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An impedance method for the characterization of porous carbons

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A method is proposed whereby electrode impedance data may be analysed to yield information about the structure and composition of porous electrode materials. The method is more suitable for comparative investigations than as a technique for obtaining absolute values of the total surface area of a porous solid in contact with an electrolyte.

Introduction

The purpose of the present work was to develop and assess a method whereby the effective surface area of a graphite sample could be obtained rapidly and reliably. There already exist several methods of determining surface area data for porous media. The two most commonly applied methods are [1–3]:

(a) the B.E.T. gas adsorption technique, and
(b) the heat of immersion technique.

However, these methods are relatively slow to operate and it was considered preferable to develop a method using impedance measurements, where the material is tested under conditions more closely resembling those in which it is to be used, viz. in an electrochemical cell. Similar methods using potentiostatic pulses have been proposed [4, 5].

It was not envisaged that the present work would lead to highly accurate absolute values of the available surface area. The purpose was to investigate whether interfacial impedance data would reflect the material characteristics, to determine how reliably such data could be used to compare the properties of different samples of material, and also to determine the effect of different impregnants, particularly linseed oil, on these properties.

Theoretical aspects

A porous carbon electrode immersed in an electrolyte can be treated as having a large number of varying pore lengths which are filled with electrolyte. The impedance of a single pore [6] is given by

$$Z_0 = \frac{E_0}{i_0} = (Z_1 R)^{\frac{1}{2}} \operatorname{cotanh} (\rho l_0). \qquad (1)$$

When the interfacial impedance is purely capacitative, i.e.

$$Z_1 = \frac{1}{j\omega C'} \qquad (2)$$

then

$$Z_0 = \frac{(2R)^{\frac{1}{2}}}{(1+j)\,(\omega C')^{\frac{1}{2}}} . \operatorname{cotanh} \frac{(1+j)\,(\omega R C')^{\frac{1}{2}} l_0}{\sqrt{2}} \qquad (3)$$

when $\rho l_0 \gg 1$ the pore appears as semi-infinite to the applied electrical signal and the length of pore which is penetrated by the signal is given by

$$l = \left(\frac{\Gamma}{2\omega\, C_{dl}\, \sigma}\right)^{\frac{1}{2}}. \qquad (4)$$

Thus for $C_{dl} = 17\ \mu\text{F cm}^{-2}$, which is a reasonable value for the double layer capacity of planar carbon surface, and $\sigma = 4{\cdot}75\ \Omega$ cm, the values of the frequency required to penetrate pores of a given depth and radius may be calculated, and are shown in Table 1.

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Table 1.

σ (*Ωcm*)	*Values of r* (*cm*)	*Values of f(Hz) for an a.c. signal which will penetrate to a depth of*		
		0·5 cm	*1 cm*	*2 cm*
4·75	5×10^{-3}	20	4·9	1·2
	5×10^{-4}	2	0·49	0·12
	5×10^{-5}	0·2	0·049	0·012
	5×10^{-6}	0·02	0·0049	0·0012

The total admittance of the carbon sample is $\sum_{n=1}^{n=N_0} \frac{1}{Z_0}$ where N_0 is the total number of pores. For the limit $w \rightarrow 0$, i.e. at a sufficiently low frequency all the pores are penetrated, and

$$\sum_{n=1}^{n=N_0} \frac{1}{Z_0} \rightarrow j\omega C_{dl} A \qquad (5)$$

from which the surface area of the carbon sample can be estimated.

Experimental

Circuit requirements

Since C_{dl} is normally a function of the potential across the interphase, it is important to establish the potential reproducibly in a comparative investigation. A potentiostat (Chemical Electronics type 2A/70) was used. A schematic diagram of the circuit is shown in Fig. 1. A low frequency oscillator (modified Solartron type B0567) was used to supply a sinusoidal voltage of peak to peak amplitude 10 V, at frequencies between 0·01 to 100 Hz. The signal was supplied to the X-plates of an oscilloscope or chart recorder and also (attenuated to 100 or 10 mV) to the potentiostat. The current supplied by the potentiostat to charge the graphite-electrolyte interfacial double layer was monitored by supplying the voltage developed across a 1 kΩ resistor in the potentiostat, to the Y-plates of the oscilloscope or chart recorder.

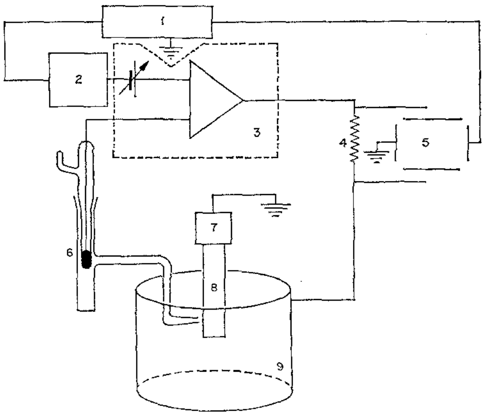

Fig. 1. A schematic diagram of the circuit and cell used with 1 : oscillator (100—10^{-2} Hz); 2 : potential divider; 3 : potentiostat; 4 : 1 kΩ resistor; 5 : oscilloscope or chart recorder; 6 : reference electrode (calomel); 7 : steel holder; 8 : graphite electrode; 9 : platinum counter electrode.

A current voltage ellipse was displayed on the recording instruments, and from its dimensions the interfacial capacitance of the cell was obtained. The overall circuit was conveniently calibrated and checked using a standard capacitor in place of the cell.

The cell

Graphite samples in the form of machined cylinders (1 cm diameter × 4 cm length and 2 cm diameter × 6 cm length) were used. The electrolyte chosen was 2·0 M KCl solution. This electrolyte gives a sufficiently high conductivity for the signal depth of penetration to be as high as is practicable in aqueous solution. The slight advantage resulting from the higher conductivity of more concentrated solutions was offset by the tendency for the electrolyte to crystallize out on, and within, the specimen (thereby altering the effective surface area). Electrical connection to the graphite samples was made by a stainless steel clip positioned at the top of the cylinder, and maintained at least 1 cm above the electrolyte surface. The mean potential of the graphite sample was maintained at that of a calomel reference electrode in 2·0 M KCl. A large platinum cylinder, concentric to the graphite, served as counter electrode. A Luggin capillary was used to take the point of reference close to the graphite surface. Measurements were made at ambient temperature (22±2°C).

Impregnation technique

A vacuum of 0·1 mm Hg was applied to the graphite samples for 30 min., after which KCl solution was admitted to the system until the samples were completely immersed. The graphite samples remained under KCl solution for a minimum of 24 h to allow complete penetration of finer pores by the solution. In the subsequent handling care was taken to prevent air from being admitted into the pore structure. To test the efficiency of the KCl impregnation, certain samples were tested, as described below, cleaned by flushing thoroughly with distilled water, dried, reimpregnated and re-tested. The apparent surface areas were found to differ by less than 3% between the two impregnations, substantiating the belief that the impregnation technique was adequate.

Samples were impregnated to varying degrees with linseed oil by a series of pressure-vacuum cycles, and the percentage voids filled by the impregnant determined, after which KCl impregnation was effected.

Measurement technique

For each type of sample or level of oil impregnation at least six specimens were tested, and the results averaged to eliminate excessive random scatter effects. The dimensions of the current voltage ellipse were recorded at frequencies of 100, 60, 30 . . . 0·01 Hz. At the higher frequencies sufficient sensitivity was obtained using a 10 mV signal level. However, at very low frequencies it was necessary to apply 100 mV to the electrode. The oscilloscope was used to record the current-voltage trace when frequencies between 100 and 3 Hz were used but in the frequency range below 3 Hz the chart recorder was used.

Results and Discussion

Assuming a value of $C_{dl} = 17\ \mu F\ cm^{-2}$, the data obtained in the present work are all expressed as values of the apparent specific area, A', which is the area of graphite available to the signal at a given frequency per unit volume.

Correlation of specific area with volume of sample immersed

It was necessary to test the importance of any anomalies due to solution creeping up to the part of the samples above the electrolyte surface because of capillary action within the pore structure. This was done by varying the depth of sample immersion and measuring the apparent area. Fig. 2 shows the dependence of the interfacial capacitance on the volume of the graphite immersed, at frequencies of 3 and 10 Hz. Within experimental error a linear relationship is observed, confirming that the error arising from the section of sample above the electrolyte level is not significant.

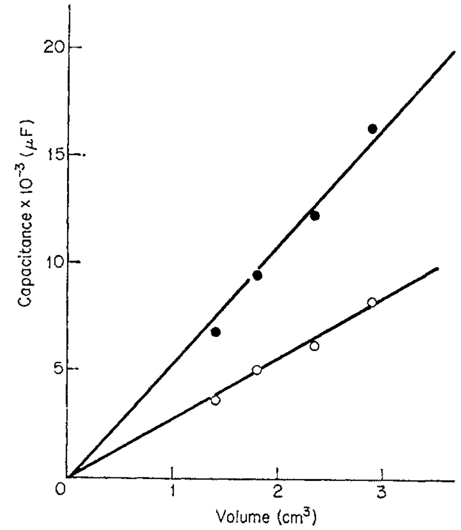

Fig. 2. Dependence of the interfacial capacitance on the volume of electrode immersed in the electrolyte. ● Frequency 3 Hz; ○ Frequency 10 Hz.

Frequency dependence of the impedance

Fig. 3 shows on logarithmic scale the dependence of the apparent specific area on frequency. It can be seen that even at 0·01 Hz the area does not reach a limiting value, showing that even at this

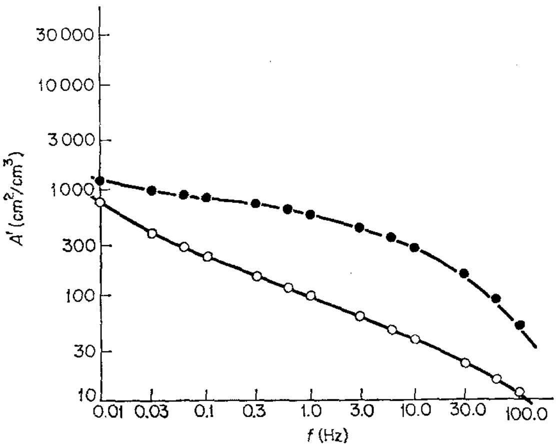

Fig. 3. Dependence of the apparent specific area, A', on frequency for plain (●) and linseed oil impregnated (○) industrial graphite.

frequency complete penetration of the pore structure by the signal is not being obtained. At higher frequencies the apparent specific area falls since the signal is restricted to progressively larger pores. The manner in which the apparent area depends on frequency is characteristic of the pore size distribution of the particular type of graphite used. In Fig. 3 data are shown both for plain and linseed oil impregnated graphite (where the voids-filled level was estimated at 50%). The voids-filled level was estimated by a gravimetric method developed at A.G.L. Ltd., based on the volume available for impregnation by paraffin of known density. It is seen that the linseed oil appreciably reduces the area in contact with the electrolyte. At limiting high frequency the two curves would converge as the apparent area approached the geometric area of the sample. At very low frequencies the value of the apparent surface area estimated from the capacitance approaches that deduced from other physical methods, e.g. the B.E.T. data value for this type of graphite by Krypton adsorption gives A' a value of 4,175 cm^2/cm^3. To apply the method to obtain absolute values of the surface area would necessitate the use of frequencies lower than 0·01 Hz, and would also require an improved accuracy in the knowledge of C_{dl}. Some advantage may result from the use of higher electrolyte concentrations and temperatures. However, the impedance method appears more useful for determination of differences between samples of graphite prepared under varying conditions by identification of the characteristic frequency dependences of their apparent area.

When examining the implications of the data presented in Fig. 3 the effect of the adsorption of neutral species from the linseed oil at the unblocked graphite surface must be considerd. This adsorption may be expected to reduce the effective double layer capacitance of the interphase, and could therefore contribute to the lower surface area results obtained, leading to a degree of uncertainty in the interpretation of the results.

Correlation of impedance data with inert impregnant voids filled level

Fig. 4 shows the variation of the apparent area with the degree of linseed oil impregnation, with the measurements pertaining to a frequency of 0·01 Hz. When the oil content in the sample is low the area measured approaches that of plain graphite, whereas at high oil content, the area approaches a limiting low value as the interior of the graphite becomes increasingly blocked to penetration by the alternating signal. It is seen

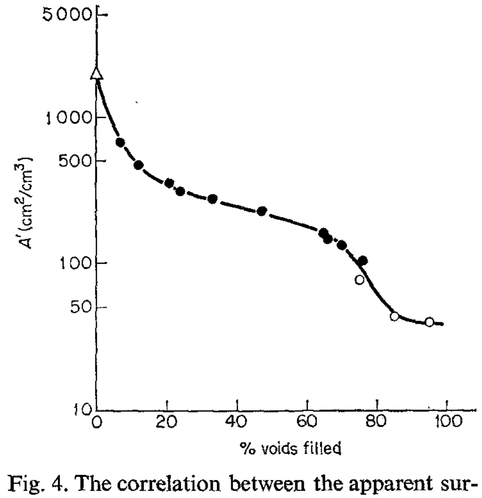

Fig. 4. The correlation between the apparent surface area A' and the percentage of voids filled by the linseed oil at frequency 0·01 Hz. △ : The result corresponding to plain graphite, i.e. zero percentage voids filled; ● : Results of samples which had been impregnated using a linseed oil/ether technique; ○ :Results of samples which had been impregnated using a linseed oil and pressure/vacuum cycle reduction technique.

that there is a monotonic relation between the apparent specific area and the amount of inert impregnant present.

Data at higher frequencies show a similar trend to that of Fig. 4. However, only at the lowest frequencies is the signal able to penetrate to the bulk of the pore structure. Thus higher frequency data will tend to reflect the presence of oil near the exterior of the samples only.

This method can be used to determine the content of an inert impregnant provided that the type of graphite concerned has previously been calibrated by measuring the impedance under conditions where the level of impregnant is known and varied. Under favourable conditions the level of linseed oil present in graphite samples could be estimated to within ±5%.

Acknowledgments

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List of symbols

A	Surface area of the electrode (cm^2)
A'	Apparent specific area of the electrode material (cm^2/cm^3)
C_{dl}	Capacitance per unit area ($F\ cm^{-2}$)
C'	Capacitance per unit pore length ($F\ cm^{-1}$)
E_0	Potential at pore orifice (V)
i_0	Current at pore orifice (Amp)
j	$\sqrt{-1}$
l	Depth of penetration of signal (cm)
l_0	Length of pore (cm)
R	Resistance of electrolyte per unit pore length ($\Omega\ cm^{-1}$)
r	Pore radius (cm)
Z_1	Capacitative impedance per unit pore length (Ω cm)
Z_0	Impedance of pore (Ω)
ρ	$= (R/Z_1)^{\frac{1}{2}}$ Reciprocal penetration depth (cm^{-1})
σ	Electrolyte resistivity (Ω cm)
ω	$2\pi f$ where f = frequency (Hz)

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