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Fourier Analysis of AC Polarography. Elimination of Non-Faradaic Effects and Determination of Kinetic Parameters for Cd(II)-Na_2SO_4 System

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The on-line Fourier analysis of the AC polarographic current was found to give accurate results for electrode kinetics provided that the compensation of the *iR* drop and of the non-faradaic current was attained: The *iR* drop was compensated by a *positive feedback technique*. The charging current was cancelled by addition of a *pseudo-charging current*, inverse in phase to the former. Both the phase angles and amplitudes of the fundamental and second harmonic AC responses for the system of Pb(II) in 1M $NaClO_4$ ($[H^+]=12$ mM) agreed with theoretical prediction. As an illustration, the kinetic parameters of Cd(II)-1 N Na_2SO_4 system have been determined to be $k_s=(0.20\pm0.03)$ cm/s and $\alpha=0.30$ $(0.27<0.30<0.35)$ from the second harmonic AC polarogram.

The on-line Fourier analysis of instantaneuos AC polarographic currents enable us to determine simultaneously the amplitudes and phase angles of the fundamental and second harmonic responses.[1] However, since no instrumental compensation of the *iR* drop and the non-faradaic current(charging current) was made, the values obtained showed significant departure from those predicted theoretically. Thus, it was necessary to improve the instrument in order to eliminate the *iR* drop and the non-faradaic current. The cell resistance decreases the intensity and shifts the phase angle of AC polarographic current, and the large capacitive current reduces the precision of the analog-to-digital(A/D) conversion of small faradaic currents.

In the present study, a simple circuit has been adopted in order to compensate the charging current due to double layer capacity. A *positive feedback technique*[2-4] was employed for compensation of the *iR* drop. The results for typical chemical systems are presented to show the applicability of the apparatus.

Experimental

Apparatus and Procedure. A block diagram of the apparatus is given in Fig. 1. It is similar to the one previously described[1] except for the addition of circuits of compensation for the *iR* drop and the charging current. An oscillator (Model SY-118, NF Circuit Design Block) was used. A frequency counter(Model 5326B, Yokogawa-Hewlett-Packard) was used as a trigger generator. A sinusoidal AC potential with small amplitude was superposed on the DC potential applied to the electrode. A dropping mercury electrode (DME) was used with a reference electrode (saturated calomel electrode(SCE), Yanagimoto Model MRP). The polarographic current was sampled during a single drop life and stored in the computer with an 8 bit A/D converter(JRA-5 of JEOLCO), which was connected to the potentiostat. The Fourier transformation was performed after the DC component of the polarographic current had been largely eliminated by shifting the zero level.

Compensation for Charging Current and iR Drop. The charging current was nearly compensated with the aid of a *pseudo-charging current*, inverse in phase to the charging current. It was supplied from the common signal source (oscillator) through the phase inverter and differential circuit, the output of this circuit thus being inverse in phase to the charging current. It was then added to the polarographic current at the amplifier. The amplitude of the output of the differential circuit was proportional to the frequency of the input AC potentials in the range 20 Hz∼3 kHz. In order to stabilize the circuit, a resistance was connected in series with the input of the differential circuit. Figure 2 shows the effect of the compensation for the charging current of the Cd(II)-1 N Na_2SO_4 system. At a potential where the faradaic current was negligible, the amplitude of the pseudo-charging current was adjusted to minimize the observed polarographic current. When the *iR* drop is effectively compensated, the second harmonic response is not influenced by the charging current. The amplitude of the charging current varies with DC potentials at which polarographic currents are measured and with the area of the DME, which makes it difficult to completely eliminate the charging current at all potential regions. It is therefore desirable for measurement of the second harmonic AC current for the charging current to be eliminated in major part, in order to retain accuracy and precision of A/D conversion and digital calculations. For the measurement of the fundamental harmonic response, the present method of charging current compensation only lowers the base line of the capacitive component.

The *iR* drop compensation was fulfilled by the use of the positive feedback circuit reported by Smith and his co-

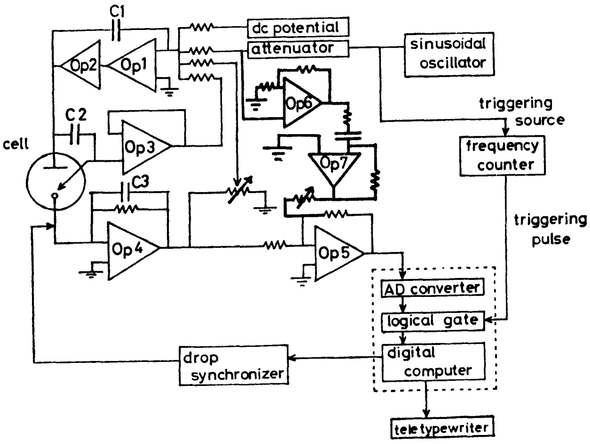

Fig. 1. The block diagram of the apparatus.
Operational amplifiers used are as follows;
Adder; Op1 = Teledyne Philbrick(TP) 1029,
Op2 = Philbrick/Nexus BQ 100.
Voltage follower; Op3 = TP 1009.
Current follower; Op4 = TP 1029.
Amplifier; Op5 = TP Nexus 1024.
The circuit of the pseudo-charging current;
Op6 = TP 1319, Op7 = Burr Brown 3112/12C.

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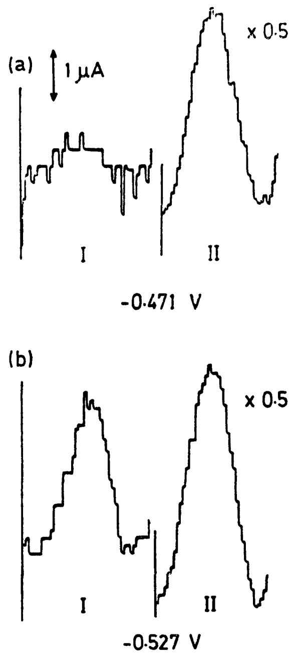

Fig. 2. The effect of the pseudo-charging current.
[Cd(II)] = 0.49 mM, $[Na_2SO_4] = 1.0$ N.
(a) charging current
(b) charging current with small faradaic current
I: with the pseudo-charging current
II: without the pseudo-charging current

workers:[2-4] The same amount of voltage as that of the ***iR*** drop was returned from the current follower to the adder *via* the variable resistance (Fig. 1). The small capacitances (C1, C2, C3 = 100 pF) were used to stabilize the circuit.

Measurement. The amplitude of the AC potential (ΔE) superposed on the DC potential was 5 mV or 15 mV, the frequency being adjusted to 27.9 or 173.6 Hz. The A/D converter began to sample 16 cycles of the AC polarographic current in 8 bit digital form 3.44 s after the time when the new drop started growing. The sampling method was similar to that reported previously.[5] The Fourier transformation was performed with a Fast Fourier Transform (FFT) program. The flow rate of mercury was 0.67 mg/s at the mercury column height of 40 cm. All the measurements were carried out at (25.0±0.5) °C. A computer simulation was performed using a HITAC 8800/8700 system at the Computer Centre, The University of Tokyo. A FORTRAN program from D. E. Smith was used to calculate the theoretical curves of the fundamental and the second harmonic responses.

All chemicals used were of analytical reagent grade. Water was distilled after deionization.

Results and Discussion

Figure 3 shows the reversible fundamental and second harmonic AC polarograms of Pb(II)–1M $NaClO_4$ ($[H^+] = 12$ mM) system, where the tracings of the original instantaneous AC currents are also demonstrated for the sake of comparison.[6] The frequency and amplitude of the AC potential in this case were 27.9 Hz and 5 mV, respectively. The magnitude of resistance of the feedback for the ***iR*** drop was determined at the DC potential (arrow, Fig. 3(B)) so that the phase angle of the second harmonic response was made equal to the theoretical value.[7]* The solid lines indicate the reversible theoretical curves for the fundamental and the second harmonic responses which were calculated according to the expanding plane model by the following equations.

$$I(\omega t) = \frac{n^2F^2AC_0^*(\omega D_0)^{1/2}(\Delta E)}{4RT\cosh^2(j/2)}\sin(\omega t + \pi/4) \quad (1)$$

$$I(2\omega t) = \frac{n^3F^3AC_0^*(2\omega D_0)^{1/2}(\Delta E)^2\sinh(j/2)}{(4RT)^2\cosh^3(j/2)}\sin(2\omega t - \pi/4) \quad (2)$$

$$j = \frac{nF}{RT}(E_{DC} - E^r_{1/2}) \quad (3)$$

where $I(\omega t)$ and $I(2\omega t)$ represent the fundamental and the second harmonic AC currents, respectively. The other notations have their usual meanings.[1] D_0 was obtained experimentally from the average diffusion current by means of the Ilkovič equation. The electrode area A was obtained by

$$A = 0.85\, m^{2/3}t^{2/3} \quad (4)$$

where m is the flow rate of mercury, t the drop time calculated from

$$t = (\text{waiting time}) + \frac{(\text{sampling time})}{2} \quad (5)$$

where the waiting time was the quiescent time from the beginning of the drop growth to the data sampling, the sampling time being the time interval of the data sampling. The waiting time and sampling time were made to be 3.44 s and 0.57 s, respectively, so that 16 cycles of AC polarographic current were stored in the memory during the course of sampling time.

The cathodic peak of the second harmonic AC wave was higher than that of the anodic one, the peak intensity of the fundamental harmonic AC wave being slightly higher than that of the theoretical one (Fig. 3). The results are interpreted to be due to the effect of the spherical diffusion in which the reduced form is soluble in the DME.[8,9]

Departure of phase angles from theoretical values was less than ±1° in the regions ($E_p \pm 0.4$) V for the fundamental harmonic AC polarogram, where E_p is the peak potential, and ($E_p \pm 0.1$) V for the second harmonic AC polarogram. The results suggest that the circuit for the ***iR*** drop compensation works satisfactorily.

The effect of the amplitude of the applied AC potential was also examined. With the increase of amplitude of AC potential up to 15 mV, the half-width of the fundamental and the peak-to-peak separation of the second harmonic AC polarogram exceeded the theoretical values by 10%.

It is thus concluded that the apparatus can be used to obtain accurate values for the kinetic parameters of the electrode reactions.

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* Cell resistance in the absence of the feedback circuit can be easily calculated from the measured vector components of the admittance for the electrolyte solution without depolarizer. However, this operation is less accurate than that mentioned above.

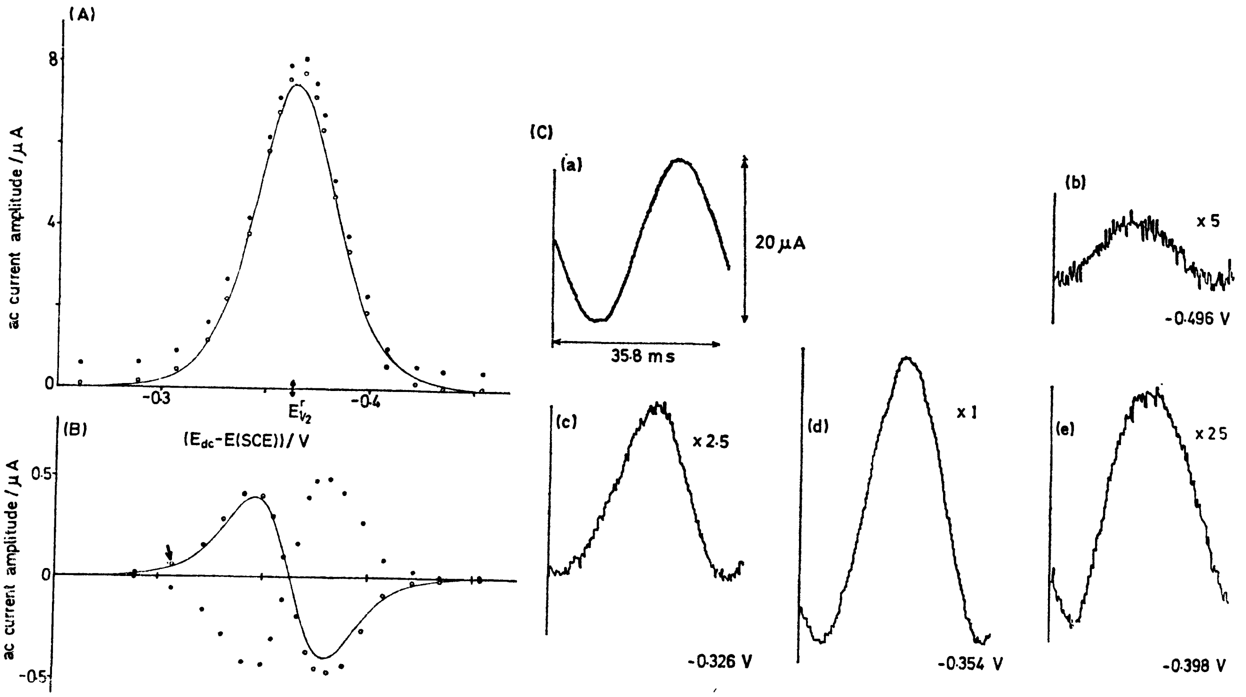

Fig. 3. The AC polarogram of lead(II).
[Pb(II)] = 0.83 mM, [$NaClO_4$] = 1.0 M, [$HClO_4$] = 12 mM.
(A) fundamental harmonic AC polarogram. (B) second harmonic AC polarogram.
○ in-phase component ● quadrature component
—— theoretical curves of the in-phase component based on the expanding plane model
$n=2$, $D_0=1.07\times10^{-5}$ cm^2/s, $A=0.016$ cm^2, $\Delta E=5$ mV, frequency = 27.9 Hz.
(C) instantaneous AC current.
(a) dummy cell with 1 kΩ resistance. (b) charging current only. (c, d, e) faradaic currents of Pb(II)/Pb(Hg) and charging current.

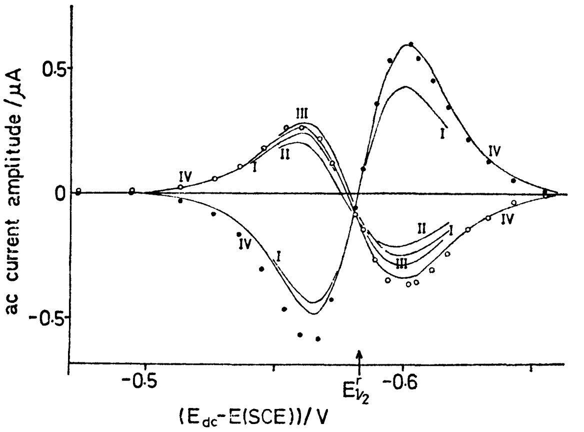

Fig. 4. The second harmonic AC polarogram of cadmium(II).
[Cd(II)] = 0.49 mM, [Na_2SO_4] = 1.0 N.
○ in-phase component ● quadrature component
—— theoretical curves based on the expanding plane model
$\alpha=0.30$
I: $k_s=0.20$ cm/s, II: 0.15 cm/s, III: 0.25 cm/s (II, III in-phase component only), IV: corrected for spherical diffusion on the curve I
$n=2$, $D_0=0.84\times10^{-5}$ cm^2/s, $D_r=1.6\times10^{-5}$ cm^2/s, $A=0.015$ cm^2, $\Delta E=5$ mV, frequency = 173.6 Hz.

Figure 4 shows the second harmonic AC polarogram for the Cd(II)–1 N Na_2SO_4 system. The frequency and amplitude of the AC potential were 173.6 Hz and 5 mV, respectively. The kinetic parameters for this system were found to be (0.20±0.03) cm/s for k_s and 0.30(0.27 <0.30<0.35) for α by computer simulation.[7] The diffusion coefficient of the reduced form was taken from the works of Furman *et al.*[10] The solid lines (I—III) are theoretical curves calculated from the expanding plane model. Curve IV was calculated considering the effect of spherical diffusion at the stationary electrode[11] on curve I. The kinetic parameters for Cd(II)–1 N Na_2SO_4 system are in good agreement with those obtained by the phase-sensitive AC polarographic method.[4,11–13]

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