a less toxic alternative to mercury electrodes. Giguère and Lamontagne [1], and Escue et al. [2] showed polarography with dropping gallium electrodes, but they encountered many difficulties in the experiments, because gallium was too reactive. Stehle et al. performed polarography in molten potassium chloride with liquid silver and gold-bismuth alloy electrodes at high temperature (~1000 °C) [3]. Recently, Surmann and Heyat employed galinstan (eutectic alloy of gallium, indium, and tin; m.p. −19 °C) for a liquid electrode at room temperature [4]. They showed that the galinstan electrode was applicable to differential-pulse anodic stripping voltammetry of lead and cadmium ions. A few papers have also appeared on liquid electrodes with other gallium alloys [5,6], although polarographic or voltammetric measurements have not been reported.

In 1958, Adams presented the first voltammetric results of carbon paste electrodes in the famous literature entitled “Carbon Paste Electrodes” [7]. In the last paragraph of the text, he described that using more fluid carbon-bromoform pastes, a dropping carbon electrode was devised. Although many reports have been published on carbon paste electrodes from his group since then [8,9], no report seems to have appeared on polarography with fluid carbon paste. Also, we could not find any paper dealing with a fluid carbon electrode from other groups.

In the present study, we revisited this topic. Fluid carbon pastes with different organic liquids were examined in order to obtain a dropping electrode for polarography. Using an electrode prepared from graphite powder and a mixture of dioctyl phthalate and diiodomethane, we performed anodic polarography of ferrocenecarboxylate in aqueous solution at room temperature.

2. Experimental

Graphite powder (TGP-7, average diameter of 7 μm) was kindly donated by Tokai Carbon Co. Ltd. (Tokyo, Japan) and used as received. Dioctyl phthalate (DOP), *n*-dodecane, and bromoform from Nacalai, diiodomethane from Tokyo Chemical Industry, liquid paraffin from Wako, and low-viscosity liquid paraffin (PARLEAM 4) from NOF were used without further purification. Ferrocenecarboxylic acid from Wako was mixed with equimolar amount of sodium hydroxide and used as a sodium salt of ferrocenecarboxylate ($\mathrm{FcCOO^-}$).

Fluid carbon pastes were prepared by mixing the graphite powder (typically 15 g) and the organic liquid (typically 35 mL) in a mortar. The amount of the liquid was varied according to its viscosity. A T-shaped tube (tip diameter 2.0 mm) and a Pasteur pipet (tip diameter 1.0 mm) were filled with the carbon paste and used as stationary and dropping carbon electrodes, respectively. The electric contact was made by a copper wire. Their schematic illustrations are shown in Fig. 1.

Cyclic voltammetry and polarography of $\mathrm{FcCOO^-}$ were carried out in a 0.1 M KCl solution saturated with air. A platinum coil and an Ag/AgCl (0.1 M KCl) electrode were used as the counter and reference electrodes, respectively. In this report, all potentials are referred to the Ag/AgCl (0.1 M KCl) electrode. Voltammograms and polarograms were recorded with a potentiostat (HA-1010mM1A, Hokuto Denko) without using a positive feedback circuit for *IR* compensation. All of the experiments were performed at room temperature.

Results and Discussion

In preliminary experiments, we examined six different organic liquids ($CHBr_3$, CH_2I_2, n-$C_{12}H_{26}$, liquid paraffin, low-viscosity liquid paraffin, and DOP) as binders for graphite powder. The fluid carbon pastes prepared from all these liquids gave voltammetric signals of $FcCOO^-$ when they were used as stationary electrodes. However, the graphite powder gradually sedimented in the fluid carbon pastes with $CHBr_3$, CH_2I_2, and n-$C_{12}H_{26}$, and thus their voltammetric results were not reproducible. Liquid paraffin and low-viscosity liquid paraffin provided more stable fluid carbon pastes, but the sedimentation of graphite powder started to appear in several hours. Among these six liquids, only DOP provided a well-mixed fluid carbon paste, which was stable for at least 2 days.

Figure 2 shows the cyclic voltammograms of $FcCOO^-$ at the stationary carbon electrode (graphite powder 12 g + DOP 28 mL). Well-defined anodic and cathodic waves were observed within the potential window. The reactions which determined the positive and negative limits of the potential window were presumably the oxidation of water and the reduction of dissolved oxygen, respectively. As the scan rate (v) was increased, the anodic and cathodic peak potentials shifted slightly to more positive and negative potentials, respectively, which may be partly due to a resistance of the fluid carbon paste itself. The potential peak separation was 60 mV, when *v* was extrapolated to zero. The mid-point potential remained constant independently of *v* and the concentration of $FcCOO^-$ ($[FcCOO^-]$), and was determined to be 231 mV. The anodic peak current was proportional to the square root of *v* between 5 and 200 mV s^{-1} at $[FcCOO^-] = 0.3$ mM, and also to $[FcCOO^-]$ between 0.1 and 0.5 mM at $v = 50$ mV s^{-1}. Therefore, the anodic and cathodic waves in Fig. 2 can be assigned to the reversible 1-electron oxidation and reduction of $FcCOO^-$.

When the fluid carbon paste (graphite powder 12 g + DOP 28 mL) was squeezed out from the tip of the Pasteur pipet, a string of the carbon paste flowed down into water (Fig. 3). This was probably due to the low density and surface tension of DOP. We tried to cut the string periodically, but all of the attempts were unsuccessful, because the paste was sticky. We also tried to prepare a streaming electrode with this, but it was difficult to obtain a fixed length, or surface area, of the string. In order to prepare a dropping electrode, it was necessary to increase the density and the surface tension of the liquid. For this purpose, we adopted CH_2I_2. When DOP was replaced by a mixture of DOP and CH_2I_2 (1:1 in volume ratio), periodic drops of the carbon paste were successfully obtained (Fig. 4). The shape of the drop was cylindrical, and its length was about 1.2 cm. The drop time could be controlled by changing the position of the reservoir. The shortest drop time of the present device was about 2 s.

Figure 5 shows the polarograms of $FcCOO^-$ at the dropping carbon electrode (graphite powder 21 g + 1:1 DOP-CH_2I_2 49 mL). The potential was linearly scanned from –450 to 1000 mV at $v = 2$ mV s^{-1}. The drop time during this experiment was about

2 s, which means about 360 drops fell for each polarogram. In the absence of FcCOO$^-$ (curve a), a potential window similar to that of the stationary electrode was observed in the range from −450 to 850 mV (±1 μA). When 0.1 mM FcCOO$^-$ was added into the 0.1 M KCl solution, an anodic wave appeared from about 200 mV (curve b), which was comparable to the cyclic voltammograms at the stationary electrode in Fig. 2. The wave became greater on the further addition of FcCOO$^-$ (curve c). These results indicate that the polarographic waves observed here are attributable to the oxidation of FcCOO$^-$. The inset of Fig. 5 shows the expanded polarogram (curve b) at about 420 mV. The current increase for each drop was more linear due to the cylindrical growth of the drop, as compared with the $t^{1/6}$-curved increase at a dropping mercury electrode with spherical growth. Unfortunately, the limiting currents in these polarograms were not clear, probably because the drop size could not be regulated strictly. To study the Ilkovič coefficients for this method, our device has to be improved. We are now constructing a new electrode holder using a Teflon opening. In addition, the potential distribution on the surface of the electrode may affect the shape of the polarogram, if the resistance of the carbon paste is significantly high. A study of the resistivity will also be presented in a subsequent paper. If these problems are solved, polarography at dropping carbon electrodes can be a complementary method to conventional polarography at dropping mercury electrodes, since carbon electrodes have wide potential windows to more positive potentials, which cannot be reached by mercury electrodes.

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Figure Captions

Fig. 1 Schematic illustrations of (A) stationary and (B) dropping carbon electrodes.

Fig. 2 Cyclic voltammograms of 0.3 mM $FcCOO^{-}$ at the stationary carbon electrode (graphite powder 12 g + DOP 28 mL) at v = (a) 20, (b) 50, and (c) 100 mV s^{-1}.

Fig. 3 Pictures of the fluid carbon paste (graphite powder 12 g + DOP 28 mL) squeezed out into water (from left to right).

Fig. 4 Pictures of the fluid carbon paste (graphite powder 21 g + 1:1 DOP-CH_2I_2 49 mL) squeezed out into water (from left to right).

Fig. 5 Polarograms of $FcCOO^{-}$ at the dropping carbon electrode (graphite powder 21 g + 1:1 DOP-CH_2I_2 49 mL) with (a) 0, (b) 0.1, and (c) 0.2 mM $FcCOO^{-}$. Scan rate: 2 mV s^{-1}. Inset is the expansion of curve b at about 420 mV. The sampling interval was 0.5 s.

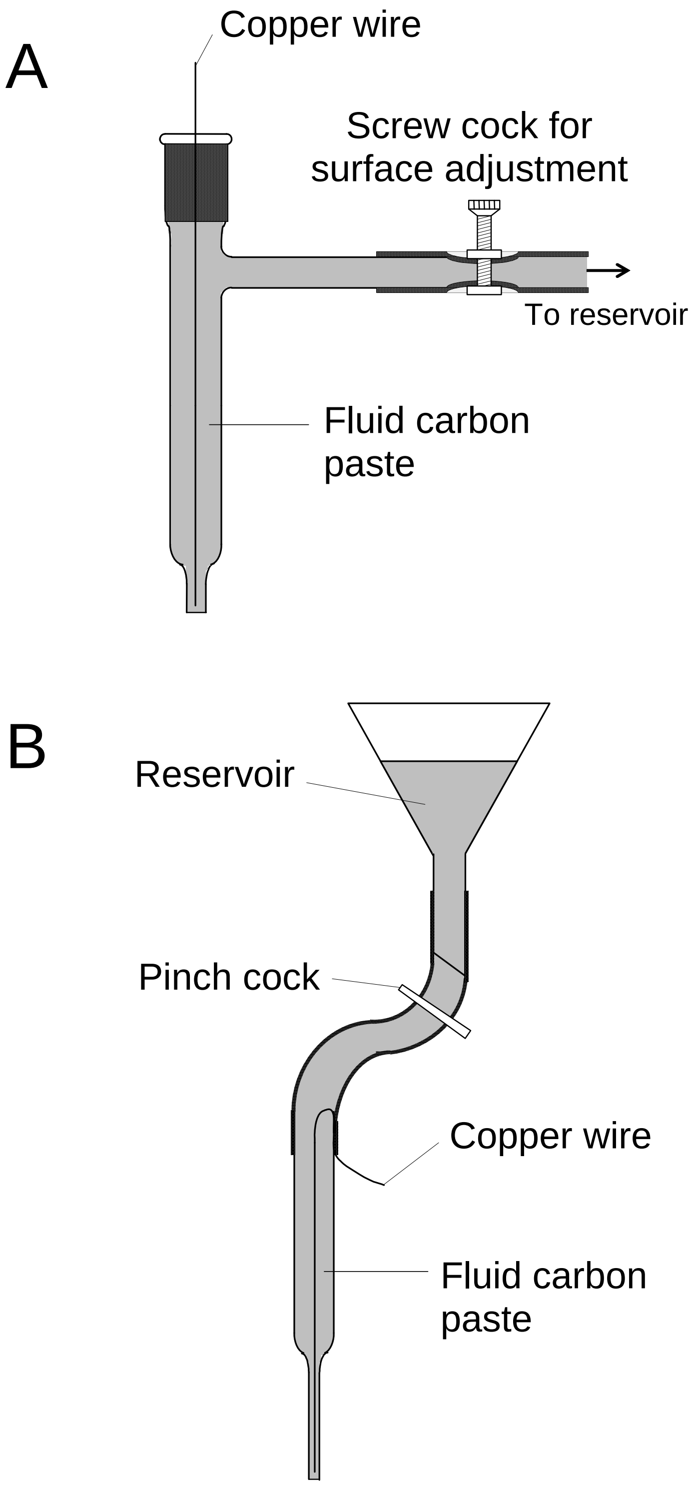

Fig. 1. Tatsumi & Shiba

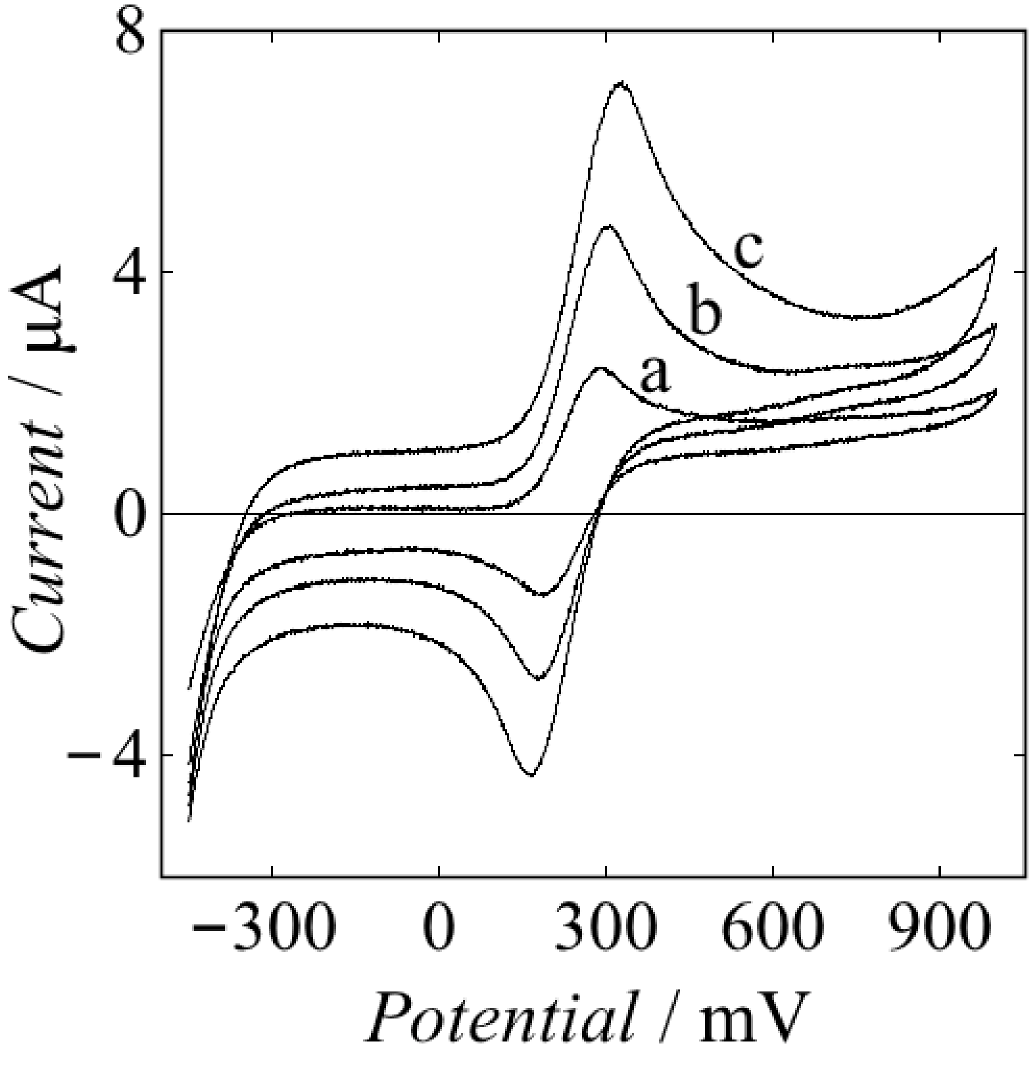

Fig. 2. Tatsumi & Shiba

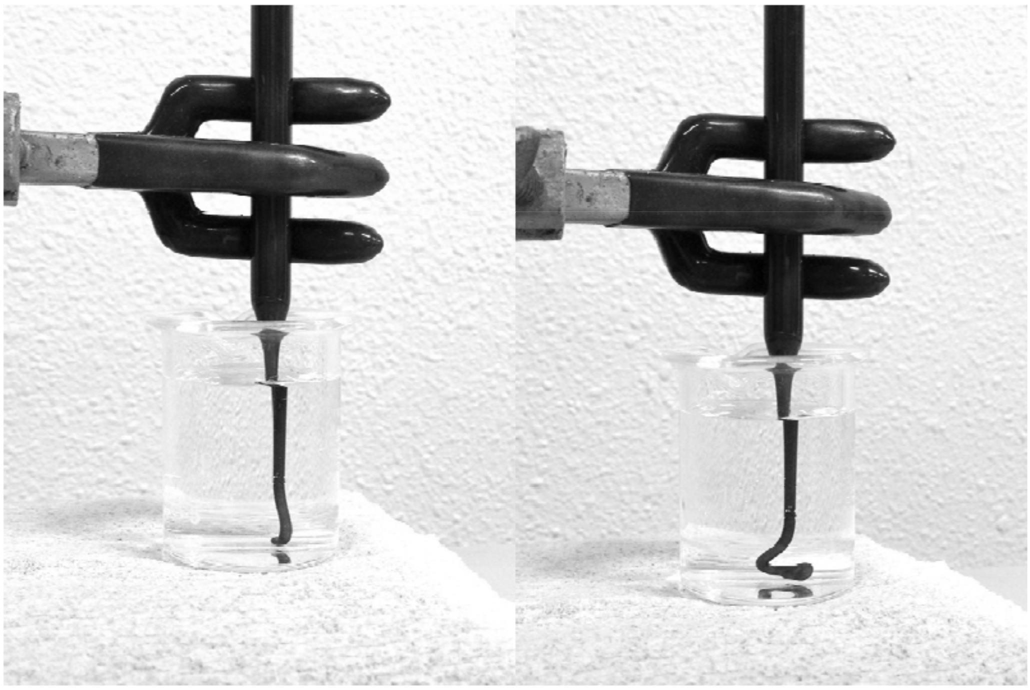

Fig. 3. Tatsumi & Shiba

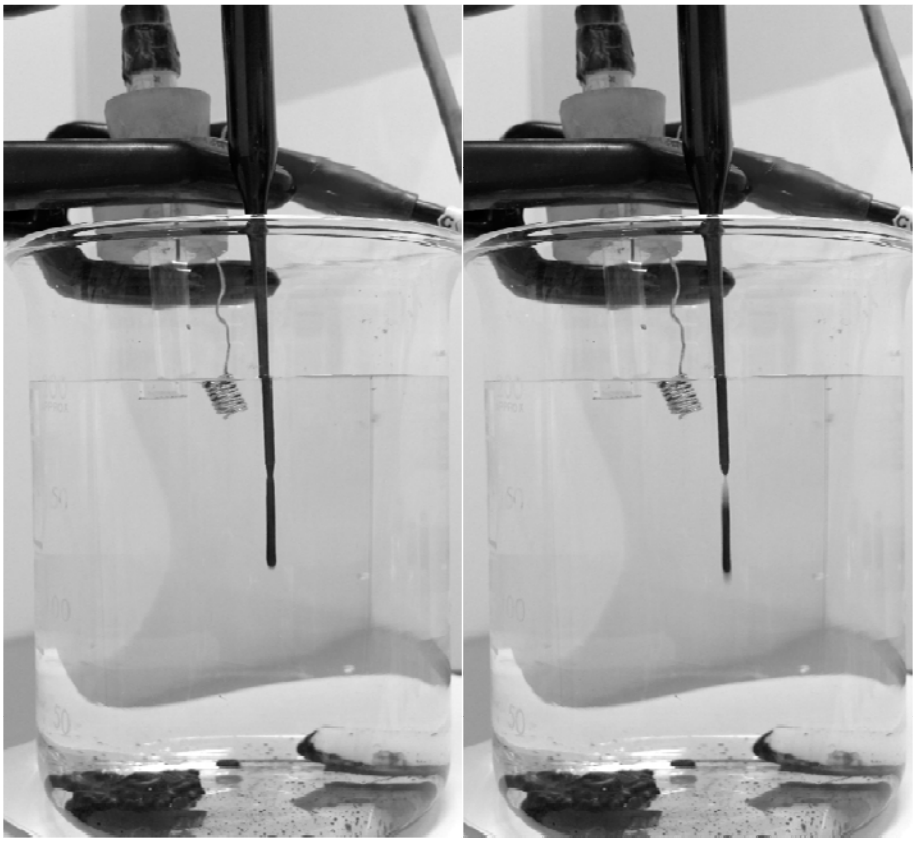

Fig. 4. Tatsumi & Shiba

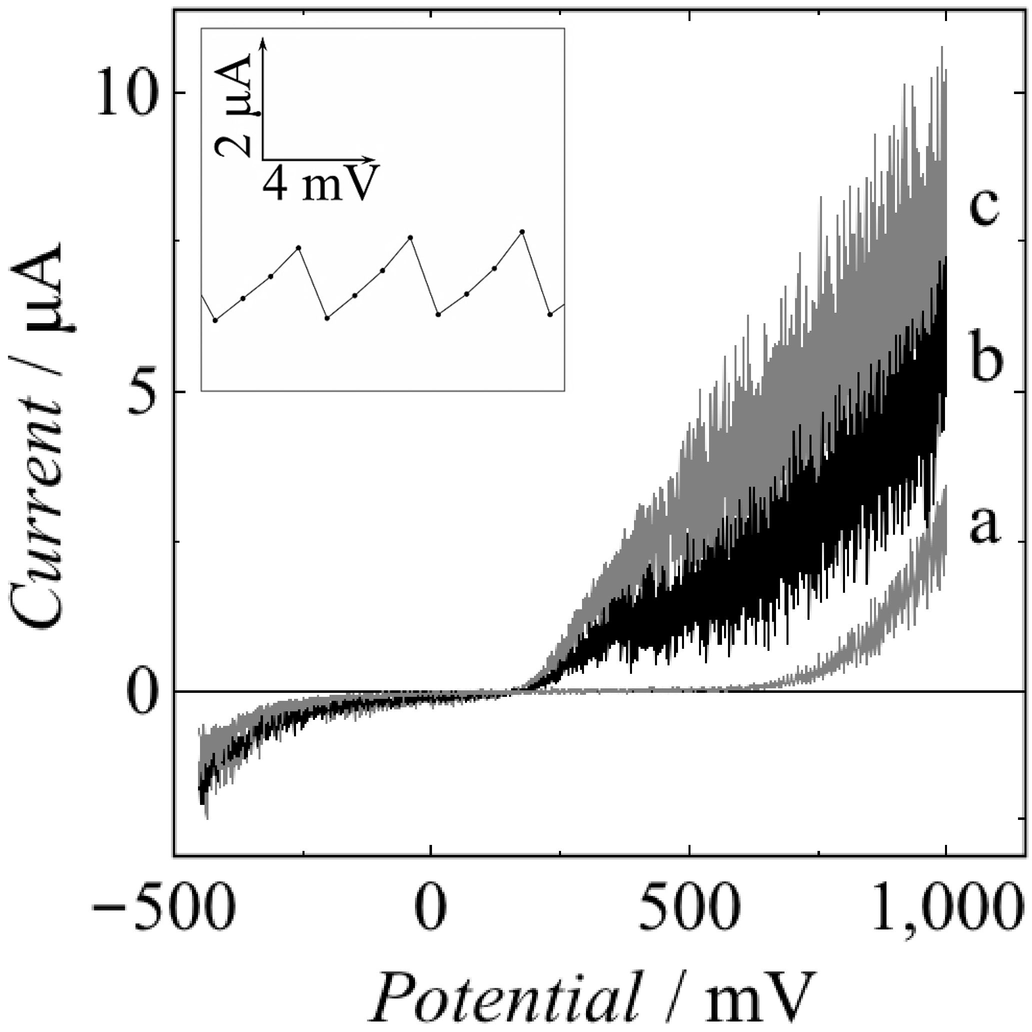

Fig. 5. Tatsumi & Shiba