

DOUBLE-LAYER CAPACITY AT A PYROLYTIC GRAPHITE DISK ELECTRODE

HENRY H. BAUER^a, MICHAEL S. SPRITZER^b AND PHILIP J. ELVING

The University of Michigan, Ann Arbor, Michigan (U.S.A)

(Received October 10th, 1966; in revised form October 28th, 1967)

An understanding of electrochemical reactions is frequently not attainable unless the structure of the electrical double-layer is understood. The nature of the double-layer at solid electrodes has not yet been adequately elucidated, knowledge about it being largely based on analogy with the well-characterized mercury electrodes; the present state of our understanding in this area has been comprehensively reviewed by DELAHAY¹.

Primary difficulties with solid electrodes involve questions as to: (a) the reproducibility of the electrode surface and (b) the dependence of the apparent double-layer capacity on frequency. The aim of the present study was to investigate these questions in relation to the pyrolytic graphite electrode, which has in recent years proved useful in a variety of electrochemical studies; particular attention was given to electrode preparation and treatment.

The observed capacity was always to some extent dependent on the frequency at which the measurement was made. However, it is indicated that such an effect may be expected at any electrode, such as a disk, at which the distribution of current over the surface is not uniform.

EXPERIMENTAL

Polarization circuit

Instrumentation for polarization by both alternating and direct voltages has been either fully manual, with corrections for iR -drop and other effects being calculated after the experiments have been made², or fully controlled with both d.c. and a.c. signals held constant by electronic circuits, usually constructed of operational amplifiers³. The latter scheme has the disadvantage that, with readily available equipment, work is restricted to frequencies no higher than about 1000 Hz. Therefore, a "hybrid" arrangement (Fig. 1) was used in the present work, in which a.c. and d.c. circuits were connected in parallel across the cell.

The d.c. circuit was controlled by a conventional operational-amplifier control-loop⁴; the direct voltage was applied by potentiometer, E; capacitor C₂ was used to

^aPresent address: Department of Chemistry, University of Kentucky, Lexington, Kentucky, U.S.A.

^bPresent address: Department of Chemistry, Villanova University, Villanova, Pennsylvania, U.S.A.

attenuate any a.c. picked up by the reference electrode; choke L ensured that a.c. applied between counter and working electrodes was not shunted through C_2 to ground.

The a.c. circuit, supplied by an audio-frequency oscillator, was manually controlled. A parallel combination of resistance (R_p) and capacitance (C_p) decades was used for phase-angle measurement; phase shifts and cell impedances were measured as previously described⁵, using an oscilloscope. A 10-mV peak-to-peak voltage was maintained across the working electrodes by manual adjustment of R_1 and of the oscillator amplitude-control. Capacitor C_1 blocked the d.c. signal from the a.c. circuit.

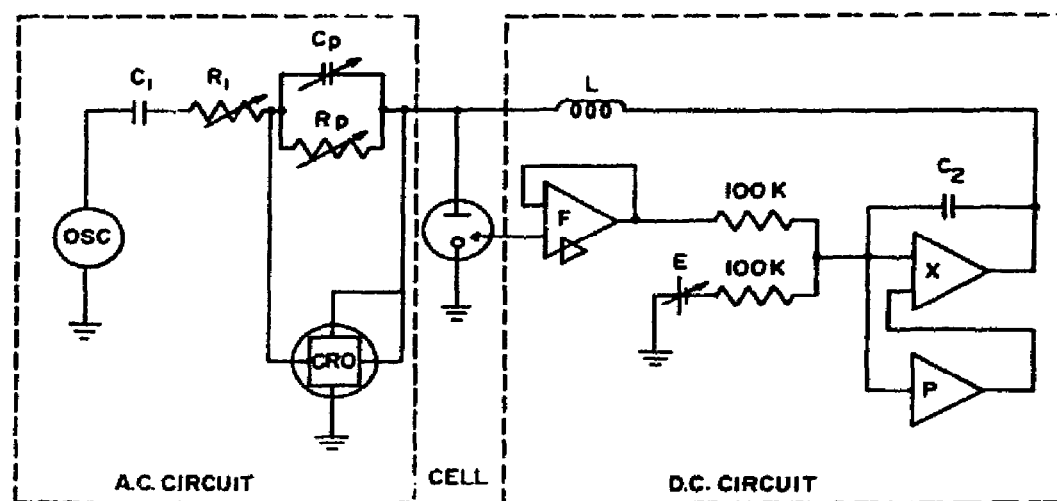


Fig. 1. Circuit for a.c. measurements. (C_1), $0.01 \mu\text{F}$; (C_2), $2 \mu\text{F}$; (C_p), General Radio decade capacitor Type 1419-A; (CRO), Tektronix Model 502A dual-beam oscilloscope; (E), 0–10 V variable potential source; (F), stabilized follower; (L), United Transformer choke Type MQM-600; (OSC), Heathkit audio-frequency oscillator Model AG-8; (P), Philbrick K2-P operational amplifier; (R_1), two $3/4$ -turn radio potentiometers in series, $5\text{k}\Omega$ and $1\text{-M}\Omega$; (R_p), General Radio decade resistor Type 1434-QC; (X), Philbrick K2-X operational amplifier.

Cells

For runs in aqueous solution, a conventional H-cell was used with a saturated calomel electrode, SCE, as reference electrode, and an agar plug between compartments. The counter electrode, which was placed in the test-solution compartment, consisted of either a large mercury pool (area: 9.6 cm^2) or a platinum gauze cylinder, 1 cm in diameter and 3 cm high (*ca.* 26 gauge wire). The three-compartment water-jacketted cell used for runs in pyridine solution has been described⁶; salt bridges were methyl cellulose gel– $0.1 \text{ M Et}_4\text{NClO}_4$ in pyridine. Runs in aqueous solution were at ambient room temperature (no significant effect of temperature changes of a few degrees on capacity has been reported); runs in pyridine solution were at 25° .

Graphite electrode

Pyrolytic graphite electrodes (P.G.E.) made from 4-mm diameter cylinders sealed into glass tubing were prepared as previously described⁷ with the graphite surface flush with the end of the glass tubing, as well as with several millimeters of graphite protruding from the tubing; in the latter case, the sides of the graphite cylinder were insulated. Shell Epon resin, Sears two-component epoxy resin, and polyethylene (obtained by melting polyethylene tubing in a low flame) were tried for sealing and insulation. Resurfacing was accomplished by polishing with a fine abrasive paper⁷

or by cleaving about a millimeter of graphite from the electrode tip by means of a sharp scalpel. The most reproducible behavior was obtained with a "protruding" electrode, sealed and insulated with Sears epoxy resin and resurfaced by cleaving.

Reagents

Aqueous potassium chloride (J. T. Baker) solutions were purified by treatment with charcoal (Darco G-60). Pyridine, argon for de-aeration, and tetraethylammonium perchlorate were obtained and treated as previously described^{6,8}. The argon was equilibrated in the case of aqueous solutions by first being bubbled through water; for pyridine solutions, it was first passed through a column of Drierite and then through pyridine containing molecular sieves.

MEASUREMENT APPROACH

The measuring technique involved determination of total cell impedance, Z , and phase angle, ϕ , and calculation of the equivalent series resistance, R_s and capacity C_s (the apparent double-layer capacity), by simple transformation of the measured quantities. Thus,

$$Z^2 = R_s^2 + 1/\omega^2 C_s^2 \quad (1)$$

where ω is the angular frequency of the applied alternating signal, and

$$\cot \phi = \omega R_s C_s \quad (2)$$

Combining eqns. (2) and (1),

$$Z^2 = R_s^2 + R_s^2 / \cot^2 \phi = R_s^2 / \cos^2 \phi \quad (3)$$

which permits R to be calculated directly from Z and ϕ via

$$R_s = Z \cos \phi \quad (4)$$

C can then be calculated, using eqn. (2), from

$$C_s = 1/\omega Z \sin \phi \quad (5)$$

If R_s and C_s are independent of frequency, support is given to a representation of the cell as being the double-layer capacity at the working (small) electrode in series with the solution resistance, and C_s and R_s can be taken to be measures of these quantities. However, if R_s and C_s change with frequency ("frequency dispersion"), such inferences cannot be drawn. It is worth emphasizing that, when the equivalent series circuit is inapplicable, use of C_s as a "double-layer capacity" involves an assumption whose validity does not necessarily improve as the frequency dispersion becomes less; it is the applicability or inapplicability that is significant, since any frequency dispersion points to a phenomenon that must be understood before C_s -values can be reliably used.

REPRODUCIBILITY AND FREQUENCY DISPERSION

The reproducibility, nature, and magnitude of the frequency dispersion obtained on pyrolytic graphite electrodes (Tables 1 and 2) indicate that good reproducibility may be attained at a given electrode by rigorous control of the preparation and handling of the electrode (*cf.* subsequent discussion).

However, both the magnitude of the measured quantities and their variation with frequency are sensitive to the method of preparation of the electrode surface: compare data in Table 1 for a cleaved electrode and Table 2 for a polished electrode cathodized before the impedance measurements were made. Thus, one possible factor

TABLE 1

SERIES CAPACITY AND RESISTANCE AT A CLEAVED PYROLYTIC GRAPHITE ELECTRODE^a

Frequency (Hz)	C_s^b (μF)			R_s^b (Ω)		
	(1)	(2)	(3)	(1)	(2)	(3)
50	2.09	2.36	2.34	256	279	285
125	1.85	2.13	2.14	129	146	143
250	1.76	1.96	2.60	81.8	90.5	96
500	1.61	1.78	1.78	56.6	62	58.1
1,250	1.53	1.54	1.80	36.7	37.6	31
2,500	1.43	1.42	2.05	30.8	28.5	39.4
5,000	1.31	1.21	1.27	26.6	23.2	22.2
12,500	1.26	1.12	1.07	23.4	17.6	17.8
25,000	1.20	1.03	1.83	22.4	15.8	15.8

^aElectrode (diam. 4 mm) was sealed and covered by a polyethylene pressure-fitted sleeve. Soln. composition: 0.4 M KCl.

^bMeasurements were made at a potential of -0.5 V vs. SCE. The numbers in parentheses refer to the series of experiments made on the same electrode with resurfacing by cleaving between each series.

TABLE 2

SERIES CAPACITY AND RESISTANCE AT A GROUND PYROLYTIC GRAPHITE ELECTRODE^a

Frequency (Hz)	C_s^b (μF)		R_s^b (Ω)	
	(1)	(2)	(1)	(2)
50	8.8	8.8	48.5	47.8
125	8.42	8.25	35.2	34.4
250	9.05	7.85	28.8	31
500	7.95	7.8	29	28.9
1,250	7.92	7.25	26.6	26.8
2,500	8.9	6.95	23.9	26.5
5,000	6.58	6.36	24.5	24.5
12,500	6.6	5.66	24.5	23.9
25,000	9.65		21	

^aElectrode (diam. 4 mm) was sealed in a glass tube by polyethylene with its end flush with the glass; it was resurfaced by grinding. Soln. composition: 0.5 M KCl.

^bMeasurements were made at a potential of -0.5 V vs. SCE. In series (1), the soln. was pre-electrolyzed initially by cyclic scan to -1.0 V; in series (2), the soln. was similarly pre-electrolyzed before each measurement.

in the differences observed is the presence or absence of an "oxidized" surface. The P.G.E. normally has an "oxidized" surface that shows a different apparent capacity than the "reduced" surface⁹; the latter can be produced, e.g., by polarizing the electrode from 0 to -1.4 V vs. SCE at 10 mV sec⁻¹. Therefore, if an "oxidized" electrode is held at a negative potential, the capacity would be expected to change with time. We have occasionally observed such effects, where the order of magnitude of the drift is about a 5% change in capacity in 15 min while the resistance remains constant or is

changed to a lesser extent; these changes appear to depend on applied electrode potential and on the frequency. No quantitative data bearing on this particular point were obtained; however, work is continuing on the study of the nature of the surface ("oxidized" or "reduced"), in particular by cyclic voltammetric investigations⁹.

Another possible factor in the small frequency dispersion that was persistently observed (*e.g.*, Tables 1 and 2) may have been penetration of the solution between the electrode and its insulation. For example, in one of a number of experiments that gave a much larger C_s -value at low frequencies (a factor of up to 4 over Table 2) together with a much greater degree of frequency dispersion (Table 3), the resin coating around

TABLE 3

EFFECT ON SERIES CAPACITY AND RESISTANCE OF SEEPAGE OF SOLUTION BETWEEN PYROLYTIC GRAPHITE ELECTRODE AND ITS INSULATION^a

Frequency (Hz)	C_s^b (μF)		R_s^b (Ω)	
	(1)	(2)	(1)	(2)
50	27.9	33.8	199	164
125	30.9	29.9	101	103
250	22.9	24.1	77.2	74.9
500	22.5	18.2	89.3	75
1,250	4.55	4.75	53.4	52.5
2,500	3.26	3.38	37.7	37.3
5,000	1.75	1.92	31.7	31
12,500	1.70	1.70	23.8	23.8
25,000	1.69	1.60	21.7	21.1

^aElectrode was encased in a two-component epoxy resin and was resurfaced by cleaving. Soln. composition: 0.4 M KCl.

^bMeasurements were made at a potential of -0.5 V *vs.* SCE. In series (1), a pool counter-electrode was used; in series (2), a platinum gauze cylinder counter electrode was used; the lack of any difference in the two series indicate that both counter-electrodes were equally effective.

the electrode became opaque and readily peeled away, evidently due to penetration of solution between electrode and resin. Continuous penetration is not necessarily involved, but merely the presence of a "wedge" of solution. The latter has been identified as a cause of frequency dispersion under some circumstances¹⁰⁻¹⁴; in fact, such an explanation is commonly invoked in a qualitative way to explain frequency dispersion, but quantitative support for the explanation is not usually available. At solid electrodes, roughness of the surface is another explanation commonly given for the observation of frequency dispersion.

Both explanations amount to the use of an equivalent circuit in which the lines of current flow have to be represented by a number of parallel paths, each with capacitive and resistive properties, whereas a lack of frequency dispersion permits the use of an equivalent circuit consisting of only one path for current flow, *viz.* through the capacity of the interface and the ohmic resistance of the solution in series. Thus, any physical situation in which the current density is not uniform over the surface of the electrode will result in frequency dispersion. In the following section, we discuss the possibility that such an effect is inherently present when a disk-shaped indicator electrode is used.

ELECTRODE SHAPE AND FREQUENCY DISPERSION

Statements in the literature refer to the need for a symmetrical arrangement of electrodes if frequency dispersion is to be avoided, for example, in the work of GRAHAME:

"...Hanging droplet... not significantly different from d.m.e... with (large cupped Hg surfaces)... frequency effect always exceeded that... with droplets, and its magnitude depended critically upon the size and shape..." (p. 305 of ref. 10; *cf.* also column 1 of p. 307).

"...Generally... dispersion is greater on wires and sheets than on spheres... more difficult to satisfy the symmetry requirements..." (almost at end of ref. 15).

"... The necessity for smoothness and spherical symmetry (or any other symmetry which assure an equal flow of current to all points of the electrode surface)... Robertson... points out the enormous increase in the apparent series resistance... with platinum electrodes as the frequency is lowered... also noted by the writer... not only with platinum but also with other types of solid electrodes and to a lesser degree even with mercury. The effect with mercury has been... apparently explained... as being due to the creeping of the solution up the inner walls of the capillary... It is not clear that any similar explanation will suffice to explain the results observed with solid microelectrodes. The (series) capacity of a spherically symmetrical smooth solid electrode is virtually unaffected by the frequency... This fact can be used as a test for smoothness and symmetry of an electrode." (p. 353 of ref. 16).

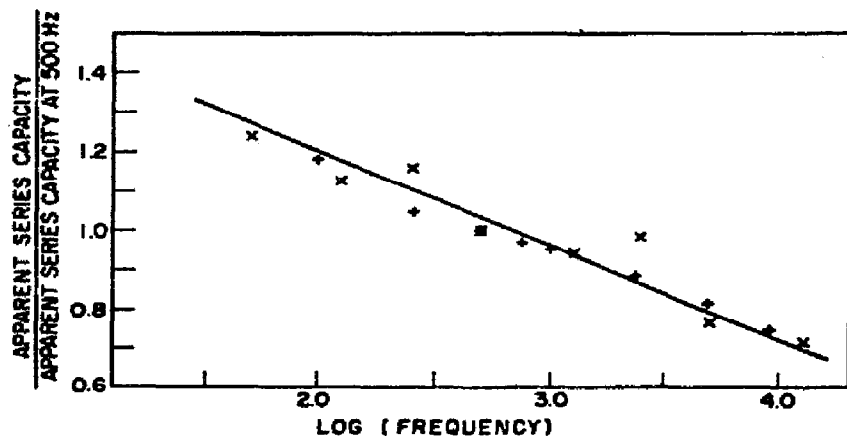


Fig. 2. Frequency dispersion of apparent double-layer capacity at planar disk-shaped working electrodes. (x), results obtained in the present study, taken from Tables 1 and 2; (+), results reported by GRANTHAM¹⁶ at mercury. The line was calculated by assuming that all results follow the same relation.

In connection with our work, the question now arises whether a symmetrical arrangement of electrodes was achieved. We were not able to detect differences between the results obtained with a large mercury pool as counter electrode as compared with a large cylindrical platinum gauze counter electrode. Such a test is inconclusive, however, since the important feature is the current distribution at the disk-shaped working electrode, which could be very similar with the two counter-electrodes used. In point of fact, in a theoretical discussion of the distribution of direct current in electrodeposition, it has been shown that there are only three arrangements of electrodes in which it is possible to obtain an absolutely uniform current dis-

tribution over the electrodes: concentric spheres, concentric cylinders, and infinite parallel planes¹⁷. Thus, it seems that frequency dispersion will be inherently connected with the use of disk-shaped working electrodes.

Some support for this expectation may be found in data obtained at a plane mercury disk electrode¹⁸, where dispersion of the observed capacity with frequency was observed. Moreover, the magnitude of this dispersion is comparable to that found in the present work (*cf.* Fig. 2).

Given that a variation of measured capacity with frequency is the result of non-uniform distribution of current, an equivalent circuit would then be composed of a set of capacities and resistors, C_i and R_i , arranged so that there are parallel paths, each of which contains one C and the corresponding R . It is readily seen that in such an arrangement, extrapolation to sufficiently low frequencies will yield the sum of the individual capacities C_i ; sufficiently low frequencies require that all of the R_i -values will be small compared with the corresponding $(1/2\pi f C_i)$ terms. The results in Table 2 may have approached this requirement; however, as mentioned, unresolved questions on the nature of the surface preclude further discussion at this stage of the significance of the numerical values obtained in these measurements.

EFFECT OF ELECTRODE POTENTIAL ON DOUBLE-LAYER CAPACITY

In studies where frequency dispersion is absent or ignored, measurements of the double-layer capacity are commonly made with signals of 1000 Hz or thereabouts. At solid electrodes¹⁹, the measured capacities generally are similar to those at mercury in that the capacity rises at both positive and negative polarizations and shows a more

TABLE 4

SERIES RESISTANCE AND CAPACITANCE AT A PYROLYTIC GRAPHITE ELECTRODE OF A PYRIDINE SOLUTION OF TETRAETHYLAMMONIUM PERCHLORATE (0.1 *M*) AT 250 Hz

Potential ^a (V)	R_s^b (Ω)	C_s^b (μF)
1.0	286	16.5
0.7	287	14.5
0.5	290	13.5
0.3	294	11.9
0.2	296	11.4
0.1	299	9.8
0	300	10.0
-0.1	302	11.2
-0.2	301	12.4
-0.3	294	11.7
-0.5	290	13.4
-0.7	289	15.0
-1.0	284	17.0

^aVs. N.Ag.E.: Ag/1 *M* AgNO₃ in pyridine²⁷.

^bThe values are averages of from one to five separate experiments, normalized for 10 μF and 300 Ω at 0 V; the actual capacity at 0 V was about 60 $\mu F/cm^2$ of macroscopically measured surface.

TABLE 5

EFFECT OF APPLIED POTENTIAL ON SERIES CAPACITY AND RESISTANCE AT A PYROLYTIC GRAPHITE ELECTRODE

Potential vs. S.C.E. (V)	C_s (μF)	R_s (Ω)
+1.0	7.92	45.7
0.8	7.74	46.7
0.6	7.24	46.6
0.4	7.13	47.0
0.2	6.68	47.4
0.0	6.99	46.4
-0.1	6.68	47.4
0.2	6.58	48.2
0.3	6.60	48.1
0.4	6.57	48.2
0.5	6.68	47.4
0.6	7.02	46.5
0.8	7.38	46.3
1.0	8.05	46.3

^aElectrode (diam. 4 mm) was sealed in a glass tube by polyethylene with its end flush with the glass; it was resurfaced by polishing. Soln. composition: 0.5 *M* KCl. Frequency: 1000 Hz.

or less pronounced minimum at intermediate potentials; the minimum capacity is sometimes taken as a measure of the potential of zero charge. In order to compare the behavior of the P.G.E. with that of other solid electrodes in this respect, measurements were made at a fixed frequency with changing electrode potential (Tables 4 and 5).

In aqueous KCl, the capacity appeared to show a very shallow minimum between *ca.* -0.2 and -0.4 V *vs.* SCE; in 0.1 M Et₄NClO₄ in pyridine, a distinct minimum in the capacity lay close to 0 V *vs.* N.Ag.E.²⁰ In the latter system, polarization beyond -1.0 V produced an irreversible change in the electrode surface, *i.e.*, results obtained after such a polarization and a return to less negative potentials were scattered and unreproducible. In aqueous KCl solution, such behavior results from reduction of an "oxidized" surface (*cf.* previous discussion) or from the formation of hydrogen through discharge of protons²¹; the reactions, which may occur in pyridine to alter the graphite surface, have not yet been elucidated.

ACKNOWLEDGEMENTS

The authors thank the U.S. Atomic Energy Commission and the Horace H. Rackham School of Graduate Studies and the Institute of Science and Technology of The University of Michigan, which helped support the work described. They are indebted to Dr. WILBUR SHULTS for drawing their attention to the work of KASPER.

SUMMARY

The apparent double-layer capacity at pyrolytic graphite electrodes has been measured over a wide range of frequencies (50–25,000 Hz) in aqueous and in pyridine solutions. The capacity varied with frequency, as did the series resistance; various methods of preparation of the electrode surface were tried, but with no indication that the frequency-dependence could be eliminated along this line of approach to the problem.

It is suggested that the frequency dispersion may be at least in part an effect of electrode geometry since the distribution of current at a disk electrode is not uniform across the surface.

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