1083. *Electrochemical Preparation of Salts from Well-oriented Graphite.*

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With well-oriented pyrolytic graphite, electrochemical methods permit the convenient preparation of graphite salts. Methods are described for obtaining graphite compounds of sulphuric, chloro- and fluoro-sulphonic, selenic, perchloric, and nitric acid and the complex acid $BF_3,2AcOH$. Progress of the reaction can be followed by measuring voltage differences; the nature of the end product can be studied by *X*-ray diffraction methods.

In a number of cases more than one stage of salt formation can be achieved by controlled electrolysis. Double decomposition can also be used to replace one acid, intercalated by electrolysis, to form a graphite salt of another acid. Qualitative observations indicate that similar methods probably afford other graphite salts, such as those derived from trifluoroacetic, arsenic, periodic, phosphoric, and pyrophosphoric acid.

ALTHOUGH salts of graphite with acids have been known for over a hundred years,[1] convenient methods of preparation are somewhat elusive. One reason is that a large increase in distance between the carbon-hexagon networks occurs on formation of any crystalline compound of graphite. This precludes the use of polycrystalline graphite as starting material for electrochemical methods, because the electrodes crumble before the higher stages of oxidation can be attained. Conventional methods using strong acids and various oxidising agents such as CrO_3, Mn^{3+}, and HIO_4, have led to the identification of various inorganic salts, prepared from flake or powdered graphite.[2] A study of their structure has been made, mainly by powder *X*-ray diffraction.[3]

The bisulphate and perchlorate have been prepared electrochemically by using well-oriented pyrolytic graphite,[4] and natural single crystals of graphite have been used for electrolytic preparation of the hydrogen sulphate.[2] However both the above electrolytic procedures involved other conditions that are not relevant to the general preparative chemistry of these compounds. The present paper describes the electrochemical formation of a number of salts of graphite from well-oriented pyrolytic graphite, and illustrates the possibilities and difficulties. Progress of the reaction can be followed fairly simply and the compounds are obtained in a compact form convenient for study.

EXPERIMENTAL

Well-oriented pyrolytic graphite was prepared by pyrolysis of short-chain hydrocarbons at ~2100°C, followed by annealing at higher temperatures,[5,6] and consisted of crystallites of near-ideal graphite with random *a*-axis orientation but with good *c*-axis parallelism. Specimens ($1·0 \times 0·5 \times 0·01$ cm.) were used for preparative work only if they gave *X*-ray diffraction patterns near to those of a single-crystal *c*-axis rotation pattern (Plate a), and provided they showed a positive temperature coefficient of electrical resistance in the basal planes. The thermal expansions of such specimens along the *c*-axis were measured by *X*-ray diffraction and agree within 0·5% with values predicted for natural single crystals.[7] Well-crystallised starting material was chosen because network disorder within the crystallites and disorder of their c-axes can obstruct crystal-compound formation [8] and may affect some of the physical properties of the products.[4] Disorder in the starting material is also likely to weaken or destroy the *X*-ray diffraction pattern used to characterise the products.

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[1] Schafhäutl, *J. prakt. Chem.*, 1840, **21**, 155.
[2] Rüdorff and Hofmann, *Z. anorg. Chem.*, 1938, **238**, 1.
[3] Rüdorff, *Z. phys. Chem. (Leipzig)*, 1939, *B*, **45**, 42.
[4] Blackman, Mathews, and Ubbelohde, *Proc. Roy. Soc.*, 1960, *A*, **258**, 329.
[5] Blackman, Saunders, and Ubbelohde, *Proc. Roy. Soc.*, 1961, *A*, **264**, 19.
[6] Blackman and Ubbelohde, *Proc. Roy. Soc.*, 1962, *A*, **266**, 20.
[7] Nelson and Riley, *Proc. Phys. Soc.*, 1945, **57**, 477.
[8] Saunders, Ubbelohde, and Young, *Proc. Roy. Soc.*, 1963, *A*, **271**, 499.

Selected specimens (0·02—0·05 g.) of graphite were weighed, measured, and placed in sliding contact with the 24-gauge platinum wire (B in Fig. 1), forming the anode. A thinner wire would help to reduce losses from electrolytic side reactions but is a less effective support. A second, larger piece of graphite C (~2 × 1 × 0·1 cm.) was cut from a well-oriented deposit of pyrolytic graphite (not, however, specially selected), and served as a floating reference electrode. The anode and cathode compartments were separated by a sintered Pyrex disc (porosity 1); bright platinum foil was used as cathode at A.

Great care was necessary in controlling the composition of the electrolyte; the best conditions observed with each of the acids used are detailed under the individual compounds below. In general, if the electrolyte was allowed to absorb too much water, side reactions during electrolysis competed to an undesirable extent with the primary electrochemical reaction. Moisture also impaired the stability of the acid salts on storage after the completion of electrolysis.

The electrolytic reaction was carried out by one of two methods:

(i) A current, constant to ±2%, was passed continuously through the cell, by applying a D.C. voltage (H.T. Battery) of 24—36 v to the cell, in series with a 10^5 ohm resistance inserted to render insignificant any changes of the internal resistance of the cell during electrolysis.

(ii) A fixed voltage, usually 1·5 or 3·0 v (from dry cells), was applied across the cell, with only a small resistance (5000 ohms) in series, as shown in Fig. 1. Both the cell current, and the voltage developed between the specimen B and the reference electrode C, were recorded continuously.

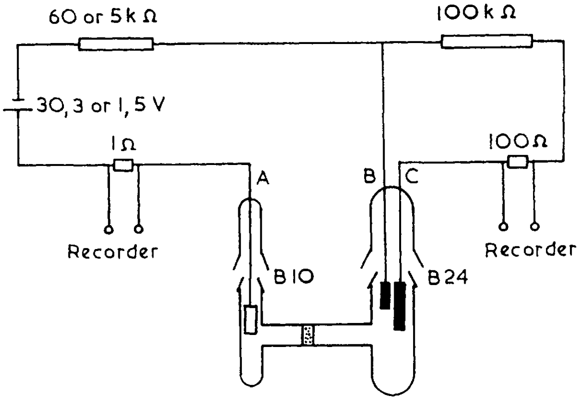

FIG. 1. Schematic diagram of preparation cell and associated electrical circuits.

Comparisons between runs at current densities of 500 and 50 μA/cm.^{2} showed very similar voltage–current plots in the case of the hydrogen sulphate. Rather better resolution of the plateaux observed in the early stages of compound formation was obtained with the lower current density, but this was normally used only when the formation of the lower oxidation states was of particular interest.

For the investigation of *X*-ray diffraction patterns, specimens were quickly transferred from the anode compartment to a satchel (~2 × 1 cm.) formed by heat-sealing polychlorotrifluoroethylene foil (0·03 mm. thick). Acid carried over with the specimen in this transfer helped to maintain anhydrous conditions inside the satchel. Photographic examination of the *X*-ray diffraction patterns from specimens prepared in this way normally showed no deterioration for up to 2 weeks, provided the acid salt itself did not decompose spontaneously.

For more accurate measurements of lattice spacings, the salts were prepared *in situ*, in the same electrochemical conditions, but with the graphite held in a special cell which could be mounted directly on a proportional-counter *X*-ray diffractometer. These studies are being described elsewhere.

Chemical Composition and Nomenclature of the Salts of Graphite and Acid.—In accord with Rüdorff and Hofmann's proposals,[2] crystal compounds in which every layer between the carbon-hexagon networks is filled are designated in the present paper as " first sequence " (" erste Stufe "); when every second layer is filled the compounds are designated as " second sequence," and so on.

Accurate chemical analysis of these crystal compounds proved difficult; if completely separated from the circumambient strongly acidic electrolyte, they decomposed quite rapidly. Mere immersion of the graphite compound in the analytical reagents is not adequate to remove all the intercalated species.[8-10] Accurate chemical analysis thus requires destruction of the graphite networks and does not always lead to meaningful results in view of the instability of the compounds during handling. On the basis of special analytical techniques, the formula $C_{24}{}^{+}HSO_4{}^{-}(2H_2SO_4)$ has been put forward for the first-sequence bisulphate.[2] In this formula, the oxidation state of the graphite can be established with fair accuracy, but even if the above limiting chemical formula describes the oxidation state correctly, the precise number of additional H_2SO_4 molecules packed between the carbon-hexagon networks is less certain. By analogy with graphite–bromine [8] the spatial arrangement of such additional molecules packed within each intercalated layer is likely to depend on the sequence of formation reactions used.

It therefore seemed unprofitable to attempt to determine what " acid of crystallisation " was present in the preparations. Instead, two other methods have been used for identifying the compounds obtained.

(i) Graphs showing the voltage difference between the compound and the reference electrode as a function of the integrated charge passed per g.-atom of graphite showed breaks which often coincided with colour changes in the product. When electrolytic side reactions had been eliminated (or allowed for) these breaks could be correlated with the coulombs per carbon atom needed to reach specific stages in the electrochemical oxidation. Such correlation permitted assignment of the composition of the oxidation product $C_n{}^{+}A^{-}$, where A is the anion, but did not, of course, give any direct information about the intercalation of additional molecules of acid between the layers. This question is left open in what follows.

Since the limiting-sequence compound for many of the acids investigated appears to lie at $C_{24}{}^{+}A^{-}$, the integrated charge per carbon atom at given times has been plotted as a fraction of the total charge required to form this compound in conditions where no loss occurred by side reactions during electrolysis.

(ii) *X*-Ray diffraction patterns of the crystal compounds were obtained in every case. The 00*l* spacings confirmed changes in the distance between carbon-hexagon networks due to intercalation of the acid anions, either directly, as in the case of the first-sequence compounds, or indirectly, as for compounds of other sequences, if we assumed unfilled layers to have the normal graphite separation. In most cases, *hkl* reflexions were observed, showing that the individual crystallites had some degree of three-dimensional order. Except in the case of the first-sequence bisulphate, no *hkl* superlattice reflexions were observed, but the question of whether the intercalated molecules are ordered relative to the carbon lattice is not relevant to the use of the technique for chemical identification, and will not be discussed here.

Graphite Bisulphate.—Preparation of this salt by other methods has been frequently described. Nevertheless it was considered desirable to explore optimum conditions for preparation by the present electrolytic techniques, in view of the accurate control of composition they permit under favourable circumstances, and also because salts with other acids can be prepared from the bisulphate by double decomposition (see below). Electrolysis was best carried out in 100% sulphuric acid (Griffin and George). Fig. 2 records a plot of the voltage measured between electrodes B and C against the quantity of electricity passed. Clear breaks can be observed at X (where the solid first suddenly acquires a blue colour) and at Y. *X*-Ray-diffraction photographs of samples electrolysed under similar conditions showed only the structure of the first-sequence compound $C_{24}{}^{+}HSO_4{}^{-}(2H_2SO_4)$ at Y (Plate b). No further change could be detected in the pattern, or in the 00*l* spacings, in the interval from Y to Z. This interval was found to vary without any obvious relation to the mass of the graphite used. Provisionally, it seems likely that the portion of the curve in Fig. 2 beyond Y refers to the build-up of an oxygen overvoltage, and not to the formation of an oxidation stage higher than $C_{24}{}^{+}HSO_4{}^{-}$.

The break at X corresponds to completion of formation of the second-sequence compound $C_{48}{}^{+}HSO_4{}^{-}(nH_2SO_4)$ and the onset of formation of the first sequence. Formation of the second-sequence compound was verified by *X*-ray diffraction; the diffraction lines were, however, too weak for reproduction here. A less distinct break at W (Fig. 2) is probably due to

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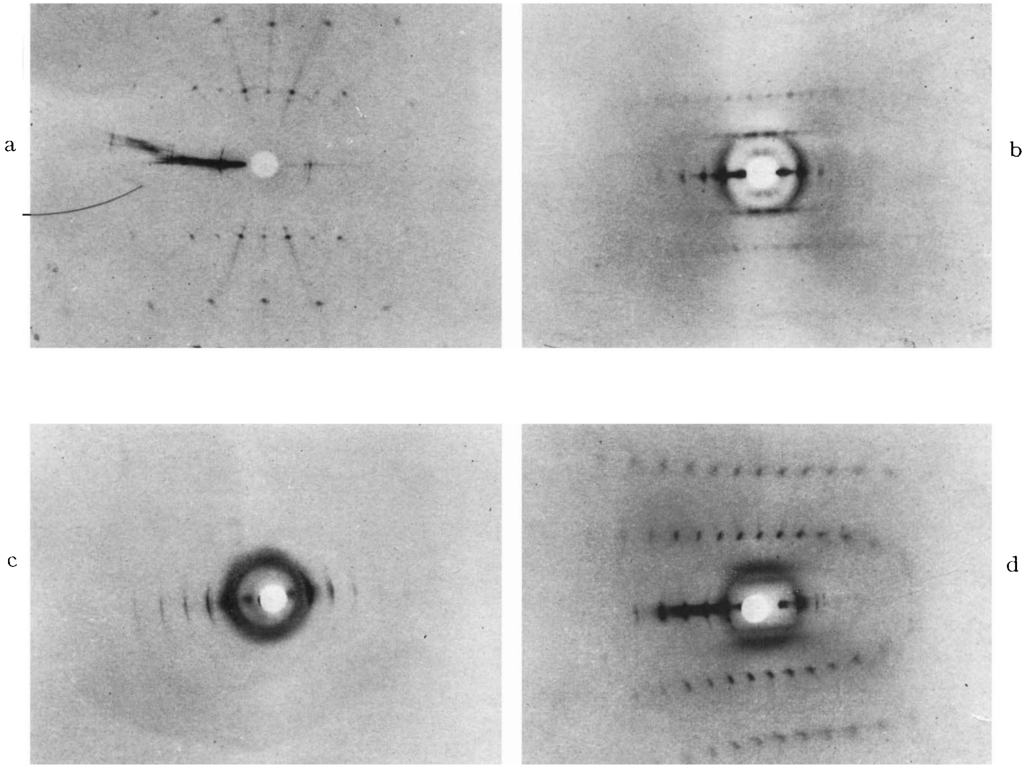
[9] McDonnell, Pink, and Ubbelohde, *J.*, 1951, 191.

[10] Hennig, *J. Chem. Phys.*, 1951, **19**, 922.



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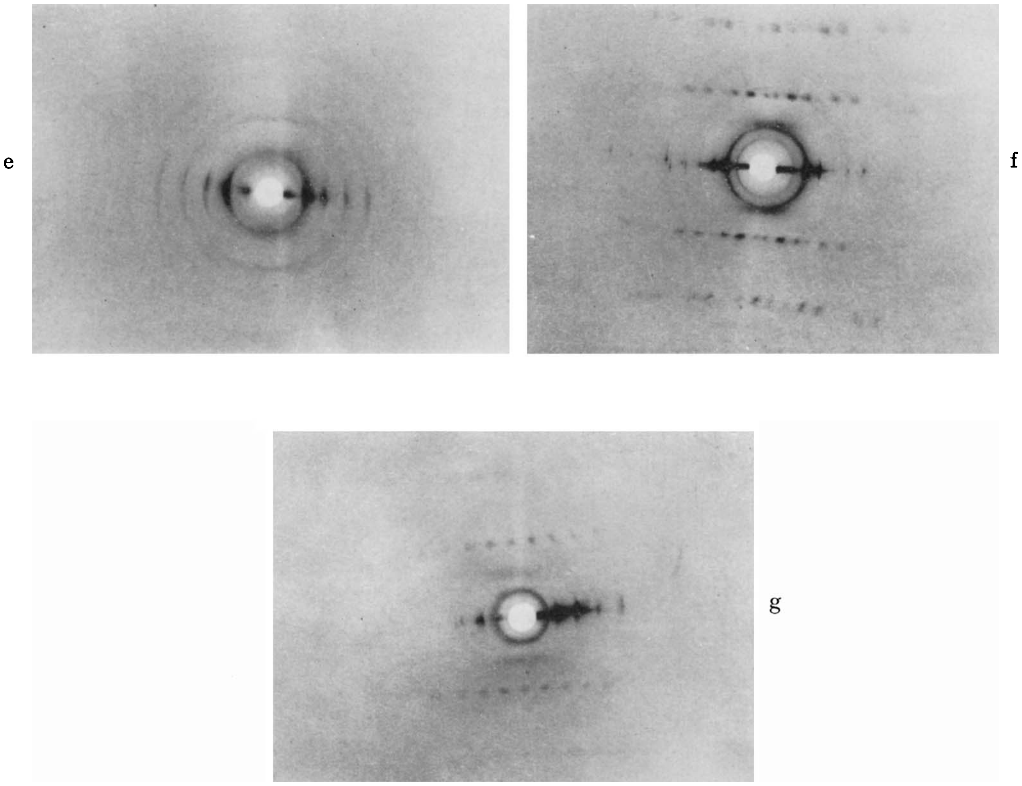

Diffraction photographs of stationary specimens recorded with Mo-K radiation (Zr-filtered except for A) on flat film. In all cases the c-axis is approximately horizontal and perpendicular to the beam. The random a-axis orientation of crystallites in any specimen gives rise to a diffraction pattern that is effectively a c-axis rotation photograph of a single crystal.

(a) Pyrolytic graphite, type AB, as used for preparations. (b) Graphite hydrogen sulphate, first sequence. The superlattice hkl reflexions are clearly visible. (c) Graphite chlorosulphate, first sequence. (d) Graphite perchlorate, first sequence. (e) Graphite perchlorate, first sequence. Double-decomposition preparation. (f) Graphite nitrate, first sequence. (g) Graphite nitrate, second sequence.

completion of a third sequence, $C_{72}{}^{+}HSO_4{}^{-}(nH_2SO_4)$; but no attempt was made to verify this by *X*-ray diffraction methods. Fig. 2 further indicates that when 24 v were applied across the cell, the total current passed was ~25% in excess of the theoretical quantity of electricity calculated for completion of the various sequences. This excess can be attributed (at least in part) to the evolution of oxygen or formation of peracids at the platinum anode surface above the graphite specimen.

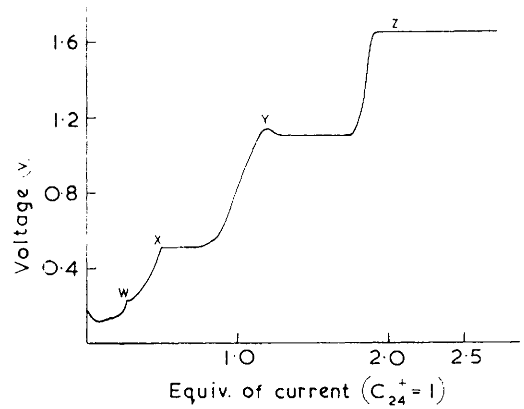

FIG. 2.

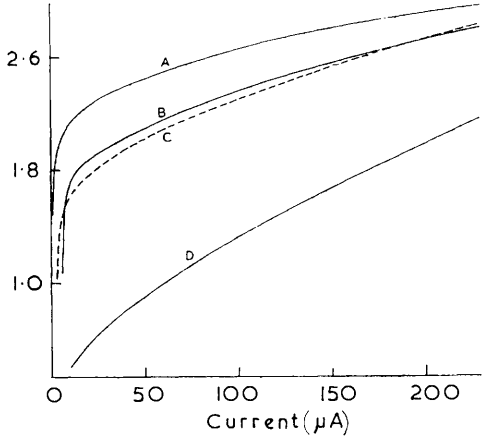

FIG. 3.

FIG. 2. Voltage–current curve for the formation of graphite hydrogen sulphate.

FIG. 3. Current flowing through cell, with bright platinum electrodes, as a function of applied voltage for various strong acids.

A, 100% H_2SO_4; B, $HClO_4$; C, 98% H_2SO_4; D, $ClSO_3H$.

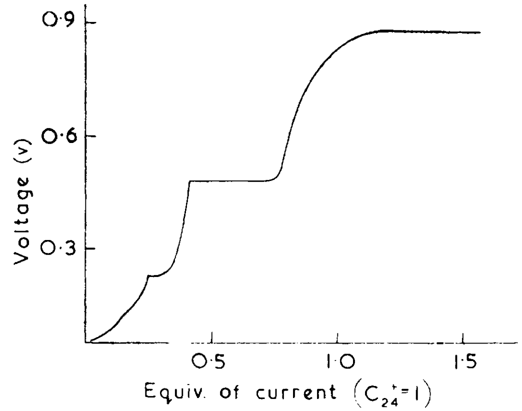

FIG. 4.

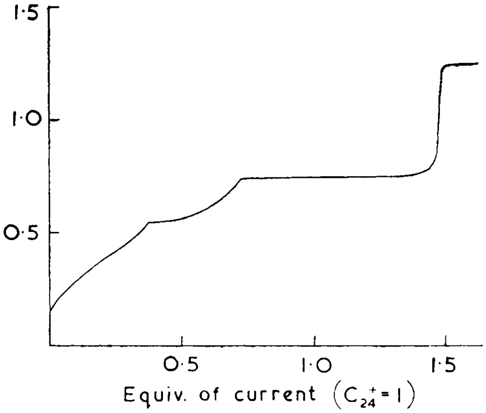

FIG. 5.

FIG. 4. Voltage-current curve for graphite chlorosulphonate.

FIG. 5. Voltage–current curve for graphite selenate.

In the absence of graphite, only a small current (5—10 μA) passed for an applied E.M.F. of 2 v (Fig. 3). When this low driving potential was used for the formation of bisulphates, the excess of coulombs passed beyond the quantities required for the formation of the crystal compounds corresponded quite closely to the discharge processes on the surface of the platinum support. However, such small E.M.F.s, though necessary to establish the amount of charge transfer, were inconvenient and time-consuming for general preparative purposes. Fig. 3

shows the effect of increased driving voltages on the current flowing between bare platinum electrodes in various strong acids.

Graphite Chlorosulphates.—With 100% chlorosulphonic acid (B.D.H.; 99·5% acid, 95% chlorine), the higher-voltage technique was more suitable, despite the fact that, with this electrolyte, application of 24 v led to a much larger excess current than with 100% sulphuric acid (cf. Fig. 3). This excess corresponds with a reduced efficiency of formation of graphite chlorosulphonate $C_{24}^{+}SO_3Cl^{-}n(ClSO_3H)$ in the present apparatus. Fig. 4 shows the final plateau corresponding with $C_{24}^{+}SO_3Cl^{-}$, with breaks for the second- and third-sequence compounds. Formation of the first-sequence compound was verified by *X*-ray diffraction (Plate c).

Graphite Selenates.—Preparation of these crystal compounds by electrolysis called for particularly careful control of the conditions. At room temperature commercial 100% selenic acid crystallised in the cell, particularly around the sintered disc which provided numerous nucleation centres. Raising the temperature kept this electrolyte molten, but above 30° no first-sequence compound was formed, presumably owing to its instability at this temperature or to competitive side reactions at the graphite anode. As the acid was progressively diluted with distilled water, the efficiency of electrochemical oxidation decreased rapidly. A workable compromise was to add just sufficient distilled water to keep the electrolyte " liquid " at 25°, and to electrolyse at this temperature with an applied voltage of 1·5 v so as to minimise side reactions. As illustrated in Fig. 5, a charge-transfer efficiency of $\sim$85% was achieved in these conditions; in some experiments, the sharp rise at the end of the preparation illustrated in Fig. 5 was sometimes more gradual. Other evidence suggests that this rise is a function of the structural perfection of the starting material.

With this crystal compound it was important to stop electrolysis at the end-point, to avoid rapid exfoliation. As in the case of the acid sulphate, the final plateau observed in the plot in Fig. 5 was probably due to oxygen overvoltage. For both acids, a tentative hypothesis is that the peracid radical $[SO_3(OOH)]^-$ or $[SeO_3(OOH)]^-$ begins to intercalate between the carbon-hexagon networks when formation of the first-sequence compound is complete. However, this would be a highly unstable system, especially for perselenic acid. The exfoliation may be due to liberation of oxygen in this decomposition within the specimen.

The problem of stopping electrolysis before serious degradation of the sample takes place was not easily overcome for the selenate. Unlike the bisulphate and perchlorate, with which either a fairly sharp plateau or clear peak marked the completion of formation of $C_{24}^{+}A^{-}$, the selenate only rarely showed a break, apparently owing to the proximity of the overvoltage potential. This aspect of the preparation of graphite biselenate has not been examined further, mainly because *X*-ray-diffraction photographs of all preparations showed no *hkl* reflexions. By analogy with the preparation of graphite perchlorate, discussed below, the best route to graphite hydrogen selenate seems to be double decomposition of graphite bisulphate and selenic acid.

Fig. 5 also illustrates breaks which mark the complete formation of two crystal compounds with longer sequences than the first. It was interesting that the second-sequence compound was also blue, unlike most of these salts with acid but like alkali-metal derivatives of graphite.

Graphite Perchlorates.—When 70% perchloric acid and a driving voltage either of 24 v or 1·5—3 v were used, the preparation proceeded, with a loss in side reactions of 5—10% of transferred charge, to the stage where a peak corresponding with the first-sequence compound was reached (Fig. 6). As in the case of the selenate, electrolysis beyond this stage led to rapid breakdown, probably involving decomposition of the perchlorate radicals within the specimen. Water liberated in such decomposition further accelerates breakdown, so that it soon becomes catastrophic. Attempts to lower the concentration of " free " water by adding anhydrous magnesium perchlorate reduced neither the side losses nor the decomposition beyond $C_{24}^{+}ClO_4^{-}$. *X*-Ray diffraction patterns were obtained for the first-sequence (Plate d) and higher-sequence compounds prepared by electrolysis.

Graphite Nitrates.—Immersion of well-oriented pyrolytic graphite in fuming nitric acid (*d* 1·52) led to the formation of the second-sequence compound directly, by chemical oxidation (Plate g). Therefore, with the second-sequence compound as reference electrode, formation of the first-sequence compound (Plate f) could be carried out by electrochemical oxidation with fuming nitric acid partly dehydrated by phosphorus pentoxide, which resulted in the formation of some (about 10%) nitrogen pentoxide in solution. The graphite nitrate first-sequence compound did not appear to be very stable even in this acid (see below). It proved practicable to form the first-sequence compound by passing a fairly high current (500 μA) with a 24 v driving potential and continuing the reaction until the E.M.F. referred to the secondary electrode ceased to rise. The correlation between the weight of sample and the total charge transferred was not good, probably because of the instability of the first-sequence compound in contact with nitric acid. Completely reproducible preparation of the first-sequence compound may demand the use of nitric acid containing some 50% of nitrogen pentoxide in which the compound is reported to be stable.[2] We have confirmed that direct formation of the first-sequence compound occurs when the graphite is immersed in this solution, but this preparation is much less convenient than electrolysis.

X-Ray diffraction photographs showed that at room temperature the second-sequence nitrate was stable indefinitely in contact with fuming nitric acid, but that in these conditions the first-sequence compound reverted to the second-sequence compound during 1—3 days. It may, however, be preserved if the excess of acid is drained away after completion of the electrochemical preparation and the solid is then stored in a sealed glass tube.

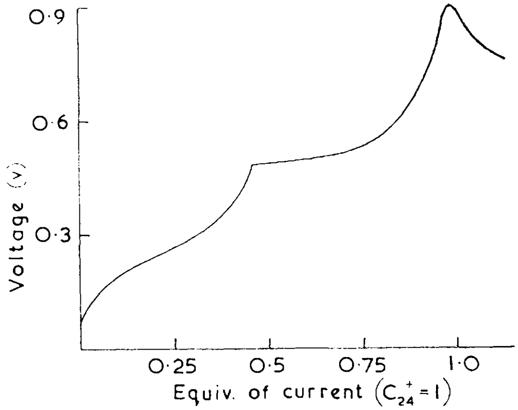

FIG. 6. Voltage–current curve for graphite perchlorate.

Graphite nitrates can also be prepared by double decomposition from the stage 1 hydrogen sulphates, as described below.

Formation of Salts with Other Acids by Electrochemical Oxidation of Well-oriented Graphite.—It seems likely that salts with a number of other acids can be prepared by similar electrochemical procedures, provided suitable electrolytes can be found. Mention is made here of preliminary studies which illustrate the kind of obstacles encountered.

Graphite Fluorosulphonates.—Anhydrous fluorosulphonic acid was prepared by distilling the commercial acid (kindly provided by Imperial Smelting Corporation) until a colourless fraction was obtained (b. p. 155—165°). Electrolytic preparation apparently gave only the first-sequence compounds as a distinct stage in the formation. No satisfactory *X*-ray diffraction patterns could be obtained, principally because of difficulties in handling the samples, which evolved hydrogen fluoride in large quantities.

Boron Trifluoride–Diacetic Acid.—As electrolyte, a 40% solution of boron trifluoride in glacial acetic acid was investigated. This contained a large fraction of the trifluoride in the form of the above complex.[11] Electrolysis led to the formation of a blue compound, probably third-sequence $C_{32}^+A^-$, and there were also indications of a fourth-sequence compound $C_{64}^+A^-$.

Acids, $CF_3{\cdot}CO_2H$, H_3PO_4, H_3AsO_4, HIO_4. With each of these acids, a cathetometer was used to follow swelling during anodic oxidation of well-oriented graphite. *X*-Ray-diffraction patterns gave indications of an expansion of the layers and the formation of crystal compounds, in the case of periodic and arsenic acid, but no detailed *X*-ray examination of any of these compounds has yet been practicable.

For trichloroacetic and dichloroacetic acids, no suitable electrolyte composition has yet been found. Possibly these acids are too weak to permit the formation of salts of graphite by the method.

Cathodic reactions during electrolysis. Cathodic hydrogen may lead to reduction products, especially with strong acids when very concentrated. Thus concentrated sulphuric acid gave

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[11] Rüdorff and Siecke, *Chem. Ber.*, 1958, **91**, 1348.

some hydrogen sulphide and sulphur; selenic acid gave finely divided selenium; but the sintered disc reduced the rate of diffusion of any such products into the anode compartment and no serious disturbances were experienced.

Indirect Formation of Salts by Double Decomposition.—From the present experiments, it seemed likely that obstacles to a generalisation of these direct electrochemical methods might include the following:

(i) Water in solution tends to promote side reactions during electrolysis and to reduce the stability of the salt. It is tempting to interpret the first step in the degradation of graphite salts as a hydrolysis, *e.g.*:

$$\underset{\text{Graphite salt}}{C_{24}^{+}A^{-} + H_2O} \rightleftharpoons \underset{\text{Graphite hydroxide}}{C_{24}^{+}OH^{-} + HA}$$

followed by proton switching and valency rearrangements in the graphite–hydroxide system, leading eventually to alicyclic types of network and conversion into graphite oxide. For various reasons, unfortunately, water cannot always be entirely eliminated from the electrolyte.

(ii) Some acids may be too unstable or too weak to conduct an adequate current at room temperature. Rise of temperature may promote degradation and cannot generally be used to increase electrical conductivity. Cooling, to improve stability, may reduce the conductivity to an undesirable level.

(iii) The affinity of the process

$$\text{Graphite} + HA \longrightarrow C_{24}^{+}A^{-} + H^{+} + e$$

and of similar oxidative processes for higher-sequence derivatives may require very high driving voltages and cause deleterious side reactions to take place during electrolysis.

Such difficulties indicated the desirability of exploiting an indirect electrochemical route for obtaining these salts. Graphite bisulphates are readily and reliably prepared by the electrochemical method; starting with well-oriented pyrolytic graphite, the products are coherent, and the sulphuric acid electrolyte can readily be replaced *in situ* by a range of other concentrated acids. Provided that thermodynamic and kinetic conditions are suitable, repeated washing can lead to the formation of salts of other acids by double decomposition:

$$C_{24}^{+}HSO_4^{-} + HA \longrightarrow C_{24}^{+}A^{-} + H_2SO_4$$

here mass-action principles can be applied to remove the sulphate from the compound, if necessary by repeated washings.

This procedure has been tested for the bisulphate first-sequence compound, in double decomposition with 70% perchloric acid. First-stage graphite perchlorate $C_{24}^{+}ClO_4^{-}$ was obtained, and the hazards of overoxidation encountered in the direct electrochemical oxidation as described above were obviated at the expense of a rather less well-oriented product (see below).

Problems of electrochemical instability limit the usefulness of this procedure. Thus graphite nitrate was obtained only as a second-sequence compound by washing the first-sequence hydrogen sulphate with fuming nitric acid until all traces of sulphate ion had disappeared. Presumably the first-sequence nitrate was too unstable to survive these operations.

Though they verify that double decomposition has occurred, *X*-ray-diffraction measurements do not, of course, guarantee that this indirect route removes the final trace of anions intercalated in the direct preparation, which may be stubbornly retained as "residue compounds." [8-10] In this connexion it may be significant that graphite perchlorate formed by double decomposition (Plate e) showed the correct 00*l* spacings but with increased *c*-axis misorientation, compared with the crystal compound prepared by direct electrolysis (Plate d). (The graphite used as starting material in this reaction sequence was of the same high degree of order as in that which yielded Plate b.)

Double decomposition is thus to be used with caution; careful chemical analysis is advisable in cases where such retentions could lead to error. Nevertheless, double decomposition offers a very promising route where direct electrochemical oxidation is unpracticable.

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