

## A STUDY OF THE V(II)/V(III) REDOX COUPLE FOR REDOX FLOW CELL APPLICATIONS

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(Received February 14, 1985; in revised form April 19, 1985)

### Summary

The electrochemical behaviour of the V(III)/V(II) redox couple has been investigated at glassy carbon electrodes using cyclic voltammetry. The oxidation/reduction is found to be electrochemically irreversible with a value  $k^{\circ} = 1.2 \times 10^{-4}$  at pH = 4. A slight trend in  $k^{\circ}$  with pH is observed. Electrode poisoning effects are observed at the glassy carbon electrode, and surface preparation is found to be critical in determining observed behaviour.

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### Introduction

A suitable energy storage system is an essential requirement for remote power system applications that are supplied by either photovoltaic arrays or wind turbine generators. For such applications, low life-cycle cost and simplicity of operation are the major requirements. Rechargeable batteries are an attractive option. In particular, redox energy storage systems have recently received considerable attention as they promise to be inexpensive and possess many features that provide for long life, flexible design, high reliability, and low operation and maintenance costs.

For a number of years now, the NASA-Lewis Research Centre has been involved in the development of a complete redox energy storage system based on the Fe(III)/(II) and Cr(III)/(II) couples for the positive and negative sides of the battery, respectively [1 - 6]. Although the Fe(III)/(II) couple proved to be suitably reversible, the Cr(III)/(II) couple is quite irreversible, leading to poor ampere-hour and watt-hour efficiencies. A suitable electrode surface was therefore developed to catalyse the Cr(III)/(II) half-cell reactions, while minimising the hydrogen evolution reaction during the charge cycle. This was achieved by depositing small amounts of lead (high hydrogen overvoltage) and gold (catalyst for chromium) onto large-area carbon felts.

The second major aspect of the NASA redox energy storage project has been the development of a highly efficient ion-exchange membrane to

prohibit the passage of iron and chromium ions and yet allow easy passage of chloride and hydrogen ions. Although significant advancements have been made by NASA over the last few years in both electrocatalysis and membrane improvement, two major problems can still be identified.

The first problem is that the gold-lead catalyst is difficult to prepare and is not very stable. Impurities are a serious problem, particularly in the chromium half-cell. Certain impurities in the chromium solution are electro-deposited over the lead catalyst; these produce an electrode surface with a low hydrogen overvoltage and result in unacceptable amounts of hydrogen being produced during charge. Large kinetic polarization effects with the chromium reactions have also been observed [1].

The second major problem with redox batteries is the diffusion of cations through the membrane, and cross-contamination of the positive and negative cell electrolytes. Although this problem has been markedly reduced with the highly efficient ion-exchange membranes developed for the NASA redox cell, the necessity to operate at elevated temperatures, so as to improve the kinetics of the chromium charging reaction has greatly diminished the ability of the membranes to keep the reactant species separate. To overcome this, NASA has recently begun to employ pre-mixed reactants, so that in the fully-discharged state, both reactant solutions contain, for example, 1M  $\text{FeCl}_2$ , 1M  $\text{CrCl}_3$  and 2M HCl [6]. Although this has eliminated the problem of cation migration, other complications could arise from the use of pre-mixed reactant solutions. The deposition of iron at the negative electrode during charging would be one example.

In order to overcome catalyst limitations, a redox-couple system is required that possesses rapid charge-transfer rates without requiring the application of complicated electrocatalysts to the electrode surface. Bard and co-workers [7] have recently investigated Co(III) and Co(II) complexes with *o*-phenanthroline, bipyridine and related ligands, for their suitability as redox couples for electrochemical energy storage systems as well as semiconductor photoelectrochemical cells. These complexes appeared to satisfy many of the general requirements of an energy storage redox couple. The formal potentials were unsuitable, however, for either the positive ( $\sim 0.38$  V for  $\text{Co}(\text{phen})_3^{2+}$  compared with 1.08 V for  $\text{Fe}(\text{phen})_3^{2+}$ ) or the negative half-cell [8].

The  $\text{Ti}^{3+}/\text{TiO}^{2+}$  redox couple has been investigated as a possible negative half-cell in an Fe-Ti redox system [9 - 11], but  $\text{TiO}_2$  passivation was found to be a serious problem. The addition of lead as a reducing agent was found to enhance the performance of the Fe-Ti redox cell by minimising the formation of  $\text{TiO}_2$ . The lead also contributed over 400 mV to the cell open-circuit potential [12].

The NASA group conducted an initial screening of a large number of redox couple/electrode combinations including the V(III)/(II) system. This latter couple was eliminated largely on the basis of cost [1]. In remote area energy storage applications, however, cost is usually a secondary consideration, the emphasis being on efficiency. The V(III)/(II) system was thus

chosen for this study because its standard reduction potential ( $E^\circ = -0.255$  V) makes it suitable for use as a negative half-cell with the positive Fe(III)/(II) system. More importantly, however, vanadium exists in a number of valence states, the wide range of standard reduction potentials of which offers the possibility of an all-vanadium redox cell system, which would minimise the problem of cross-contamination of positive and negative cell electrolytes.

Preliminary studies conducted by the NASA group indicated that V(V)/(IV) and V(IV)/(III) couples generally exhibited irreversible behaviour; however, the reversibility of V(III)/(II) on a B<sub>4</sub>C electrode was better than that of Cr(III)/(II) [1].

Chen [13] reported that V(III)/(II) in HCl showed properties consistent with application to redox flow cells. Polarographic studies of V(III) in 0.5M H<sub>2</sub>SO<sub>4</sub> have shown that vanadic ion undergoes a reversible 1-electron reduction to vanadous ion [14]. In weakly acid but non-complexing media such as acetate buffers of pH 4.1 - 6.3, the cathodic V(III) wave divides into a doublet whose relative heights are a function of pH. This doublet apparently results from reduction of the hydrolytic species VOH<sup>2+</sup> and VO<sup>+</sup> in a sluggish equilibrium [14].

In the present study, the electrochemical behaviour of V(III)/(II) has been investigated in both H<sub>2</sub>SO<sub>4</sub> and HCl electrolytes, over a range of pH and on various electrodes, so as to determine the reversibility of the electrode reactions and the suitability of this system for redox battery applications.

## Experimental

The electrochemical behaviour of V(III)/V(II) was investigated at glassy carbon (area 0.07 cm<sup>2</sup>), gold, and platinum electrodes using cyclic voltammetry. The VCl<sub>3</sub> (Alfa Products, Danvers, MA, U.S.A.) was dissolved in either H<sub>2</sub>SO<sub>4</sub> or HCl solutions that had been prepared with triply-distilled water and pre-electrolyzed before use. The supporting electrolytes were de-aerated by bubbling with nitrogen for 10 min before addition of the VCl<sub>3</sub>.

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 thoroughly rinsed before use. In the case of glassy carbon, however, the electrode preparation was found to be very critical, and various procedures were used. In addition to the method described above, some experiments were performed on electrodes that had been polished only with the 1200 grit polishing paper and then rinsed. Where alumina polishing was employed, this was usually followed by ultrasonification (Ultramet III sonic cleaner, Buehler Ltd, Evanston, IL, U.S.A.) for periods ranging from 10 min to 1.5 h.

Voltages were measured (and reported in this paper) *versus* a saturated calomel reference electrode (SCE), and a graphite rod was used as a counter electrode. Solutions were de-aerated by bubbling with nitrogen before and

during use. Cyclic voltammograms were obtained with a Pine RD3 potentiostat (Pine Instrument Co, Grove City, PA, U.S.A.) and a Riken Denshi (Model D-72BP) X-Y recorder.

## Results and discussion

The V(II)/V(III) redox system was studied under acidic conditions in order to keep the hydrolysis of V(II) and V(III) to a minimum [15]. Cyclic voltammograms of  $VCl_3$  in both HCl and  $H_2SO_4$  solutions of various concentrations were initially obtained on platinum and gold working electrodes. As illustrated in Fig. 1 for a gold disc, the low hydrogen overvoltage at these electrodes masks the V(III) reduction peak so that it cannot be observed under these conditions. The V(III) reduction reaction was thus studied at a glassy carbon working electrode.

### Electrode preparation effect

As seen in Fig. 2, the method of preparation of the glassy carbon was critical in determining the observed behaviour. Curve (a) was obtained at a glassy-carbon surface that had been previously polished on P1200 sandpaper followed by  $0.3 \mu m$  alumina. Even after cleaning the electrode in an ultrasonic bath for 45 min to remove any alumina particles from the surface, no peaks corresponding to the reduction of V(III) could be observed. When the electrode was polished on the sandpaper alone, a cathodic peak correspond-

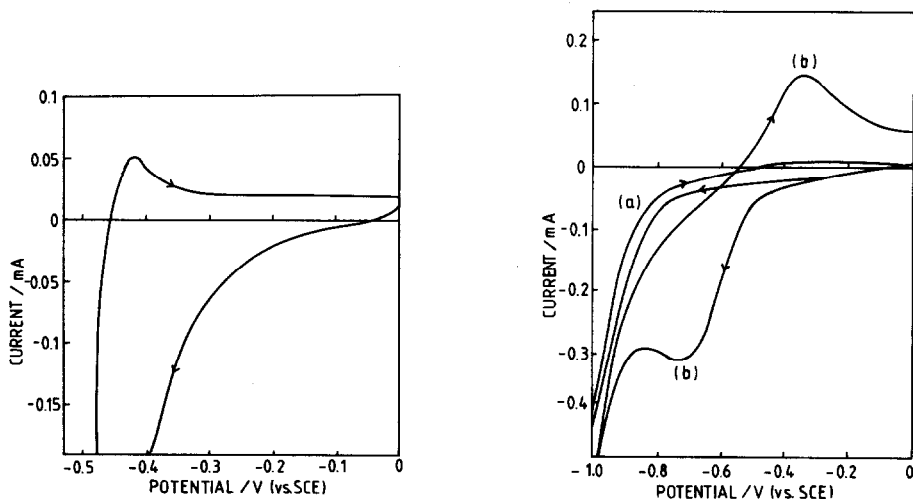


Fig. 1. Voltammogram of gold (area  $0.45 \text{ cm}^2$ ) in  $0.015M VCl_3 + 0.1M H_2SO_4$ ; sweep rate  $2 \text{ V min}^{-1}$ .

Fig. 2. Effect of electrode polishing on voltammograms for glassy carbon in  $0.08M VCl_3 + 1.8M H_2SO_4$ ; scan rate  $5 \text{ V min}^{-1}$ . (a) Electrode prepared with P1200 sandpaper,  $0.3 \mu m$  alumina, 45 min ultrasonic cleaning; (b) electrode polished on P1200 sandpaper.

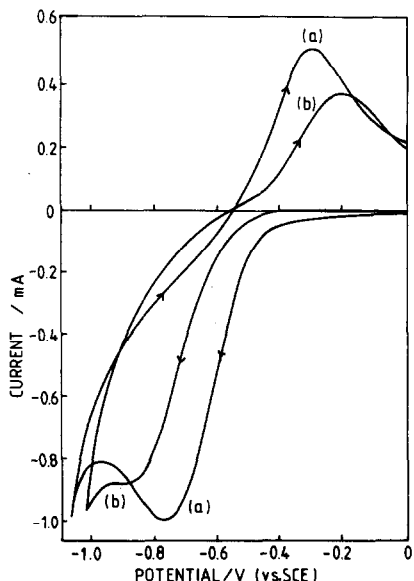


Fig. 3. Effect of time on behaviour of glassy carbon electrode in 0.11M  $\text{VCl}_3$  + 1.6M  $\text{H}_2\text{SO}_4$ ; scan rate  $8 \text{ V min}^{-1}$ . (a) First scan; (b) second scan after 10 min rest period.

ing to the reduction of V(III) to V(II) was observed at approximately  $-0.7 \text{ V}$  (curve (b), Fig. 2). It can also be seen that reversal of the potential scan gives rise to an anodic peak corresponding to the re-oxidation of V(II) to V(III) at around  $-0.35 \text{ V}$ . In order to obtain reproducible cyclic voltammograms for the V(III)/(II) system, not only was electrode preparation important, but it was also found that the potential scans had to be performed immediately after immersing the freshly polished glassy carbon electrodes in the  $\text{VCl}_3$  solution. As illustrated in Fig. 3, for a given scan rate the magnitude of the peak current ( $i_p$ ) decreased, and the peak potential separation increased, after a delay of several minutes.

### Complex species effect

The cyclic voltammograms of  $\text{VCl}_3$  solutions were also found to be affected by the composition of the supporting electrolyte. The variation in the observed behaviour was reflected by changes in the colour of the solutions, indicating that soluble complexes were present. When  $\text{VCl}_3$  was added to  $\text{HCl}$  solutions with  $[\text{H}^+] < 0.1\text{M}$ , a brown solution resulted; for  $[\text{H}^+] > 0.1\text{M}$ , the resulting dark brown-violet solution changed to green on standing. Similarly, solutions of  $\text{VCl}_3$  in  $\text{H}_2\text{SO}_4$  with  $[\text{H}^+] < 0.1\text{M}$  were brown in colour, but for  $[\text{H}^+] > 0.1\text{M}$ , blue solutions were obtained. Furthermore, when sodium sulphate was added to the  $\text{VCl}_3/\text{H}_2\text{SO}_4$  solutions, the colour changed from brown ( $[\text{H}^+] < 0.1\text{M}$ ) or blue ( $[\text{H}^+] > 0.1\text{M}$ ) to green-brown or blue-green, the green shade becoming more intense as the concentration of  $\text{Na}_2\text{SO}_4$  was increased. The chemistry of V(III) in aqueous solutions is described in the literature [15 - 17]. The colour change brought about by

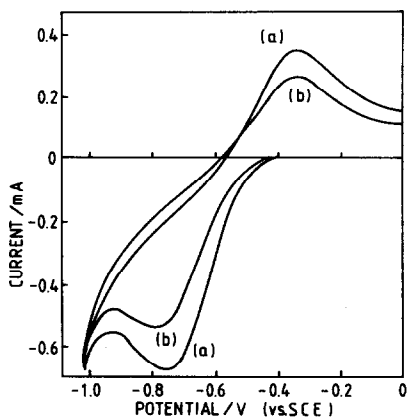


Fig. 4. Effect of  $\text{Na}_2\text{SO}_4$  addition on voltammograms at glassy carbon in  $0.11\text{M VCl}_3 + 1.6\text{M H}_2\text{SO}_4$ ; scan rate  $4\text{ V min}^{-1}$ . (a) Without  $\text{Na}_2\text{SO}_4$ ; (b)  $1.0\text{M Na}_2\text{SO}_4$ .

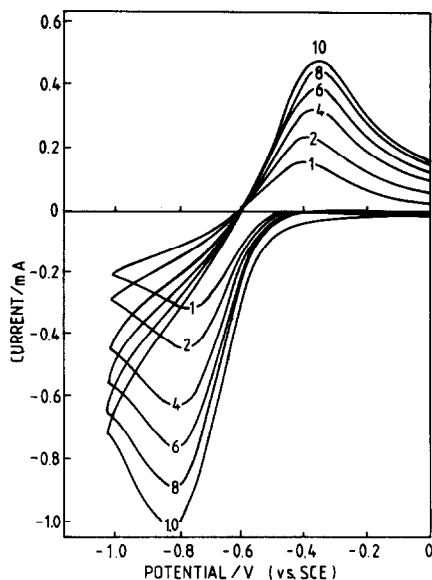


Fig. 5. Cyclic voltammograms at glassy carbon in  $0.12\text{M VCl}_3 + 0.5\text{M H}_2\text{SO}_4 + 1.04\text{M Na}_2\text{SO}_4$ . Numbers on curves correspond to scan rates in  $\text{V min}^{-1}$ .

the addition of, for example,  $1.0\text{M Na}_2\text{SO}_4$  to  $0.11\text{M VCl}_3$  in  $1.58\text{M H}_2\text{SO}_4$  was accompanied by a reduction in the peak currents for the same scan rate (Fig. 4). This small change in  $i_p$  could be attributed to a slight change in the value of the diffusion coefficient,  $D_{\text{O}}$ , of the new complex of  $\text{V(III)}$ , since  $i_p$  is a function of  $D_{\text{O}}$ . The colour change that results from the addition of  $\text{Na}_2\text{SO}_4$  is an indication of the formation of a new complex species.

### *pH effect*

Cyclic voltammetry was used to study the kinetics of the reaction  $\text{V(III)} + e \rightleftharpoons \text{V(II)}$  at a glassy carbon electrode in a supporting electrolyte of  $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$  as a function of pH. The concentration of  $\text{H}^+$  was varied between  $1 \times 10^{-4}$  and  $3.2\text{ moles l}^{-1}$ . Solid  $\text{Na}_2\text{SO}_4$  was added to maintain a constant ionic strength.

Figure 5 shows a typical series of cyclic voltammograms obtained at different scan rates in a solution of  $0.12\text{M VCl}_3$  in  $0.5\text{M H}_2\text{SO}_4 + 1.04\text{M Na}_2\text{SO}_4$ . As the peak separations are between 300 and 400 mV, the  $\text{V(III)} + e \rightleftharpoons \text{V(II)}$  reaction is irreversible at the glassy carbon electrode. For an irreversible reaction, the peak current,  $i_p$ , is given by [18]:

$$i_p = 0.4958nFAC_{\text{O}}^{\circ}D_{\text{O}}^{1/2}v^{1/2} \left[ \frac{cn_a F}{RT} \right]^{1/2} \quad (1)$$

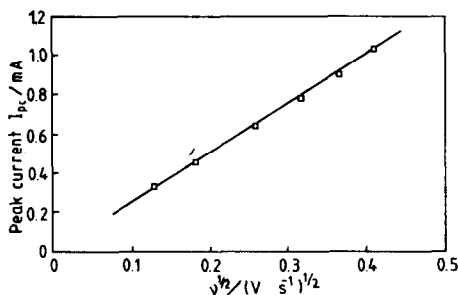


Fig. 6. Peak current vs. square root of scan rate for voltammograms in Fig. 5.

where  $i_p$  is in amperes,  $A$  is the electrode area ( $\text{cm}^2$ ),  $C_O^0$  is the bulk concentration of oxidant ( $\text{moles cm}^{-3}$ ),  $\nu$  is the potential sweep rate ( $\text{V s}^{-1}$ ),  $D_O$  is the diffusion coefficient of the oxidant,  $\alpha$  is the charge transfer coefficient, and  $n_a$  is the number of electrons involved in the rate-determining step. At  $25^\circ\text{C}$ , eqn. (1) reduces to:

$$i_p = 2.99 \times 10^5 n (\alpha n_a)^{1/2} A C_O^0 D_O^{1/2} \nu^{1/2} \quad (2)$$

A plot of  $i_p$  vs.  $\nu^{1/2}$  should therefore give a straight line with slope proportional to  $D_O$ . For a totally irreversible process, the peak potential,  $E_p$ , is a function of scan rate, the difference between  $E_p$  and the formal potential,  $E^{o'}$ , being related to the standard heterogeneous rate constant,  $k^0$ .

The peak current may also be expressed as [18]:

$$i_p = 0.227 n F A C_O^0 k^0 \exp \left[ - \frac{(\alpha n_a F)}{(RT)} (E_p - E^{o'}) \right] \quad (3)$$

A plot of  $\ln(i_p)$  vs.  $(E_p - E^{o'})$ , determined at different scan rates, should thus have a slope of  $-(\alpha n_a F/RT)$  and an intercept proportional to  $k^0$ .

A plot of cathodic peak current,  $i_{pc}$ , vs.  $\nu^{1/2}$  for the cyclic voltammograms of Fig. 5 is given in Fig. 6. 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 was  $1.41 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . The formal potential of the electrode  $E^{o'}$  was estimated from the cyclic voltammograms by taking the mean of the average of the anodic and cathodic peak potentials,  $E_{pa}$  and  $E_{pc}$ , i.e.,

$$E^{o'}(\text{estimate}) = \frac{\sum_{i=1}^m (E_{pa_i} + E_{pc_i})/2}{m} \quad (4)$$

where  $m$  is the total number of scans.

The ratio of the peak current  $i_{pa}/i_{pc}$  was calculated from the expression:

$$\frac{i_{pa}}{i_{pc}} = \frac{(i_{pa})_0}{i_{pc}} + 0.485 \frac{(i_{sp})_0}{i_{pc}} + 0.086 \quad (5)$$

TABLE 1

Values of anodic: cathodic peak current ratio ( $i_{pa}/i_{pc}$ ) and the formal potential ( $E^{o'}$ ) calculated from cyclic voltammograms of Fig. 5 for the reaction  $V(III) + e \rightleftharpoons V(II)$

$\nu$ (V min <sup>-1</sup> )	$\nu$ (V s <sup>-1</sup> )	$(i_{sp})_o$ (10 <sup>-3</sup> A)	$(i_{pa})_o$ (10 <sup>-3</sup> A)	$i_{pc}$ (10 <sup>-3</sup> A)	$E_{pa}$ (V)	$E_{pc}$ (V)	$\Delta E_p$ (V)	$(i_{pa}/i_{pc})$	$E^{o'}$ (V)*
1	0.0167	0.23	0.16	0.33	-0.41	-0.77	0.36	0.92	-0.588
2	0.0333	0.31	0.24	0.45	-0.40	-0.77	0.37	0.95	-0.585
4	0.0667	0.46	0.33	0.63	-0.38	-0.79	0.41	0.96	-0.585
6	0.1000	0.57	0.40	0.78	-0.38	-0.80	0.42	0.95	-0.585
8	0.1330	0.67	0.46	0.90	-0.37	-0.80	0.43	0.96	-0.585
10	0.1670	0.80	0.49	1.02	-0.37	-0.81	0.44	0.95	-0.588

\*Estimated.

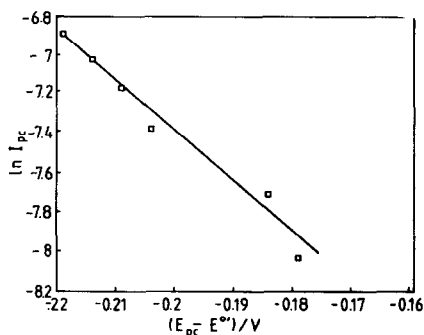


Fig. 7.  $\ln i_{pc}$  vs.  $(E_{pc} - E^{o'})$  for voltammograms in Fig. 5.

where  $(i_{pa})_o$  is the uncorrected anodic-peak current with respect to the zero current baseline and  $(i_{sp})_o$  is the current at the switching potential [18]. Table 1 shows the values of  $i_{pa}/i_{pc}$  and  $E^{o'}$  calculated from the cyclic voltammograms of Fig. 5. The mean value of  $i_{pa}/i_{pc}$  is 0.95, very close to the value of unity expected when there are no kinetic or other complications in the electrode process.

The average value of  $-0.586$  V for the formal potential of the electrode process shown in Table 1, was used to plot  $\ln i_p$  vs.  $(E_p - E^{o'})$  for the relationship given by eqn. (3). Figure 7 presents the plot of  $\ln i_p$  vs.  $(E_{pc} - E^{o'})$  obtained from the cyclic voltammograms of Fig. 5. From the slope of this straight line, the value of  $\alpha$  was found to be 0.6, while from the intercept, the heterogeneous rate constant,  $k^o$ , was calculated as  $1.71 \times 10^{-5}$  cm s<sup>-1</sup>.

Similar plots were performed from cyclic voltammograms obtained at various concentrations of  $VCl_3$ , as well as in solutions of varying pH. The effect of pH on the parameters  $i_{pa}/i_{pc}$ ,  $\alpha$ ,  $D_O$  and  $k^o$  is summarised in Table 2. Statistical analyses of these results showed no significant dependence of  $i_{pa}/i_{pc}$ ,  $\alpha$ , or  $D_O$  on pH. However, a slight trend in  $k^o$  with pH was observed,



TABLE 2

Effect of pH on  $i_{pa}/i_{pc}$ ,  $\alpha$ ,  $k^0$  and  $D_O$  for 0.1M  $VCl_3$  in  $H_2SO_4/Na_2SO_4$  solutions

$[H^+]$ (mol l <sup>-1</sup> )	pH	$\alpha$	$D_O$ (10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup> )	$k^0$ (10 <sup>-5</sup> cm s <sup>-1</sup> )	$i_{pa}/i_{pc}$
$1 \times 10^{-4}$	4.0	$0.43 \pm 0.05$	$1.50 \pm 0.14$	11.0	$0.98 \pm 0.05$
$1 \times 10^{-2}$	2.0	$0.42 \pm 0.17$	$1.34 \pm 0.08$	9.0	$0.91 \pm 0.25$
0.10	1.0	$0.55 \pm 0.12$	$1.16 \pm 0.18$	2.4	$0.95 \pm 0.04$
0.32	0.5	$0.54 \pm 0.16$	$1.67 \pm 0.12$	6.1	$0.94 \pm 0.06$
1.00	0.0	$0.67 \pm 0.15$	$1.41 \pm 0.12$	1.7	$0.95 \pm 0.04$
3.16	-0.5	$0.55 \pm 0.32$	$2.11 \pm 0.14$	3.9	$0.99 \pm 0.01$

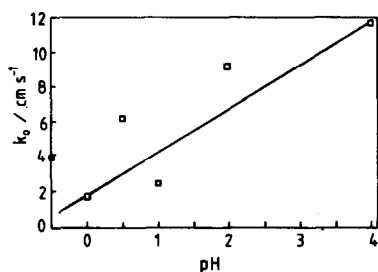
Fig. 8. Trend in value of heterogeneous rate constant,  $k^0$ , with pH.  $[VCl_3] = 0.1M$ .

Fig. 8. The linear regression analysis performed on these results gave a very low correlation coefficient (namely, 0.8559).

The theory employed here for the mathematical treatment of the results assumes that the electrode surface is smooth. As mentioned previously, the conventional technique of polishing with alumina powder and ultrasonic cleaning could not be used on the glassy carbon electrode here, due to the adverse effect of  $\alpha$ -alumina on the reversibility of the V(III)/V(II) redox couple. The use of the P1200 sandpaper would give rise to a certain degree of electrode roughness, which could create problems in the application of the theory to the treatment of results in this study, particularly in the determination of actual current densities. Experiments performed with the same electrode in a  $K_3Fe(CN)_6$  solution, however, showed that the variability in the peak currents arising from electrode roughness (*i.e.*, for electrode polished with P1200 sandpaper or with alumina powder) was no greater than the variability observed within a number of experiments employing alumina-polished electrodes. This highlights a problem often encountered in studies employing glassy carbon electrodes, namely, the difficulty in obtaining a reproducible surface on which to carry out electrochemical measurements. This difficulty would help to explain the considerable scatter of results as presented in Figs. 7 and 8.

## Conclusions

The reactions of the V(III)/V(II) redox couple were found to be electrochemically irreversible at a glassy carbon electrode, with a value of  $k^{\circ}$  equal to  $1.2 \times 10^{-4} \text{ cm s}^{-1}$  at pH = 4.

The kinetics of the V(III)/V(II) system at a glassy carbon electrode are strongly influenced by the method of preparation of the electrode surface. Polishing the electrode with alumina powder had an adverse effect on the reversibility of the reactions, even after ultrasonification for 1.5 h. The most reversible behaviour for the vanadium redox couple was obtained after the electrode had been polished with fine sandpaper only.

The reversibility of redox reactions at glassy carbon electrodes has generally been found to be much poorer than at platinum or gold electrodes [19, 20]. Wightman *et al.* [21] recently reported that the rate of reduction of  $\text{Fe}(\text{CN})_6^{3-}$  in 0.5M  $\text{K}_2\text{SO}_4$  at glassy carbon electrodes can be increased by polishing with alumina followed by ultrasonic cleaning. The impregnation of the glassy carbon electrode surface with  $\alpha$ -alumina has also been reported to increase the reversibility of the ascorbic acid oxidation reaction [22]. The overpotential for this reaction was lowered by 200 - 300 mV with the  $\alpha$ - $\text{Al}_2\text{O}_3$ /glassy carbon electrode compared with the highly polished, bare, glassy carbon electrode. The adverse effect of  $\alpha$ -alumina on the reversibility of the vanadium redox couple is difficult to explain at this stage. It is possible that alumina particles block the active sites on glassy carbon for the oxidation or reduction of the vanadium species. The observation that reversibility is improved by polishing with sandpaper only, agrees with results obtained by Evans *et al.* [23] that demonstrated that the glassy carbon surface is activated by mechanical abrasion and by etching with a radio frequency argon plasma. The reactivity of the surface carbon is thought to increase because of the removal of "surface oxides".

The glassy carbon electrode was also seen to become contaminated or poisoned with time (see Fig. 3). Electrode poisoning of glassy carbon surfaces can be caused by the formation of oxygen-containing functional groups on the surface when the electrode is immersed in a solution containing strong oxidizing agents, or if the potential is made positive with respect to SCE [24]. Once these oxygen-containing groups are formed on the surface, they can only be removed by mechanical abrasion. Poisoning of electrodes could also occur by adsorption of reactants or reaction products. The observed deterioration of reversibility with time for the vanadium redox couple can thus be explained by processes that change the surface of the electrode. Electrode poisoning would be a problem in a redox cell because the efficiency of the cell would drop dramatically with time. Thus, as the reversibility of the reaction decreases with electrode poisoning, the voltage obtained from the cell would be reduced dramatically due to the larger activation overvoltage losses. It may be possible to overcome this, however, by employing an alternative electrode material that may also improve the reversibility of the reactions.

The V(III)/V(II) redox couple is an attractive system for use in a redox battery, since it possesses many of the requirements for such applications. It has a formal potential of around  $-0.6$  V, making it suitable for use as a negative half-cell with the positive Fe(III)/(II) system.  $VCl_3$  is sufficiently soluble and stable in de-aerated acid solutions. The solutions of vanadium are safe to handle, although solid  $VCl_3$  must be handled with care since it fumes in air if left exposed, and produces solid  $VCl_2$  and gaseous  $VCl_4$  and  $Cl_2$  [15]. Although the V(III)/V(II) system exhibits electrochemically irreversible behaviour at glassy carbon electrodes, the value of  $k^\circ$  is sufficient to warrant further study to improve the reaction rate.

Finally, and quite importantly, the fact that vanadium exists in a number of oxidation states with a wide range of standard reduction potentials offers the possibility of an all vanadium redox cell system, which would overcome the problem of intermixing of electrolytes and loss of capacity. The value of the V(IV)/V(V) formal potential is around  $0.8$  V, offering a large cell voltage when combined with the V(III)/V(II) negative half-cell. The kinetics of the V(IV)/V(V) redox system are currently under investigation in our laboratories with a view to assessing the suitability of this couple as a positive half-cell in an all-vanadium redox-cell system.

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