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Double layer capacity of graphite in cryolite-alumina melts and surface area changes by electrolyte consumption of graphite and baked carbon

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The double layer (d.l.) capacity of pyrolytic graphite in cryolite-alumina melts at 1010°C was found to exhibit a minimum of 20 μF cm^{-2} at 0·9 V positive to the aluminium electrode. The d.l. capacity attained a plateau of ~60 μF cm^{-2} at 1·1–1·4 V, while it rose steeply at potentials below 0·7 V. During electrolytic consumption involving CO_2 evolution the d.l. capacity of pyrolytic graphite remained unaffected, while that of baked carbon was changed, reflecting changes in surface area. At low current densities (cds) the surface area increased substantially and the surface was noticeably roughened, while the opposite behaviour was observed at above 2·5 A cm^{-2}.

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1. Introduction

When a carbon electrode dipping into a $Na_3AlF_6-Al_2O_3$ melt is polarized anodically, evolution of CO_2 will occur [1, 2] according to the reaction

$$Al_2O_3+3/2\ C=2\ Al+3/2\ CO_2 \qquad (1)$$

and liquid aluminium will be deposited at an aluminium cathode. The reversible e.m.f. of this reaction at 1010 °C is 1·163 V [3]. The anodic reaction is accompanied by appreciable overvoltage, amounting to 0·3–0·4 V at 0·5 A cm^{-2} [4]. The overvoltage is apparently caused by a slow chemical reaction at the anode [4].

A carbon electrode might be expected to be ideally polarizable in the potential range between CO_2 evolution and aluminium deposition, and this is shown on the potential scale given below [3, 5]

−0·27V	0	+1·16V	+2·20V
Na	Al	C,CO_2	Pt(O_2)

However, subvalent species can be formed at potentials positive to that of aluminium deposition [6]. Furthermore, carbon exerts a depolarizing effect on sodium deposition, because sodium is soluble in carbon. Therefore, appreciable cathodic currents begin to flow before the aluminium deposition potential is reached, e.g. 40 mA cm^{-2} at 0·3 V.

The surface of ordinary graphite and carbon materials has a certain roughness, which can vary within rather wide limits. For this reason d.l. capacity data may show considerable variation, since the d.l. capacity will reflect the area wetted by the electrolyte. During electrolysis the surface roughness will normally change, due to uneven electrolytic consumption [4]. The change can be estimated by measuring the d.l. capacity before and after electrolysis, as outlined in the following.

The available literature data on the d.l. capacity of carbon and graphite in cryolite-alumina melts show considerable variation. Rempel and Khodak [7, 8] found the d.l. capacity of carbon in cryolite-alumina melts to be about 20 μF cm^{-2}, with odd values as low as 15 and as high as 70 μF cm^{-2}. By electrolysis of

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carbon anodes the d.l. capacity increased tenfold, and it increased further by 50% when the current was interrupted. Drossbach *et al.* [9, 10] reported the average value on graphite in a 65% Na_3AlF_6, 30% Li_3AlF_6, 5% Al_2O_3 melt to be 20 μF cm^{-2} at anodic cds below 1 mA cm^{-2}, rising to a maximum of 70 μF cm^{-2} at 5 mA cm^{-2}. The present author [4] showed that the d.l. capacity depended greatly on the carbon material; it varied from approximately 40 μF cm^{-2} on vitreous carbon to 350 μF cm^{-2} on ordinary graphite and baked carbon. Recent data by Vetyukov and Akgva [11, 12] on the d.l. capacity of vitreous carbon at varying melt composition and potential will be discussed in Section 2.2.

The purpose of the present investigation was to determine the d.l. capacity as a function of the applied potential, and to use d.l. capacity measurements for assessment of changes in surface area during electrolysis.

2. Double layer capacity

2.1. *Experimental technique*

The chemicals used were hand-picked natural cryolite, reagent grade alumina and super purity aluminium. The experimental cell shown in Fig. 1 was placed in a wire-wound furnace at 1010 °C under a nitrogen atmosphere. The cryolite melt saturated with alumina (~14 wt % Al_2O_3) was contained in the graphite crucible H, which also served as counter electrode. The working electrode E was enclosed in boron nitride, so that only the lower surface of the graphite rod of 0·5 cm^2 was exposed to the melt.

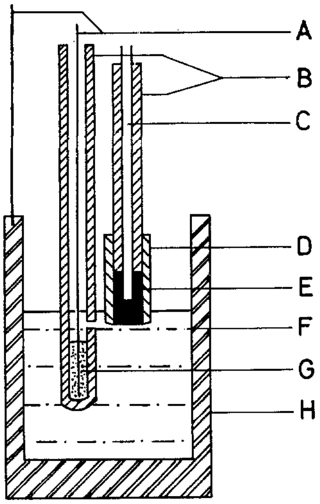

Fig. 1. Experimental cell for d.l. capacity measurements. A, Mo wire; B, alumina tubes; C, steel rod; D, boron nitride shield; E, working electrode, pyrolytic graphite; F, cryolite-alumina melt; G, aluminium reference electrode; H, graphite crucible, counter electrode.

The polarizing potential applied to the cell was measured against the aluminium reference electrode G, which was housed in an alumina tube. Likewise, the unpolarized reference electrode was used in the determination of the a.c. impedance arising from an a.c. current of low amplitude imposed on the cell. The d.l. capacity of the working electrode was evaluated from the impedance data for the frequency range 0·8 to 35 kHz according to procedures described previously [4].

2.2. *Results and discussion*

The most reproducible results were obtained with electrodes made of pyrolytic graphite (High Temperature Materials Inc.) with the basal plane facing the melt. In Fig. 2 the d.l. capacitance is plotted versus the polarization potential referred to aluminium. The polarizing current is indicated below. Only in a fairly narrow range is the electrode ideally polarizable in the sense that no appreciable current flows.

The capacity exhibits a minimum of approximately 20 μF cm^{-2} at around 0·9 V. The capacity rises steeply at potentials below 0·7 V. Such

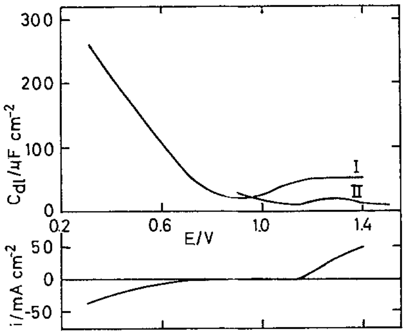

Fig. 2. d.l. capacity of pyrolytic graphite in cryolite-alumina melts versus potential, referred to the aluminium electrode. Curve I, the present work. The corresponding polarizing current is given below. Curve II, data obtained by Vetyukov and Akgva [12] on vitreous carbon in melts with NaF/AlF_3 molar ratio 2·5.

behaviour is not uncommon in molten salt systems and has been attributed to specific adsorption of cations [13]. In the present case this branch of the curve was not very reproducible, and the result depended to a certain extent on the time the electrode had been subjected to the cathodic current. When the potential subsequently was made more anodic, the d.l. capacitance was higher than before the cathodic polarization was started. This behaviour can probably be ascribed to pick-up of sodium by the electrode, causing a disruption of the surface. Signs of such disruption were clearly visible on electrodes that had been polarized cathodically for some time.

In the anodic region the d.l. capacity attained an approximately stable value of around 60 μF cm^{-2}. This value is in agreement with previous results [4]. The potential range above 1·4 V, corresponding to cds higher than 50 mA cm^{-2}, was not accessible for accurate measurements, because the gas evolution gave rise to rapid potential oscillations which disturbed the reading of the phase angle on the oscilloscope [4].

As mentioned in the introduction Vetyukov and Akgva [12] determined the d.l. capacity of vitreous carbon in melts with a NaF/AlF_3 molar ratio of 2·5 for potentials from 0·9 to 1·5 V referred to aluminium. The shape of curve II, Fig. 2, indicates that the capacity minimum, corresponding to the potential of zero charge, is shifted towards higher potentials in this melt. Concerning the numerical values, Vetyukov and Akgva [11] reported the d.l. capacitance of vitreous carbon in cryolite ($NaF/AlF_3 = 3$) to be 40 μF cm^{-2}, which is in agreement with the findings of the present author [4].

3. Surface area changes by electrolysis

3.1. *Introduction*

A carbonaceous anode is consumed during electrolysis according to Equation (1). It has been shown that the working surface of baked carbon anodes of the type used in aluminium production becomes noticeably roughened during electrolysis at normal cds [14–16]. This anode material contains two carbon phases, one being the aggregate coke, the other originating from the pitch binder.

Visual examination can give only a rather rough estimate of the changes in surface area during electrolysis. A more quantitative measure can be obtained by determining the d.l. capacity before and after electrolysis. The change in capacity can then be taken as roughly proportional to the change in contact area with the melt.

3.2. *Experimental technique*

The anode was enclosed in a boron nitride cylinder as shown in Fig. 3, to ensure that the geometric area did not change when the electrode was consumed. The cylinder was inclined slightly upwards and furnished with a hole at the bottom in order to facilitate the circulation of electrolyte and the escape of gas bubbles from the anode. If the cylinder was put in a horizontal position the upper part of the anode was hardly consumed, probably due to adhering gas bubbles.

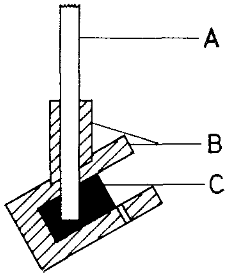

Fig. 3. Anode arrangement for surface area studies. A, steel rod; B, boron nitride shield; C, carbon anode.

3.3. *Results*

Preliminary tests were performed with graphite anodes at cds in the range 0·6–1 A cm^{-2}. The surfaces of anodes made of pyrolytic graphite, with the basal plane exposed to the melt, retained to a large extent their lustrous appearance after electrolysis, and the d.l. capacity did not change appreciably. However, a microscopic examination revealed that preferential attack had occurred to a certain extent, particularly at the grain boundaries. Anodes made of ordinary graphite (AUC, Union Carbide) acquired a peculiar appearance with a dense assembly of needle-shaped protrusions. The protrusions were easily detached from the surface, so a systematic study of the d.l. capacitance was not carried out. Results obtained after electrolysis at 1 A cm^{-2} indicated changes in the d.l. capacitance roughly similar to that found for baked carbon, as described below.

Because of the industrial application of baked carbon, the investigation was concentrated on this material. Samples of normal grade anodes were used, made of petroleum coke with 17% pitch and baked at 1250 °C. The density was 1·5 g cm^{-3}. After a short pre-electrolysis the d.l. capacity was measured at a slight anodic polarization of 1·2 V. The anodes were then electrolysed until 2·7 Ah cm^{-2} had been passed, which corresponds to an average wear of 2 mm. Cds from 0·3 A cm^{-2} to 4 A cm^{-2} were applied. After electrolysis the d.l. capacity measurement was repeated.

The d.l. capacity before electrolysis was on average 140 μF cm^{-2}. This is somewhat lower than data given previously [4], obtained with another make of carbon. The change in d.l. capacity in per cent is depicted in Fig. 4 as a function of the cd during electrolysis. Taking the change in d.l. capacity as a measure of the change in surface area during electrolysis, it is seen that the surface area increases at low and medium cds and decreases at high cds. The intercept with the dotted line, representing no net change in surface area, occurs around 2·2 A cm^{-2}. This value probably depends on the carbon quality and to a certain extent on the way in which the samples are prepared. In the present investigation the samples were cut on a lathe.

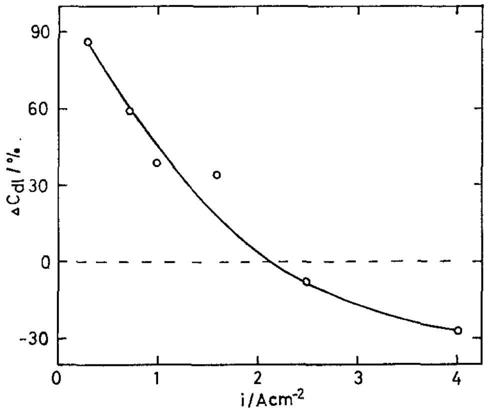

Fig. 4. Changes in d.l. capacity (in per cent) of baked carbon anodes, after passage of 2·7 Ah cm^{-2} of electricity at various cds.

There was considerable scatter in the results, particularly at low cds, and up to 8 replicate runs were made in order to establish the average values given in Fig. 4. The standard deviation was 18%. A major reason for this large scatter was undoubtedly the inhomogeneity and the unevenly distributed porosity of the baked carbon. The assessment of the d.l. capacitance was also difficult in some cases. The capacity tended to decrease gradually with increasing frequency, and the range where it attained an approximately stable value was narrow. This frequency dispersion can probably be ascribed to the fact that these samples were porous, since much better results were obtained with pyrolytic graphite.

The trend in surface area change indicated by the d.l. capacity data was supported by microscopic examination. Anodes subjected to low cds exhibited large voids which probably originated from pores that had been enlarged. In addition a multitude of small protruding coke grains were observed, which normally extended about 0·2 mm from the surface. In contrast, the surfaces of samples electrolysed at high cds were remarkably smooth, although enlargement of pores occurred also in that case. Cammarota and Schlain [15] observed numerous protruding coke particles on carbon anodes electrolysed at 0·4 A cm^{-2}, but hardly any at 1·6 A cm^{-2}. The same trend was observed in the present work, although surfaces completely free from protrusions were not obtained until the cd was raised to 2·5 A cm^{-2}.

3.4. *Discussion*

The surface roughening occurring during electrolysis of anodes made of ordinary graphite and baked carbon is due to uneven consumption of the anode material. The microscopic examination indicated that the protruding parts on baked carbon anodes consisted of grains of aggregate coke, i.e. the binder phase seemed to have been preferentially consumed. It has been established that the binder phase is more reactive towards oxygen and carbon dioxide than the aggregate coke phase. Assuming that the same would be true of electrolytic oxidation, Bowitz and Sandberg [17] suggested that the binder phase is selectively consumed, and that grains of aggregate coke may become detached from the anode.

The anodic overvoltage has been found to be due to some kind of slow chemical reaction [4]. It is then reasonable to assume that the more reactive parts of the anode will exhibit a lower overvoltage and consequently acquire a higher cd than average, which gives rise to preferential attack. This effect will be counteracted by the ohmic resistance term which will favour attack on the protruding parts. Reaction in pores and voids can also be retarded by mass transport, particularly the slow removal of gas bubbles. As the cd is increased these latter factors become increasingly important, so that the tendency to preferential attack and reaction in pores will be diminished. Thus the well-known polishing ability of high cds will come into effect, and apparently dominate at cds above 3 A cm^{-2}.

The uneven consumption of anodes made of AUC graphite can be explained along the same lines. Oxidation tests in air at high temperature show that this material, like any other ordinary graphite, is unevenly attacked. Also baked carbon is subjected to pronounced selective oxidation in air, while the lustrous surface of the basal plane of pyrolytic graphite is maintained. This is analogous to the behaviour during electrolysis.

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