Correction for Series Resistance in A.C. Polarography

by

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Abstract

The apparent or measured series resistance of an electrochemical cell is influenced by the geometry of the electrodes. At a dropping mercury electrode, the resistance increases as the frequency of the measuring signal decreases. The question arises as to how to correct for the series resistance when calculations are made of faradaic impedance. It is shown here that the use of the high-frequency limit of the resistance gives better results than use of the apparent resistance at each frequency. Nevertheless, the correction made in this way represents only an approximation.

Calculations of the faradaic impedance of redox processes are based on an equivalent electrical circuit of the electrochemical cell as shown in Figure 1. The validity of the calculations depends on the use of correct values for the double-layer capacity and the series resistance. These quantities are obtained from measurements carried out so as to minimize the effect of the faradaic impedance (absence of depolarizer or some type of extrapolation procedure).

With conventional, blunt-tipped, capillaries, measurements made at dropping mercury electrodes in the absence of depolarizer show a pronounced variation of the apparent series resistance with changing frequency of the alternating signal: the resistance increases as the frequency decreases. Newman¹⁾ has shown that such an effect can be produced by shielding of the drop by the capillary. The extent of the frequency dispersion of the resistance depends on the relative magnitudes of the double-layer capacity and the series resistance; or, more generally (in the presence of a depolarizer), on the relative magnitudes of the interfacial impedance and the series resistance. Therefore, in the frequency range where dispersion is observed, the series resistance in absence of depolarizer will differ from that in the presence of depolarizer; proper correction must take into account this factor.

In this note, it is shown that the use of the high-frequency limit of the measured resistance is a better approximation than use of the apparent resistance at a given frequency measured in absence of depolarizer.

Experimental

Two systems have been examined: one where charge transfer is comparatively fast (Cd(II)/Cd(Hg) in 1 *M* KNO_3), and one where the process is of moderate speed (Zn

(II)/Zn(Hg) in 1M NaClO₄).

Reagent-grade chemicals were used in all cases. The cadmium system was studied with a Princeton Applied Research Corporation Electrochemistry System 170; the zinc system was studied by means of manual apparatus described in detail elsewhere²¹.

Experiments were carried out at 25°C. All potentials were measured *vs.* S.C.E.

Results

Table I reports results of measurements at a d.m.e. in 1 M KNO₃, obtained with the P.A.R. instrument which is limited to a frequency range of up to 1 kHz. The double-layer capacity is constant, but the series resistance increases at lower frequencies as would be expected at a shielded drop according to the treatment of Newman¹¹. Table II shows the results of calculations made for the system Cd(II)/Cd(Hg) in 1 M KNO₃, on two bases: using the actual measured series resistance at each frequency, and using the high-frequency (1 kHz) magnitude of the resistance for calculations at all frequencies. It is evident that calculations based on the high-frequency resistance yield results that satisfy a simple diffusion-controlled model (Randles³¹), whereas calculations based on the “actual” values of the resistance (measured in absence of depolarizer) at various frequencies result in scattered values, including negative values for the charge-transfer resistance.

Similar results and conclusions emerge from measurements on 1 M NaClO₄, in presence and absence of Zn(II): Table III shows results obtained in the supporting electrolyte, Table IV those obtained in the presence of Zn(II). It is apparent that the use of “actual” as opposed to “high-frequency” resistance values leads to more serious errors, the smaller is the charge-transfer resistance of the system. This is obvious even on a priori grounds—any error in series-resistance magnitude is relatively

Table I D.M.E., 1M KNO₃, -0.58V *vs.* S.C.E.

Frequency	Double-Layer Capacity	Series Resistance
26Hz	0.471μf	735Ω
46	0.481	384
73	0.466	271
137	0.461	174
275	0.462	140
562	0.466	122
1008	0.485	101.5

Table II D.M.E., 1M KNO₃ plus Cd(II), -0.58V *vs.* S.C.E.

Frequency	Calculations using Resistance Values from Table I			Calculations using Resistance Value of 101.5 ohms		
	In-Phase Faradaic Impedance (i)	Out-of-Phase Faradaic Impedance (ii)	Charge-Transfer Resistance (i)-(ii)	In-Phase Faradaic Impedance (iii)	Out-of-Phase Faradaic Impedance (iv)	Charge-Transfer Resistance (iii)-(iv)
$5 \times 10^{-5} M$ Cd(II)						
26Hz	6720 Ω	8670 Ω	-1950 Ω	8170 Ω	7490 Ω	680 Ω
46	5230	6190	-960	5960	5420	540
73	4410	4900	-490	4900	4230	670
137	3550	3600	-50	4060	3340	720
275	2580	2480	100	2710	2010	700
562	1640	1910	-270	1770	1460	310
1008	454	3340	-2890	454	3340	-2890
Average, 26 to 275 Hz : 662 Ω						
$10^{-4} M$ Cd(II)						
26	3030	4060	-1030	4050	3650	400
46	2490	2990	-500	3000	2690	310
73	2130	2400	-270	2470	2150	320
137	1710	1700	10	1870	1530	340
275	1250	1230	20	1360	1070	290
562	827	913	-86	903	771	132
1008	667	1130	-462	667	1130	-463
Average, 26 to 275 Hz : 332 Ω						

Table III D.M.E., 1M NaClO₄

Frequency	-0.92V <i>vs.</i> S.C.E.		-0.94V <i>vs.</i> S.C.E.	
	Double-Layer Capacity	Series Resistance	Double-Layer Capacity	Series Resistance
26Hz	.532 μ F	313	.527 μ F	355
46	.534	172	.533	204
71	.543	132	.539	155
143	.548	116	.537	115
283	.546	89	.537	94
567	.544	85	.529	85
1114	.543	81	.532	80
1424	.540	78	.531	79
1813	.541	78	.531	78
2020	.544	77	.535	79
2531	.545	77.5	.538	77
3051	.533	78	.539	78
4044	.530	77	.529	77
5058	.521	76	.516	77
10454	.512	75	.506	76
20768	.518	75.5	.515	76
31266	.492	75	.492	75

Table 4 D.M.E., 1M NaClO₄ plus Zn(II)

Frequency	Calculations using Resistance Values from Table III			Calculations using Resistance Value of 76.5 ohms		
	In-Phase Faradaic Impedance (i)	Out-of-Phase Faradaic Impedance (ii)	Charge-Transfer Resistance (i)-(ii)	In-Phase Faradaic Impedance (iii)	Out-of-Phase Faradaic Impedance (iv)	Charge-Transfer Resistance (iii)-(iv)
$2 \times 10^{-4} M \text{ Zn(II)} ; -0.94V \text{ vs. S.C.E.}$						
26Hz	10600 Ω	4560 Ω	6040 Ω	10900	3850	7050 Ω
46	9660	3620	6040	9670	3040	6630
71	9100	2910	6190	8950	2370	6580
143	8160	2550	5610	7740	1900	5840
283	7490	2350	5140	6830	1660	5170
567	6750	2710	4040	5780	1650	4130
1114	5320	2640	2680	4370	1490	2880
1424	4830	4010	820	4160	2130	2030
1813	4210	2280	1930	3340	1170	2170
2020	4470	2730	1740	3270	1100	2170
$10^{-3} M \text{ Zn(II)} ; -0.92V \text{ vs. S.C.E.}$						
46Hz	9670	9210	460	9980	8520	1460
71	8960	9240	-280	9240	7760	1480
143	7140	7040	100	7340	5840	1500
283	5730	4900	830	5770	4260	1510
567	4300	4060	240	4230	2960	1170
1114	2010	1770	240	2730	1330	1400
1424	2010	905	1105	1920	764	1160
1813	1690	559	1130	1550	419	1130
2020	1500	482	1020	1440	418	1020

more important when the charge-transfer process is rapid (charge-transfer resistance small).

Some experiments were carried out with "pencil -sharpened" capillaries: the blunt end of the capillary was carefully ground away. No measurable difference in frequency dispersion could be detected, indicating that the shielding effect is due primarily to the glass immediately adjacent to the top of the drop. Siliconizing the capillary also had no effect on the frequency dispersion, indicating that the latter was indeed a result of shielding and not of a solution film inside the capillary.

Conclusions

1. At blunt-tipped capillaries, the frequency dispersion of series resistance (pronounced at low frequencies) and double-layer capacity (small or negligible) follows, at least qualitatively, the calculations (1) for a spherical electrode tangent to an insulating plane.

2. In calculations of charge-transfer-resistance values, the high-frequency limit of the series resistance should be used. Consequently,

3. Instruments used for impedance studies of redox processes should permit measurements over a sufficiently large range of frequencies that the high-frequency limit of the series resistance can be obtained.

Finally, it is evident that the reliability of impedance measurements of electrochemical processes becomes greater if electrodes can be used where a uniform distribution of current prevails across the surface of the working electrode. Then, measurements will not be complicated by frequency dispersion resulting from purely geometric factors.

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