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Chemical evolution of CO_2 by electrocatalytic oxidation of vanadium-impregnated coke anode material

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Baked carbon containing impregnated vanadium may be electrochemically oxidized to CO_2 in 1 M H_2SO_4 at 80–90% current efficiency during prolonged electrolysis (> 20 h) at 70° C under an applied potential of 1.0 V versus saturated calomel electrode (SCE). The vanadium is electrocatalytically maintained in the highest oxidation state with an activation energy of 44–80 kJ mol^{-1} at temperatures up to 80° C.

1. Introduction

The anodic discharge of oxygen-containing ions at the anode in aqueous solution is important to (a) electrowinning of metals, (b) the production of energy via fuel cells and (c) the electrolysis of water to produce hydrogen. Of these the production of hydrogen by electrical energy produced from nuclear fuel may become an important means of reducing atmospheric pollution [1].

The calculated reversible thermodynamic decomposition e.m.f. ($E^0_{H_2O} = 1.229$ V) is not realized in practice and the overpotential at which oxygen is evolved at almost all noble metal anodes (including platinum) is much higher than that of hydrogen. In the Tafel equation ($\eta = a + b\log i$; where η is overvoltage and i is current density), $a \geqslant 1$ V and $b \geqslant 0.12$ V [2] so that about 2 V versus the standard hydrogen electrode (SHE) is needed for discharge of oxygen at a platinum anode, even when i is low, say 10 mA cm^{-2}.

The electrochemical gasification of coal using a coal slurry as an anodic depolarizer has recently been proposed by Coughlin and Faroogue [3, 4] with the purpose of saving energy in the electrodeposition of copper.

The thermodynamically calculated standard electrode potential of

$$C + 2H_2O = CO_2 + 4H^+ + 4e \qquad (1)$$

is calculated to be only 0.228 V versus SHE. Coughlin and Faroogue [3, 4] have estimated that copper may be deposited with an energy saving as high as 50% of the conventional electrowinning process by carrying out the chemical gasification of coal in $CuSO_4$ solution.

More recently, this process has been studied in detail by Okada *et al.* [5], Dhooge *et al.* [6] and Anthony and Linge [7]. It was recognized that the redox pair Fe^{2+}/Fe^{3+}, derived in part from the iron naturally present in coal or carbon, acted as the electron transfer medium and was responsible for enhancing the coal electrochemical gasification process so that CO_2 was evolved catalytically at the potentials of the depolarizers. The main problem was that the catalytic current was not constant but gradually decreased with time and the current efficiency calculated according to Reaction 1 was as low as 10–15%. Pilot-plant development suggested that cost savings in the overall oxidation of coal may be non-existent [8] but different electrode configurations may be beneficial [9].

In the present work, a study of the impurities in carbon anodes for the aluminium industry drew attention to the catalytic role of vanadium in the high temperature oxidation of coke [10]

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and it seemed desirable to determine what effect vanadium might have on the electrochemical oxidation of coke, both in aqueous and molten salt media. Because the natural vanadium content of coke was probably too small to give a substantial catalytic effect, we used porous anodes from baked petroleum coke plus pitch together with vanadium oxides as the working electrode to see whether there were some catalytic activity promoting Reaction 1 in addition to that which was already due to any iron impurity present in commercial coke. The present paper deals with the aqueous oxidation of coke using vanadium catalyst.

2. Experimental details

The cell was conventional (e.g. [5]), comprising a 500 ml glass reaction vessel partly immersed in a water bath which could be maintained at temperatures of 20–80° C. The working electrode consisted successively of platinum and a series of carbon anodes ranging from spectrographic-grade graphite (total impurity < 1.39 p.p.m.) to compacts made from petroleum coke plus pitch (see Tables 1 and 2), usually with added quantities of vanadium compounds. Sulphuric acid (200 ml at 1 M) was normally the electrolyte but on one occasion vanadyl sulphate was dissolved in the acid. Argon, flowing at $30\,\mathrm{ml\,min^{-1}}$, was used as a carrier gas and the offtake gas was exhausted through a water condenser, concentrated H_2SO_4, $Mg(ClO_4)_2$ and finally Ascarite plus $Mg(ClO_4)_2$, to absorb product CO_2. A platinum foil of surface area $25\,\mathrm{cm^2}$ was used as counter electrode and the saturated calomel electrode (SCE) was the reference electrode. Stirring was by a 2 cm glass impeller at 300 r.p.m.

Table 1. Typical and actual properties of petroleum coke for anode grist

	Typical	*Actual*
Moisture (wt %)	< 0.5	
Volatile matter (wt %)	< 0.5	
Fixed carbon (wt %)	> 99	
Real (skeletal) density ($\mathrm{g\,cm^{-3}}$)	1.9–2.1	1.92
Resistivity of (-30 $+60$*, $\Omega\,\mathrm{mm^{-1}}$)	1.1	1.1
Ash content (wt %)	0.2–0.7	0.8
Al (p.p.m.)	15–100	290
B (p.p.m.)	0.2–0.7	
Ca (p.p.m.)	25–500	400
Fe (p.p.m.)	50–500	590
Mg (p.p.m.)	10–250	
Mn (p.p.m.)	2–100	
N (wt %)	< 0.1	
Na (p.p.m.)	< 130	130
Ni (p.p.m.)	10–700	400
S (wt %)	0.2–0.6	1.0
Si (p.p.m.)	10–700	490
Ti (p.p.m.)	2–60	43
V (p.p.m.)	5–1000	990

* Tyler sieve fraction.

Table 2. Nominal analysis of coal tar pitch used as binder in the baked carbon anodes

Ash	< 0.3%
C	93%
H	4.5%
S	0.5%
N	1.3%
O	0.9%
Cube-in-air point*	108–112° C
Quinoline insoluble content	12–17%

* American National Standard ANSI/ASTM D 2319-76.

The grist for the carbon anode was prepared from commercial sponge petroleum coke as normally supplied to aluminium smelters for the construction of plant anodes. The coke powder (-100 $+$ 200# Tyler sieve) was mixed with an alcoholic solution of NH_4VO_3–HNO_3 and dried with stirring to obtain a uniform distribution of the vanadium. The dried coke was then mixed with a commercial coal tar pitch (see Table 2), pressed at 120° C and 40 MPa into 40 mm cylinders and baked to 1150° C over a period of 50 h in a standard temperature–time profile (20–425° C at $15°\,\mathrm{h^{-1}}$, 425–1120° C at $25°\,\mathrm{C\,h^{-1}}$). Cores of 5 mm were cut from the 40 mm compacts for use as the anodes.

The anode porosity distributions (Fig. 1) were determined using a Micromeritics 9200 porosimeter. The voltammograms were obtained using a Utah Electronics Model 0151 sweep generator driving a Utah Electronics Model 0152 potentiostat and a Hewlett-Packard 7035B x–y recorder.

Prior to each run the carrier gas was bubbled through for 5 h, not only to deoxygenate the

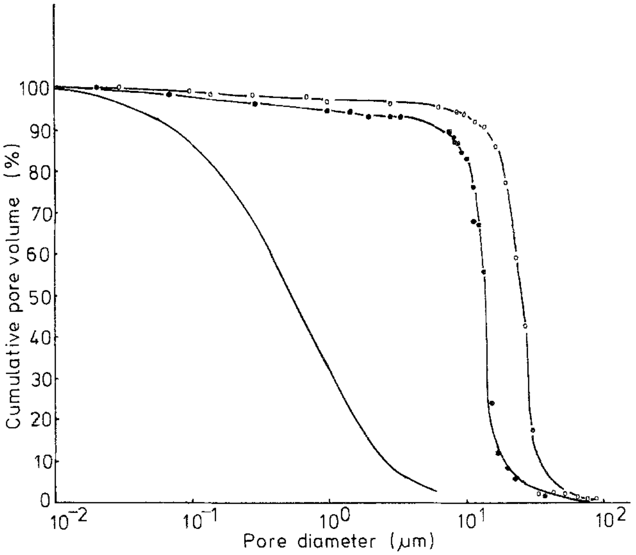

Fig. 1. Porosity distribution for baked anode from +100–200# (Tyler) petroleum coke with 18% coal tar pitch before electrolysis (-●-●) (100% = $0.15\,cm^3\,g^{-1}$) and after electrolysis (-○-○) (100% = $0.17\,cm^3\,g^{-1}$), both compared to typical coal (——) (100% = $0.09\,cm^3\,g^{-1}$).

solution but also to ensure constant weight in the Ascarite absorption vessel. For the purpose of a blank comparison, the rate of CO_2 evolution by reaction of the test anodes with 1 M H_2SO_4 was determined in the absence of dissolved catalysts and applied potential by operating the cell for 6 h with passage of argon and determining the increase in weight of the Ascarite. The results (Table 3) showed that the evolution of CO_2 was initially about $1.6\,mg\,h^{-1}$ but gradually decreased to $<0.5\,mg\,h^{-1}$.

3. Results

The results of single-sweep and cyclic voltammograms at the platinum and carbon working electrodes containing dissolved vanadium in 1 M H_2SO_4 solutions are shown in Fig. 2. The

Table 3. Evolution of CO_2 by reaction of coke anode containing impregnated vanadium (0.6% total) in 1 M H_2SO_4 at 71° C in absence of applied potential

Time interval (min)	*Total time (min)*	*Total CO_2 evolved (mg)*
30	30	0.8
60	90	1.7
40	130	2.4
140	270	3.0
50	320	3.6
50	370	3.9

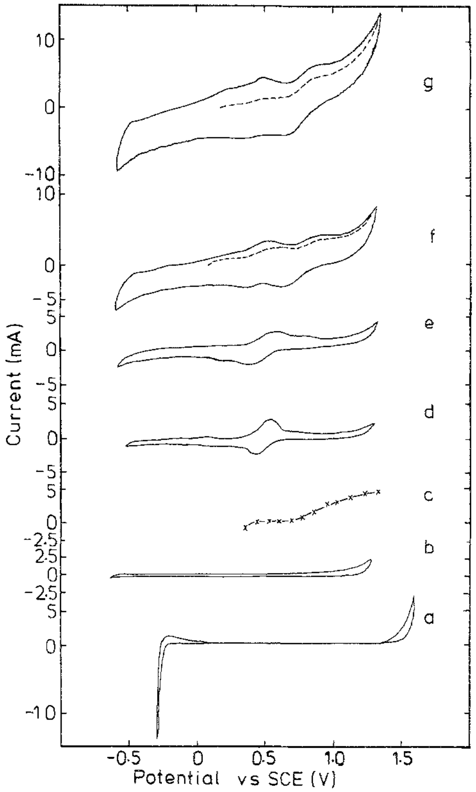

Fig. 2. Voltammograms at different anodic working electrodes in 1 M H_2SO_4 at 45°C and scan rate $0.005\,V\,s^{-1}$ (except (c), steady state readings). (a) Platinum foil, $1\,cm^2$; (b) spectro-graphite $1.13\,cm^2$; (c) 6.18×10^{-3} M V added to solution for curve b run; (d) coke anode blank $1.45\,cm^2$; (e) 0.01 wt% vanadium added to coke anode; (f) 0.2 wt% added to coke anode; (g) 0.5 wt% added to coke anode. Initial sweeps are shown dotted; cyclic sweeps are shown continuous.

curve for the platinum working electrode (Fig. 2a) served as a calibration for the operation of the measuring equipment as a whole, showing normal overpotentials for both H_2 and O_2 discharge. The spectro-graphite voltammogram (Fig. 2b) shows the decreased anodic discharge potential (and increased hydrogen overvoltage) with respect to the electrolysis of aqueous solution at the platinum electrode (Fig. 2a). Fig. 2c shows that vanadium is oxidized at potentials greater than 0.7 V versus SCE; the potential of 1.0 V versus SCE was chosen for the electrocatalytic oxidation of the carbon.

With spectro-graphite, increase in the concentration of dissolved vanadium in H_2SO_4 causes the catalytic current to increase in a nearly linear manner (Fig. 3) with a current density (per molar aqueous vanadium solution at 1.0 V versus SCE) which is three times greater than for vanadium (aqueous solution) at the platinum anode (Fig. 4f).

In contrast to spectro-graphite, the coke anode (Fig. 2d) shows an inflection in the range 0.59–0.73 V versus SHE which is identified from standard oxidation potential tables (see Reaction 2) to be caused by the Fe^{2+}/Fe^{3+} couple. This is consistent with the coke analysis (Table 1) which showed that iron is a major species to contribute multiple valence states in this region of potential.

$$Fe^{2+} = Fe^{3+} + e \quad (E^0 = +0.771\text{ V versus SHE}) \tag{2}$$

In the vanadium-impregnated anodes, it is found that the anode current preserves the Fe^{3+}/Fe^{2+} inflections and, in addition, shows inflections developing in the ranges 0.28–0.37 V and 0.98–1.13 V versus SHE (see Fig. 2e–g). From oxidation potential tables and an *E*–pH diagram [11], these new inflections correspond to the multiple valence states of vanadium, namely V^{3+}/VO^{2+} and $VO^{2+}/V(OH)_4^+$, respectively

$$V^{3+} + H_2O = VO^{2+} + 2H^+ + e \quad (E^0 = +0.337\text{ V versus SHE}) \tag{3}$$

$$VO^{2+} + 3H_2O = V(OH)_4^+ + 2H^+ + e \quad (E^0 = +1.000\text{ V versus SHE}) \tag{4}$$

It is evident from the initial sweeps (Fig. 2f, g) that if electrolyses were performed at 1.0 V versus SCE any electrochemical oxidation of carbon in the aqueous solution would take advantage of all the catalytic actions associated with Reactions 2–4 with Reaction 5 (based on Reaction 4 being the major contributor.

$$4V(OH)_4^+ + C + 4H^+ = CO_2 + 4VO^{2+} + 10H_2O \tag{5}$$

Reference to Fig. 2e and Table 4 shows that the current at 1.0 V versus SCE is greatly

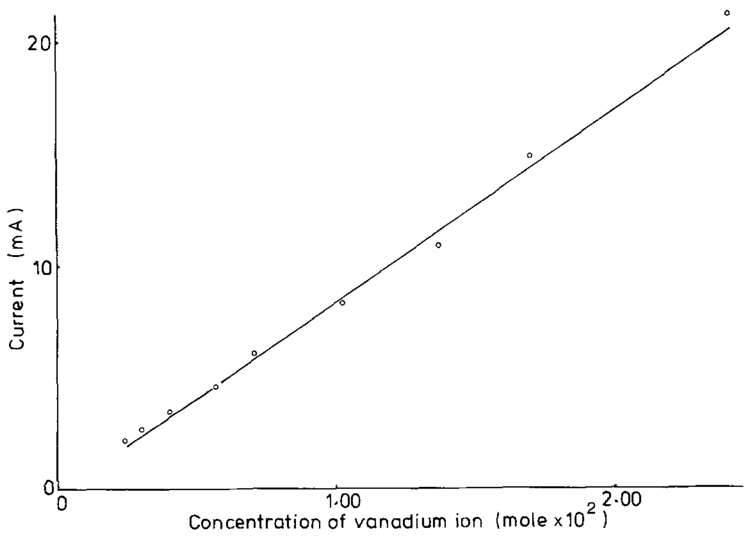

Fig. 3. Dependence of the catalytic current on the vanadium ion concentration in 1 M H_2SO_4 at the spectro-graphite electrode (surface area = 4.5 cm^2); 1.0 V versus SCE at 70° C.

Table 4. Current density at carbon anodes containing varying vanadium content, at 1.0 V versus SCE, 40° C, and 1 M H_2SO_4

Anode	*Vanadium added (wt %)*	*Vanadium total (wt %)*	*Current density ($A\,cm^{-2}$)*
Spectro-graphite	0.0	zero	1.8×10^{-5}
Petroleum coke blank	0.0	0.10	0.8×10^{-3}
Petroleum coke	0.01	0.11	1.2×10^{-3}
Petroleum coke	0.2	0.30	2.8×10^{-3}
Petroleum coke	0.5	0.60	4.7×10^{-3}

increased by the first small addition of vanadium (0.01 wt %) to the coke, thereafter the current increases more slowly with vanadium concentration (Fig. 2f, g and Table 4).

To take advantage of catalytic oxidation via pentavalent vanadium, prolonged electrolyses were performed at 1.0 V versus SCE; the yield of CO_2 was determined at temperatures from 20–80° C. At 20° C the yield of CO_2 was negligible after 150 min. At 30° C the current decreased with time (Fig. 4a), similar to the behaviour of coal slurries at the platinum electrode [5, 8]. At higher temperatures, reference to curves b, c and d) (Fig. 4b–d) showed that the current density was virtually constant over several minutes, except for oscillations caused by the release of CO_2 bubbles from the surface (see inserts, Fig. 4). Over longer periods of time, the average current density varied and normally increased (Fig. 4b–d) as the concentration of H_2SO_4-leached vanadium increased in the bulk of the electrolyte. For example, after 3 days the bulk concentration of vanadium had increased to 10^{-3} M.

The quantity of CO_2 produced at any given time should have been the sum of the quantity of carbon which is chemically oxidized by H_2SO_4 alone (Table 3), together with carbon which was electrochemically oxidized directly on the carbon surface and indirectly oxidized by catalytically recycled vanadium. It was not possible to separate these mechanisms and to smooth out the effects of temporary fluctuations in the different mechanisms; it was most convenient to determine the yield of CO_2 as a function of the total electricity passed (Fig. 5). Comparison with a theoretical slope for 100% current efficiency shows that during prolonged electrolysis of the anode containing 0.5 wt % added vanadium, the apparent yield of CO_2, was initally greater than 100%; after some 150 C (5 h electrolysis) the slope indicated that the yield decreased to about 88% and remained so for more than 20 h.

Logarithmic plotting of the current (at 1.0 V versus SCE) against reciprocal absolute temperature (Fig. 6), gave two linear plots intersecting at temperatures which decreased from 60 to 40° C with increasing concentration of vanadium catalyst. The range of activation energies, calculated in the high-temperature region, was 80–44 kJ mol^{-1}. In the low-temperature region the range was nearly constant at 31–26 kJ mol^{-1}.

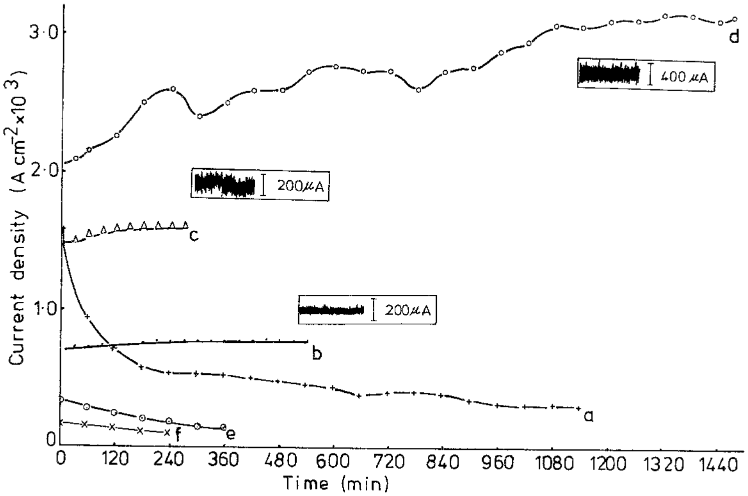

Fig. 4. Anodic current density as a function of time at various working anodes in 1 M H_2SO_4 at 1.0 V versus SCE. (a) Coke anode impregnated by 0.5 wt % vanadium (4.4 cm^2 area at 31° C); (b) coke anode with 0.01 wt % vanadium (1.45 cm^2 area, 80° C); (c) coke anode with 0.2 wt % vanadium added (1.45 cm^2 at 80° C); (d) coke anode with 0.5 wt % vanadium added 4.4 cm^2 at 71° C); (e) spectro-graphite, 1.13 cm^2 at 71° C with 2.4×10^{-3} M vanadium (aqueous solution); (f) platinum foil 1 cm^2 at 71° C with 3.2×10^{-3} M vanadium (aqueous solution).

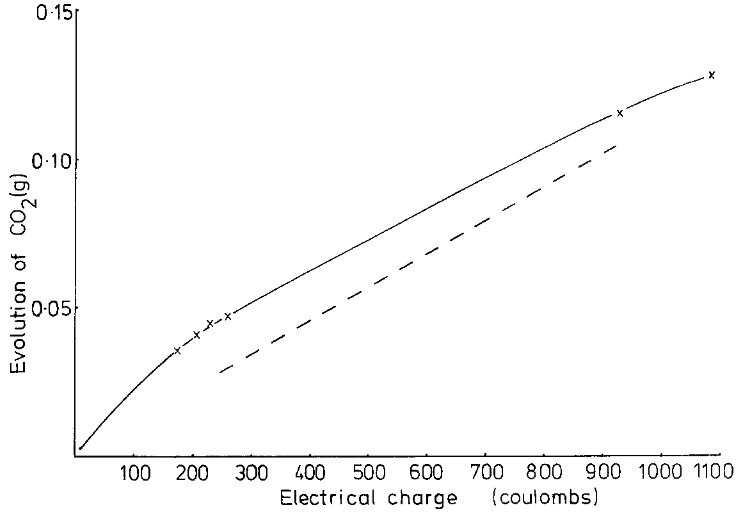

Fig. 5. Yield of CO_2 from coke anode containing 0.5 wt % vanadium at 70° C as a function of the electricity passed, compared to the theoretical yield (– – –) for 100% oxidation of C to CO_2 in 1 M H_2SO_4 at 1.0 V versus SCE; surface area = 4.4 cm^2.

4. Discussion

The cyclic regeneration of the oxidant may be shown as

$$\begin{tikzcd} 4V^{IV} - 4e \arrow[r] & 4V^{V} & \\ & + & \\ & C + 2H_2O \arrow[r] & CO_2 + 4H^{+} + V^{IV} \arrow[uull, bend left] \end{tikzcd} \quad (6)$$

where the chemical reaction, regenerating the reduced vanadium species, involves heterogeneous reaction with the carbon anode.

From the practical viewpoint, the ease of access of the vanadium catalyst to the baked carbon of the impregnated anode leads to two improvements over the electro-oxidation of coal slurries, namely:

(i) the current density does not decrease with time during prolonged electrolysis at 70–80° C,

(ii) the carbon is oxidized with high current efficiency.

The particular electronic properties of vanadium together with the characteristic properties of petroleum coke are probably responsible for the development of these features.

Pentavalent vanadium is particularly effective as an oxidant for carbon. As a transition element, vanadium possesses empty d-orbitals ($4s^2$, $3d^3$) and has a tendency to form π-multiple bonds as in the sandwich compound (π-C_5H_5)-V(π-C_7H_7) [12]. During electro-oxidation, discharged oxygen is chemically adsorbed on the aromatic graphite carbon surface of the coke in the form of the organic function groups (say carboxyl, hydroxyl, carbonyl, etc.) [4, 13]. The carbon atom in the groups is strongly bonded to other carbon atoms by sigma-bonds. The

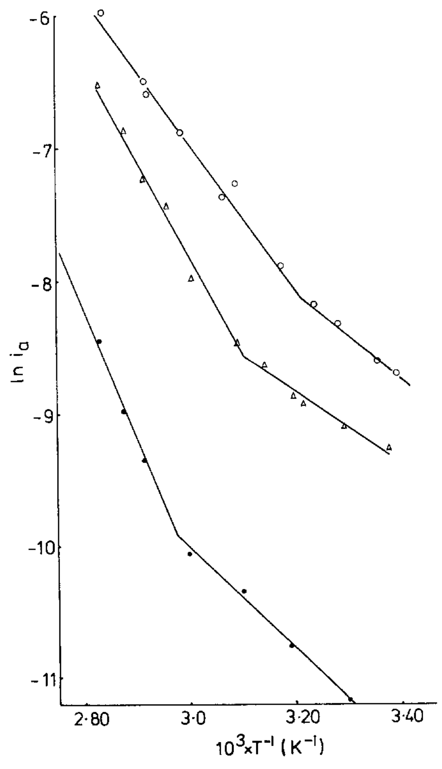

Fig. 6. Anodic catalytic currents as a function of reciprocal temperature at 1.0 V versus SCE in 1 M H_2SO_4 solution: (–○–○), 0.5 wt % vanadium; (–△–△), 0.2 wt % vanadium; (–●–●), coke anode blank.

remaining carbon p-orbitals stabilize the bond by π-multiple bonding. The vanadium atom possesses more empty d-orbitals which readily accept p-electrons in the aromatic graphite so that the π-multiple conjugate bonds between the surface-chemisorbed functional group and the carbon atom associated with the aromatic coke structure are weakened. Therefore the chance of the π-bond to be broken is increased and it would be easier for these kinds of oxygen-containing function groups to be desorbed from the surface of carbon containing vanadium. However, despite its high reactivity, dissolved $V(OH)_4^+$ cannot maintain a constant current at either spectro-graphite or platinum anodes during prolonged electrolysis (Fig. 4, cf. curves e and f, respectively), in part possibly due to some loss of vanadium to the cathode. Hence the impregnation of the carbon with vanadium prior to electrolysis is essential to providing a constant concentration of oxidant in the solution. We believe that this regeneration is especially effective with a petroleum coke anode because of its characteristic porosity distribution (Fig. 1). Furthermore, coke has the advantages of high electrical conductivity and the absence of side reactions of the many types of molecules occurring in a coal.

It may be seen (Fig. 1) that in coal the relative absence of pores which are larger than about 1 μm means that dissolved multivalent ions, say $V(OH)_4^+$, newly formed by electro-oxidation must share a confined space with C–O species formed and dislodged during the oxidation. In contrast, the coke compact offers some additional surface area to the carbon whilst at the same time permitting free mass transfer of oxidants and products. The higher the ionic charge and the smaller and size of the ion, the less the congestion within the pores of the carbon. (As oxidation proceeds the anode becomes slightly more porous (Fig. 1) due to removal of carbon within the pore system.) Coke thus offers a better combination of internal surface area and concentration of oxidant than does coal and the leaching of the vanadium at the site of oxidation of the carbon provides the most efficient utilization of the oxidant.

In addition to the freedom of transfer of vanadium and CO_2 within the porous coke compact, the anode also differs from the slurry/platinum system in that the coke plus carbonized pitch acts both as the reactant and the electrical conductor. Hence, it is easier to transfer charge through a short distance and vanadium ions will not be lost so readily by dissolving in the bulk of the aqueous solution. It would appear that a high local concentration of vanadium ions is maintained within the pores of the electrode itself, hence, if the cell voltage is adequately controlled, a large electrolysis current can be ensured without undue loss of vanadium into the bulk electrolyte. Ultimately, however, the increase of vanadium in the bulk electrolyte becomes significant and in one experiment the vanadium (aqueous solution) concentration is 10^{-3} M after some 20 h of electrolysis, indicating that some 14 mg of vanadium has been leached from the anode. This is about 75% of the vanadium originally present.

During the first few hours of electrolysis, the current efficiency apparently exceeds 100% (Fig. 5) probably because the coke reacts with H_2SO_4 itself [13], together with any oxidants leached for the coke. However, corrections made from the blank determinations in Table 3 were insufficient to bring the current efficiency to 100% (or below).

In contrast to the performance of the coke anodes, the oxidation of slurry coal proceeds via a relatively long charge transfer path between the coal and the anode (platinum). Such slurry electrodes showed a very rapid decrease of current density for reasons not fully understood but possibly due to accumulation of chemisorbed oxygen [3–5]. With vanadium, a decrease of current is also observed during electrolysis in H_2SO_4–$VOSO_4$ solution at the spectro-graphite anode and the platinum anode, even if high concentrations of vanadium were initially present as shown in Fig. 4. However, high currents at the baked carbon anode could be maintained or increased over a long period from initially zero or low concentrations of vanadium in solution.

Petroleum coke exhibits activation plots with two linear sections intersecting at a temperature which is characteristic of the impregnated vanadium concentration (Fig. 6). The lower section has an activation energy (about 30 kJ mol^{-1})

which is similar to the range obtained by Anthony *et al.* [8] for the oxidation of coal slurry by dissolved iron but is significantly lower than obtained by other workers using coal slurries [3, 5, 6]. The upper section has an activation energy (80–44 kJ mol^{-1}) which decreases with the concentration of impregnated vanadium.

The results to date suggest that the best CO_2 yield is obtained when the catalyst concentration and temperature are adjusted so that the prolonged electrolysis proceeds on the upper linear section of the activation plot (Fig. 6), but in the present work the conditions have not been optimized in terms of temperature and catalyst concentration.

5. Conclusion

The relative constancy of the oxidation of carbon by the catalytic vanadium current over a substantial time interval (>20 h) offers a prospect for industrial application which is apparently denied to the aqueous oxidation of coal or carbon slurries. However, it is recognized that a substantial energy penalty would be incurred by the insertion of the impregnation and baking stages, together with any suitable membrane to isolate the vanadium anolyte.

It is anticipated that further understanding of the process will be gained by a study of the surface properties of the petroleum coke during the electro-oxidation and also the use of coal and wood chars as the carbonaceous media for the impregnation of catalysts.

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