

## INVESTIGATION OF THE V(V)/V(IV) SYSTEM FOR USE IN THE POSITIVE HALF-CELL OF A REDOX BATTERY

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### Summary

The V(V)/V(IV) redox couple system has been studied at glassy carbon and gold electrodes in sulphuric acid solutions, using both cyclic voltammetry and rotating disc voltammetry. The system exhibits electrochemical irreversibility at a glassy-carbon surface with a value of  $k^0 = 7.5 \times 10^{-4} \text{ cm s}^{-1}$ . The behaviour is strongly dependent on the method of surface preparation of the glassy carbon. At a gold electrode, surface reactions interfere with the reduction and oxidation of V(V)/V(IV). The diffusion coefficient of V(V) was calculated as  $5.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

### Introduction

The advantages and main features of redox energy storage systems have been extensively reported in recent years [1 - 5]. Despite significant advances in the field over the last few years, particularly in the chromium/iron cell developed by NASA, there are two major problems that are yet to be overcome [1]. First, the electrocatalyst for the chromium half-cell reaction is difficult to prepare and is subject to poisoning by impurities, leading to large overvoltage losses and unacceptable amounts of hydrogen being produced during charge. Second, long-term problems associated with diffusion of cations through the ion-exchange membrane and cross-contamination of electrolytes result in serious limitations of cell life.

The use of a single-metal system for both the negative and positive halves of the cell has been proposed [6] and would certainly overcome the problem of cross-contamination as well as any problems associated with the use of pre-mixed solutions [5]. Cr(III) was suggested for such a cell [6], but the Cr(IV)/Cr(III) couple showed poor electrochemical behaviour [7]. Recently, Chen *et al.* have investigated a number of Co complexes, but the ligands employed in their study displayed poor stability for the Co(I) species [8].

A preliminary study of vanadium redox couples was conducted by the NASA group [1]. Their results indicated that V(V)/V(IV) and V(IV)/V(III) couples generally exhibited irreversible behaviour, although the reversibility of V(III)/V(II) on a B<sub>4</sub>C electrode was better than that of Cr(III)/Cr(II).

The voltammetric and chronopotentiometric characteristics of the various oxidation states of vanadium have been studied at mercury and various solid electrodes.

The nature of the platinum electrode surface has been found to influence the voltammetric response of this metal to V(IV) and V(V). There is general agreement that oxide-free electrodes, prepared by ignition or by dissolving a previously formed oxide film in hot concentrated hydrochloric acid, yield low values of the charge-transfer rate constant ( $k^0$ ) for the V(V)/V(IV) couple. Anson and King studied the reduction of V(V) in 1 M H<sub>2</sub>SO<sub>4</sub> and concluded that the rate constant was highest at electrodes that had been platinized immediately before use [9]. The voltammetric behaviour of V(IV) in sodium sulphate at platinum electrodes was also studied by Songina *et al.* [10]. The limiting current was found to be dependent on both direction of polarization and pH. This was interpreted as signifying that oxidation of V(IV) in acidic media occurs with the participation of oxygen formed by polarization at the anode.

Davis [11] also studied the kinetics of the V(V)/V(IV) couple in sulphuric acid solutions with platinum electrodes by measuring the dependence of the initial current on potential in a controlled-potential electrolysis. The value of  $k^0$  increased, passed through a maximum, and then decreased again as the oxide film was removed. The maximum value occurred when most, but not all, of the oxide film had been removed. It was suggested that reduction and oxidation were facilitated by the formation of oxygen bridges between the electroactive species and a very thin oxide coating. Other workers have proposed [12] that during the reduction of V(V) to V(IV) at both platinum and gold electrodes in sulphuric acid solutions, a film forms on the electrode surface due to the formation of vanadyl vanadates which occurs when both V(V) and V(IV) are present at the surface.

Catalytic involvement of the surface oxides on platinum and gold electrodes has been observed with several other systems including oxidation of As(III). Cebelka *et al.* [13] have presumed that oxygen, adsorbed in the form of ·OH groups at the surface of the platinum electrode takes part in the electrocatalytic oxidation of As(III) in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Using a pyrolytic graphite electrode, Miller and Zittel [14] found that the reduction of V(V) to V(IV) in 1 M H<sub>2</sub>SO<sub>4</sub> and 1 M phosphoric acid was irreversible. Cathodic voltammograms could be reproduced without cleaning the electrode and there was no evidence to suggest that the surface of the electrode was oxidized by contact with V(V).

The wide range of standard reduction potentials exhibited by the various vanadium redox couples, *viz.*,  $-0.291$  V *vs.* SHE for V(III)/(II) in 3 M H<sub>2</sub>SO<sub>4</sub> and  $\sim 1.0$  *vs.* SHE for V(V)/(IV) [9], together with the fact that

they satisfy most of the requirements of soluble redox couples for use in redox flow cells (such as high solubility and stability) make this an attractive system for further study. In the present paper, we report the results of a cyclic voltammetric study of the kinetics of the V(V)/V(IV) redox couple at a glassy-carbon electrode. Cyclic voltammetry and rotating disc voltammetry were also performed at a gold-disc electrode and the results are included here.

## Experimental

The V(V)/V(IV) system was investigated at glassy-carbon (area = 0.07 cm<sup>2</sup>) and gold (area = 0.45 cm<sup>2</sup>) electrodes using both cyclic voltammetry and rotating disc voltammetry. VOSO<sub>4</sub> (BDH Chemicals Ltd., Poole, U.K.) and V<sub>2</sub>O<sub>5</sub> (Ajax Chemicals, Sydney, Australia) were dissolved in H<sub>2</sub>SO<sub>4</sub> solutions that had been prepared using triply distilled water.

The solutions were de-aerated by bubbling with nitrogen both before and during use. Cyclic voltammograms and rotating disc voltammograms were obtained with a Pine RD3 potentiostat (Pine Instrument Co., Grove City, Pennsylvania, U.S.A.) and a Riken Denshi (Model D-72BP) X-Y recorder. For the rotating disc experiments, a Pine Instrument Model ASR2 electrode rotator was employed. Voltages were measured with respect to a saturated calomel reference electrode (SCE); in this paper all potentials are reported against the SCE unless otherwise stated. A graphite rod was used as a counter electrode.

A number of procedures were employed for preparation of the electrode surface. The electrodes were usually polished with 1200 grit (1.5 - 5 μm) silicon carbide polishing paper (Tufbak Durite T421), followed by 0.3 μm α-alumina (Buehler Micropolish, Buehler Ltd, Lake Bluff, IL, U.S.A.), and then rinsed thoroughly with distilled water. This was usually followed by ultrasonication for periods ranging from 10 min to 1.5 h using an Ultramet III sonic cleaner (Buehler Ltd, Evanston, IL, U.S.A.). In the case of glassy carbon, most experiments were performed on electrodes that had been polished only with P1200 polishing paper, ultrasonically cleaned, and then rinsed thoroughly with distilled water.

## Results and discussion

Sulphuric acid was used as the supporting electrolyte in this study. VOSO<sub>4</sub> is very soluble in sulphuric acid forming a blue solution. On the other hand, the rate of dissolution of V<sub>2</sub>O<sub>5</sub> was found to be very low at room temperature. For example, with sonification, 0.5 g V<sub>2</sub>O<sub>5</sub> in 100 ml 1.8 M H<sub>2</sub>SO<sub>4</sub> required approximately 3 - 4 h to dissolve completely. The solubility limit of V<sub>2</sub>O<sub>5</sub> in 1.8 M H<sub>2</sub>SO<sub>4</sub> was estimated by preparing a series of solutions of different concentrations and noting the appearance of each

over a period of time. After 12 days, complete dissolution was observed for 1 g  $V_2O_5$  per 100 ml, while 2 g per 100 ml required 30 days for complete dissolution. This problem of slow dissolution of  $V_2O_5$  in acids is often overcome by first dissolving in NaOH solution and then acidifying the solution [15]. At low pH, V(V) and V(IV) exist predominantly as  $VO_2^+$  [16] and  $VO^{2+}$  [17], respectively.

### Cyclic voltammetric study

The effect of concentration on the cyclic voltammetric behaviour of V(IV) at a glassy-carbon electrode was investigated in 0.1 M, 0.2 M and 2.0 M  $VOSO_4$  in 2 M  $H_2SO_4$ . The glassy-carbon electrode had been previously polished with P1200 paper and then subjected to ultrasonic cleaning for 30 min.

Figure 1 presents typical cyclic voltammograms at different scan rates in 0.1 M, 0.2 M and 2.0 M  $VOSO_4$  solutions. Anodic peaks associated with

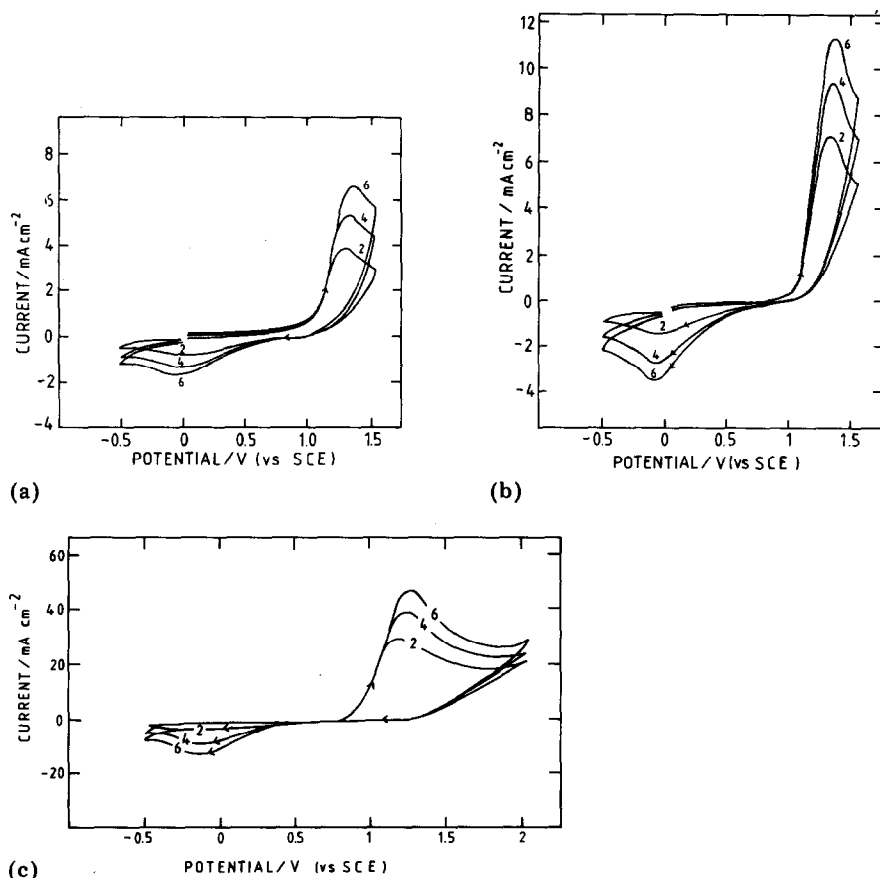


Fig. 1. Voltammograms at the glassy-carbon electrode in  $VOSO_4 + 2\ M\ H_2SO_4$  solutions; scan rates 2, 4, 6  $V\ min^{-1}$ : (a) 0.1 M  $VOSO_4$ ; (b) 0.2 M  $VOSO_4$ ; and (c) 2.0 M  $VOSO_4$ .

the oxidation of V(IV) to V(V) appear at approximately 1.3 V *vs.* SCE and corresponding reduction peaks at around -0.1 V *vs.* SCE. Apart from the increased anodic and cathodic peak currents observed with increasing VOSO<sub>4</sub> concentration, the general shape of the curves remains unchanged. The large peak potential separation ( $\Delta E_p$ ) at the glassy-carbon electrode is indicative of an electrochemically irreversible process.

TABLE 1

Values of anodic:cathodic peak current ratio ( $i_{pc}/i_{pa}$ ) calculated from cyclic voltammograms of Fig. 1 for the reaction  $V(IV) \rightleftharpoons V(V) + e$

Scan rate (V min <sup>-1</sup> )	$i_{pc}/i_{pa}$		
	VOSO <sub>4</sub> concentration		
	0.1 M	0.2 M	2.0 M
2	0.68	0.61	0.53
4	0.75	0.73	0.58
6	0.76	0.76	0.63
8	0.77	0.77	—

The ratios of cathodic peak current ( $i_{pc}$ ) to anodic peak current ( $i_{pa}$ ) were calculated and are presented in Table 1. These values differ from unity, suggesting complications in the electrode processes. The  $i_{pc}/i_{pa}$  value increases with an increase in the scan rate, however the dependence is not linear. This ratio also decreases for higher VOSO<sub>4</sub> concentrations at the same scan rate.

The diminishing value of the cathodic peak current is most likely due to diffusion of the oxidised form from the electrode surface into the bulk of solution, this becoming more significant at lower scan rates, particularly due to the large peak-potential separation. It may also be possible, however, that the decreasing cathodic peak current is due to a following chemical reaction producing an electrochemically inactive species. This would be consistent with the suggestion by Dzhabarov and Gorbachev [18] that a mixed vanadyl-vanadate complex with formula  $[(VO^{2+})(VO_3^-)_y]^{(y-2)-}$  can interfere with the oxidation and reduction process of V(IV)/V(V) couples. Further work is required to distinguish between these two phenomena, however.

An additional factor which complicates the study of the electrochemical reactions of V(V)/V(IV) is the strong dependence on electrode preparation. Figure 2 illustrates the effect of surface preparation for a glassy carbon electrode cycled in a solution of 0.55 M V(V) in 1.8 M H<sub>2</sub>SO<sub>4</sub>. Curve (a) was obtained at an electrode that had been polished with P1200 paper, followed by 0.3  $\mu$ m alumina, and cleaned in an ultrasonic bath for 1.5 h. Curve (b) was obtained when the electrode was polished with the P1200 paper alone and shows a dramatic improvement in the reversibility of the reaction. The same dependence on electrode preparation was observed for the V(III)/V(II)

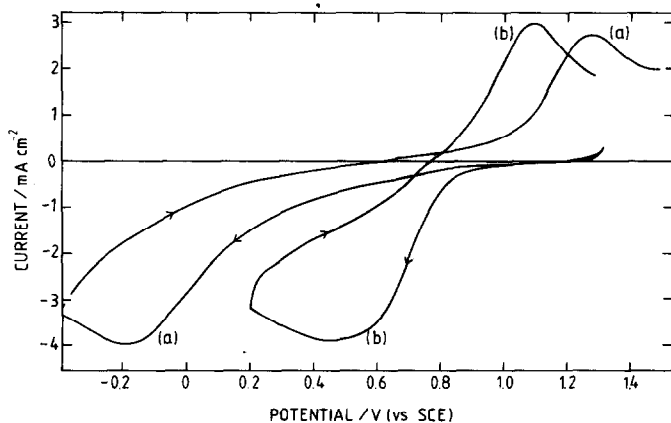


Fig. 2. Effect of surface preparation on voltammograms for glassy carbon in 0.055 M V(V) + 1.8 M H<sub>2</sub>SO<sub>4</sub> solution; scan rate = 4 V min<sup>-1</sup>. (a) Electrode prepared with P1200 paper, 0.3 μm alumina, and ultrasonic cleaning for 1.5 h. (b) Electrode polished with P1200 paper.

system at a glassy-carbon electrode [19]. It is interesting to note also from this Figure that any surface roughness introduced by polishing with P1200 paper does not have any significant effect on the magnitude of the cathodic peak current at the glassy-carbon electrode.

The cyclic voltammetric behaviour of V(V) in H<sub>2</sub>SO<sub>4</sub> was studied at both glassy-carbon and gold working electrodes in solutions containing 0.055 M and 0.11 M V(V). Figure 3 shows a series of cyclic voltammograms obtained at different scan rates at a glassy-carbon electrode in 0.055 M V(V). As the peak separations are between 300 and 600 mV, the V(V) + e ⇌ V(IV) reaction is electrochemically irreversible at the glassy-carbon electrode.

Figure 4 shows a plot of  $i_{pc}/AC_0$  vs.  $\nu^{1/2}$ , where  $i_{pc}$  is the cathodic peak current;  $A$  is the electrode area (cm<sup>2</sup>);  $C_0$  is the bulk concentration of the oxidant (moles cm<sup>-3</sup>); and  $\nu$  is the potential sweep rate (V s<sup>-1</sup>). Assuming a value of  $\alpha n_a$  equal to 0.5, the value of the diffusion coefficient calculated from the slope of this straight line [20] was  $1.4 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>.

The standard heterogeneous rate constant,  $k^0$ , was evaluated from the intercept of a plot of  $\ln i_{pc}$  vs.  $E_p - E^{o'}$ , where  $E_p$  is the peak potential and  $E^{o'}$  is the formal potential [20]. The value of the formal potential of the electrode, estimated from the cyclic voltammograms, was  $E^{o'} = 0.85$  V. Figure 5 shows the plot of  $\ln i_{pc}$  vs.  $(E_{pc} - E^{o'})$  obtained from the cyclic voltammetric data of Fig. 3. From the intercept of this straight line, the value of  $k^0$  was calculated as  $7.5 \times 10^{-4}$  cm s<sup>-1</sup>.

In the above mathematical treatment of the results, the theory employed does assume that the electrode surface is smooth. This would not be expected to be the case if the electrode is polished with P1200 paper. As illustrated in Fig. 2, however, there is negligible difference between the cathodic peak currents obtained when the electrode was polished with

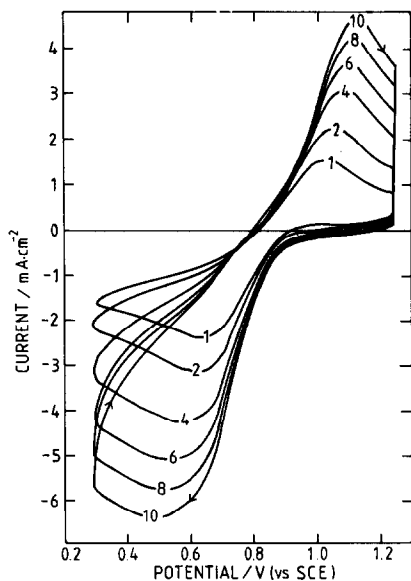


Fig. 3. Voltammograms at the glassy-carbon electrode in 0.055 M V(V) + 1.8 M H<sub>2</sub>SO<sub>4</sub> solution. Numbers of curves correspond to scan rate in V min<sup>-1</sup>.

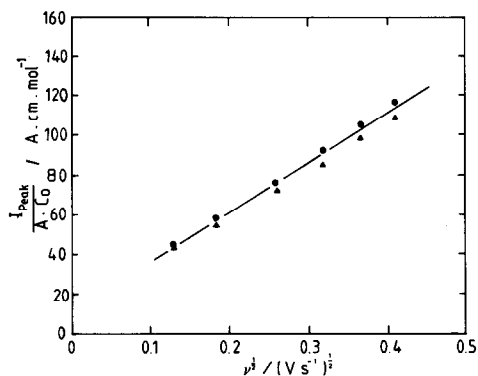


Fig. 4. Cathodic peak current vs. square-root of scan rate for voltammograms at the glassy-carbon electrode in V<sub>2</sub>O<sub>5</sub> + 1.8 M H<sub>2</sub>SO<sub>4</sub> solution. ●, 0.055 M V(V); ▲, 0.110 M V(V).

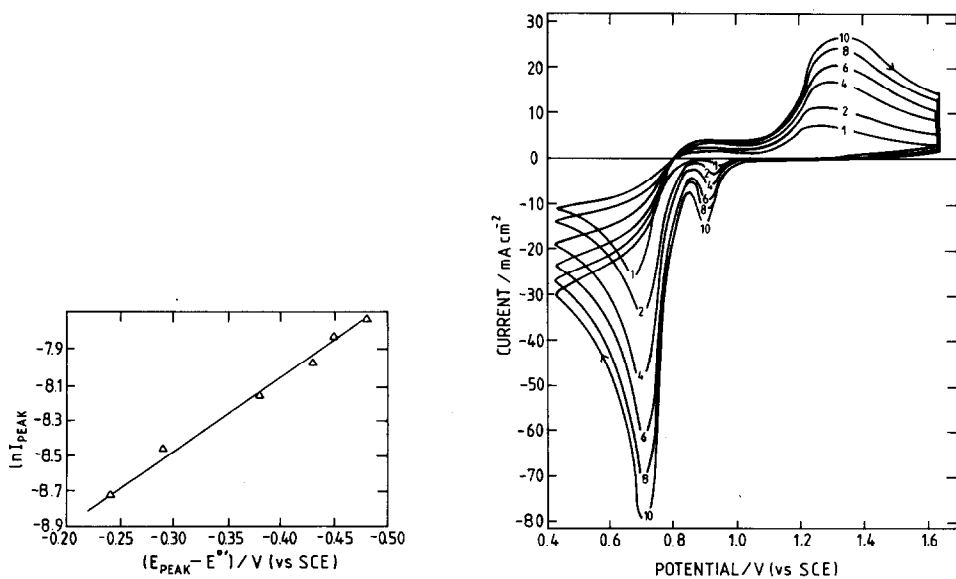


Fig. 5.  $\ln I_{pc}$  vs.  $(E_{pc} - E^{O'})$  for the voltammograms of Fig. 3.

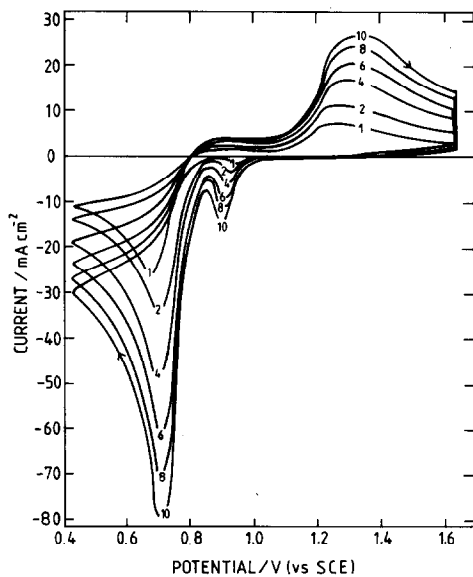


Fig. 6. Voltammograms at the gold electrode in 0.055 M V(V) + 1.8 M H<sub>2</sub>SO<sub>4</sub>. Numbers on curves correspond to scan rate in V min<sup>-1</sup>.

alumina powder or with P1200 paper alone. This difficulty in obtaining a reproducible smooth surface with glassy carbon is a problem often encountered in studies employing glassy-carbon electrodes and usually gives rise to considerable scatter in results.

Cyclic voltammetry was also performed at a gold electrode in the  $V_2O_5$  solutions and a typical series of voltammograms at different scan rates is shown in Fig. 6. Two reduction peaks can be observed as the potential is scanned negative from 1.6 V. The cathodic peak at around 0.9 V can be attributed to the reduction of the gold oxide layer formed at more positive potentials, while the peak at approximately 0.7 V is associated with the reduction of V(V) to V(IV). On reversal of the potential scan, two anodic peaks can be observed. It is very interesting to note that although there is negligible variation in peak potentials with scan rate for the V(V)  $\rightarrow$  V(IV) reduction peak (suggesting electrochemical reversibility), reoxidation of the V(IV) is not observed until several tenths of a volt more positive than the formal potential of the electrode. The gold surface reactions thus interfere with the V(V)/V(IV) redox reactions, making analysis of the data difficult. Nevertheless, the cathodic peak current was plotted as a function of  $\nu^{1/2}$  for two different concentrations of  $V_2O_5$  in 1.8 M  $H_2SO_4$ , and the results are presented in Fig. 7. Again, using a value of  $\alpha n = 0.5$ , the value of the diffusion coefficient obtained from the slope of this straight line was  $5.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

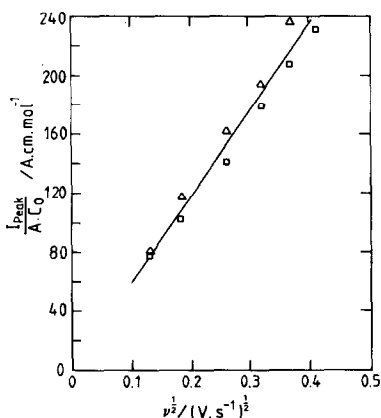


Fig. 7. Cathodic peak current vs. square-root of scan rate for voltammograms at the gold electrode in  $V_2O_5 + 1.8 \text{ M } H_2SO_4$  solution.  $\square$ , 0.55 M V(V);  $\triangle$ , 0.110 M V(V).

### Rotating disc voltammetry

In order to obtain reproducible rotating disc voltammetric data at the gold disc electrode, it was found that "conditioning" of the gold electrode was necessary after polishing with P1200 paper and  $0.3 \mu\text{m}$  alumina. Figure 8(a) shows a rotating disc voltammogram obtained when the electrode had



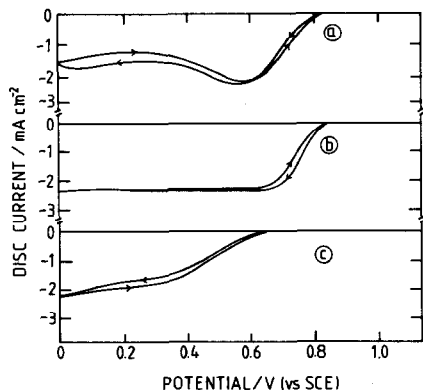


Fig. 8. Effect of surface preparation on rotating disc voltammograms at the gold electrode in 0.055 M V(V) + 1.8 M H<sub>2</sub>SO<sub>4</sub> solution. Rotation speed,  $\omega = 400 \text{ rev min}^{-1}$ . (a) Electrode freshly polished with P1200 paper and 0.3  $\mu\text{m}$  alumina powder; (b) electrode "conditioned", and (c) after a long period of operation.

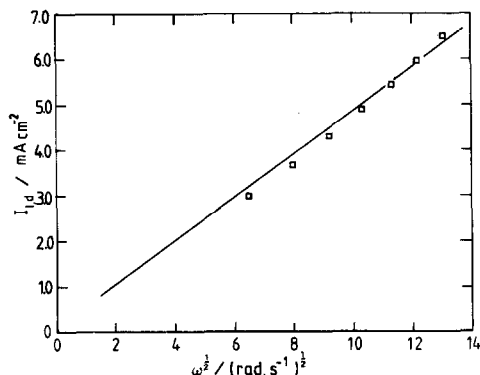


Fig. 9. Limiting disc current vs. square-root of rotation speed for the gold disc electrode in 0.019 M V(V) + 1.84 M H<sub>2</sub>SO<sub>4</sub> solution.

had been polished with P1200 paper and alumina. After the electrode had been "conditioned" by switching the potential between  $-1.5 \text{ V}$  and  $+1.5 \text{ V}$  so as to generate gas bubbles at the electrode surface, the voltammogram of Fig. 8(b) was obtained. After a long period of continuous operation, the current-voltage curve became drawn out (Fig. 8(c)), probably due to contamination of the electrode surface.

A series of rotating disc voltammograms was obtained, at different electrode rotation speeds. The limiting disc current ( $I_{l,d}$ ) plotted as a function of the square-root of rotation speed yielded a straight line that passed through the origin (Fig. 9). This indicates that the V(V) reduction reaction is convective-diffusion controlled [21]. From the slope of this straight line, the value of the diffusion coefficient was calculated as  $4.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , a value close to that obtained above by cyclic voltammetry.

### Stability of solutions

The stability of the V(IV) and V(V) species is very important from the point of view of redox flow cell applications. V(V) is unstable in HCl solutions, the V(V) being reduced by the  $\text{Cl}^-$  ion to V(IV) [22]. V(IV) has been reported to be unstable in NaOH solutions [16], being slowly oxidised to V(V). Sulphuric acid was thus selected as the supporting electrolyte for this study. The stability of the V(IV) and V(V) species in the H<sub>2</sub>SO<sub>4</sub> solution was determined by comparing cyclic voltammograms obtained in freshly prepared solutions of VOSO<sub>4</sub> and V<sub>2</sub>O<sub>5</sub> with voltammograms obtained in the same solution after periods ranging from 1 to 10 days. Negligible difference could be observed, indicating the stability of both species in the H<sub>2</sub>SO<sub>4</sub>. The V(III) species was also found to be stable in de-aerated solutions

of  $\text{H}_2\text{SO}_4$  [19], although complete sealing from the atmosphere and de-aeration was required for the V(II) solutions.

## Conclusions

The V(V)/V(IV) redox couple appears to meet many of the requirements for redox flow cell applications. The formal potential of V(V)/V(IV) in  $\text{H}_2\text{SO}_4$  is about 0.85 V, making it suitable for the positive half-cell of a redox battery. With a formal potential of around  $-0.6$  V for the V(III)/V(II) redox couple, a significant open-circuit cell voltage could be achieved with an all-vanadium system.

$\text{VOSO}_4$  is very soluble in sulphuric acid, while  $\text{VCl}_3$  and  $\text{V}_2\text{O}_5$  are sufficiently soluble for redox cell purposes.  $\text{VOSO}_4$ ,  $\text{VCl}_3$  and  $\text{V}_2\text{O}_5$  are also soluble in HCl, however V(V) is unstable in HCl. Sulphuric acid solutions of  $\text{VCl}_3$ ,  $\text{VOSO}_4$  and  $\text{V}_2\text{O}_5$ , however, are stable during generation and storage. Solutions of V(II) are readily oxidised, so the negative half-cell would need to be sealed and de-aerated.

The results of the cyclic voltammetric study of the V(V)/V(IV) redox couple at glassy-carbon electrodes indicated that this system is electrochemically irreversible with a value of  $k^0 = 7.5 \times 10^{-4} \text{ cm s}^{-1}$  and a diffusion coefficient of  $1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for V(V). As in the case of the V(III)/V(II) system, the reversibility was found to be critically dependent upon surface preparation of the glassy-carbon surface.

At a gold disc electrode, surface reactions interfere with the oxidation and reduction reactions of the V(V)/V(IV) couple. Results obtained here are consistent with previous studies at platinum electrodes [9] that showed the voltammetric response to V(IV) and V(V) to be influenced by the nature of the electrode surface. The presence of the oxide film has been found to affect the kinetics of the V(V)/V(IV) couple [11], and it has been suggested that oxygen bridges are formed between the electroactive species and a very thin oxide coating. The formation of vanadyl vanadate films on platinum and gold surfaces has also been suggested [12].

Although further work is needed to fully understand the nature of the V(V)/V(IV) reactions at platinum and gold surfaces, the results obtained at the glassy-carbon electrode are quite encouraging from the point of view of redox flow cell applications, particularly as the V(III)/V(II) shows similar promise for use as a negative half-cell in an all-vanadium system.

To test the performance of V(IV)/V(V) and V(II)/V(III) half-cells in an all-vanadium redox cell, a small experimental cell was constructed. Charging-discharging experiments were performed and the current-voltage characteristics were tested. Interim results show that the cell works well, being charged and discharged several times and giving a current efficiency of approximately 60%.

The reversibility of both redox couples could be improved by appropriate surface treatment, or by using alternative electrode materials. Such

a study is currently underway in our laboratories and a range of electrode materials are being screened to find one which gives the best reversibility for the V(III)/V(II) and V(V)/V(IV) redox couples.

A detailed description of the all-vanadium redox cell performance will be presented in a separate paper.

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