The electrochemical formation of graphite-bisulphate intercalation compounds

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The intercalation of bisulphate ion in graphite has been studied. Oxidation occurs in two stages, at 0.9V and 1.8V versus NHE, but the formation of thermally expandable compounds is associated with the second oxidation process. The first oxidation process is associated with the formation of a lower order of intercalation compound. The transport of HSO₄⁻ between the graphite planes is diffusion controlled and the diffusion coefficient value estimated is in the range of 0.3 to 2.8 $\times 10^{-6}$ cm² s⁻¹ which indicates that the intercalated ions can move quite freely between the graphite planes. The oxidation of the graphite flakes in a fluidized bed electrode was studied by AC and voltammetric techniques. Good interparticle contact was achieved when a slight compressive load was applied and fluidization resulted in a large decrease of the solid phase resistance of the bed electrode.

Nomenclature

- $A$: electrode area
- $C_{i}^{D}$: HSO₄⁻ concentration corresponding to the $i$ intercalation compound
- $C_{(x,t)}$: HSO₄⁻ concentration in bulk graphite
- $C_{(x,0)}$: initial HSO₄⁻ concentration in graphite at any distance from the surface
- $C_{Ox}, C_{R}$: bulk concentrations of the oxidised and reduced species of a redox couple in solution
- $D_{Ox}, D_{R}$: diffusion coefficients of oxidised and reduced species of a redox couple in solution
- $F$: faraday constant
- $n$: number of electrons involved in a redox process
- $R$: gas constant
- $R_{e}$: effective resistance of the solution inside the bed
- $R_{s}$: solid phase resistance of a bed electrode
- $t$: time
- $T$: absolute temperature
- $\sigma$: Warburg coefficient

1. Introduction

The existence of compounds of graphite has been known for a long time [1], and of these, the lamellar complexes have been the most widely studied. The bonding between the flat graphite aromatic layers is rather weak and allows the insertion of simple chemical compounds giving rise to the formation of intercalates [2]. The stoichiometry of these is determined in principle by the requirements of formation of the correspond- ing sublattices, and the number of graphite layers separating each sublattice. In the case of the sulphuric acid lamellar complex the maximum stoichiometry corresponds to $C_{x}^{2+}HSO_{4}$ [3]; the compound formed is known also to contain undissociated $H_{2}SO_{4}$ and the stoichiometry of this graphite salt is $C_{x}^{2+}HSO_{4} \cdot 2.5H_{2}SO_{4}$ [4].

Increasing uses are being found for intercalation compounds; for instance, graphite—bisulphate is a very good catalyst for a range of esterification reactions performed at room temperature [5, 6]. Bromination reactions with graphite—bromine compounds have been described [6] and cetal formation and nitration reactions are known to occur [7]. Some recent developments [8] have shown the possibility of use of graphite—bisulphate as the positive electrode in secondary battery technology and the use of dilute sulphuric acid as an electrolyte has been suggested [9]. In the metallurgical industry, these compounds have been...
employed as expandable materials in insulating topping mixtures. On heating, intercalated graphites are known to increase in volume up to 300 times [10]. The resulting open structure has good insulating properties, which are used in the foundry industry to control the ingot solidification rate of the hot top. The graphite–bisulphate compound has been prepared by chemical oxidation in sulphuric acid using a variety of oxidizing agents, such as Mn\textsuperscript{3+}, KMnO\textsubscript{4}, HNO\textsubscript{3}, CrO\textsubscript{3} and others [1]. The oxidizing agents themselves are not intercalated and therefore the oxidation can be performed electrolytically [1, 11]. The purpose of this work was to study the general characteristics of the electrochemical oxidation process, and the feasibility of using a packed or semi-fluidized bed approach [12] for the bulk electrochemical oxidation of graphite to yield the thermally expandable forms [10].

2. Experimental procedure

Flake natural graphite from Madagascar was employed in all the experiments. Two different electrode configurations were used in this work: (1) For the electrochemical characterization of the material, solid pellets obtained by high pressure compaction of the flakes was used, and (2) A bed electrode made up of free graphite flakes was employed for the bulk electrochemical oxidation studies. The pellets were prepared by compressing the flakes under a total compressive force of 30 Tons,\textsuperscript{*} in a die of 2.8 cm diameter. The pressure was maintained for 5 minutes and the electrical resistance across the pellet was less than 0.01 Ω. The circular pellets were cut in sections with the aid of a small saw and the sides were covered with acid resistant insulating masking enamel. Electrical contact was made with a copper wire inserted at one end of the electrode, and electrical continuity was ensured with silver paint. The electrode surface was polished with 1200 grit emery paper before each measurement and a conventional three electrode cell was employed. A Hi-Tek DT 11005 potentiostat with a Hi-Tek PPR1 waveform generator and a Bryans 26000 x–y recorder was used in the voltammetric work.

\* 1 ton = 9.80665 × 10\textsuperscript{3} newtons.

Figure 1 shows the flow cell used in the packed/semi-fluidized bed experiments. The working electrode comprised the bed of graphite flakes (length ≈ 3.0 cm) with a platinum gauze feeder electrode (40 strands per square inch) placed at the bottom of the bed. A 4.0 cm length of the flow cell prior to the electrode compartment was filled with glass ballottini to ensure a smooth velocity profile in the solution entering the bed. The counter electrode was a platinum spiral placed downstream and the reference electrode was a saturated mercury–mercurous sulphate saturated K\textsubscript{2}SO\textsubscript{4} electrode (\(E_{\text{rev}} = 0.616\) V versus NHE).

Fig. 1. Cell used for the fluidised bed experiments. (1) Bed of graphite flakes; (2) glass ballotini; (3) platinum gauze feeder electrode; (4) reference electrode; (5) platinum counter electrode and (6) capillary for controlling the flow rate.