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Electrochemical Investigation of The Catalytical Processes During Sulfuric Acid Production.

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Electrochemical Investigation of the Catalytical Processes in Sulfuric Acid Production

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ABSTRACT

The electrochemical behavior of molten $K_2S_2O_7$ and its mixtures with V_2O_5 [2-20 mole percent (m/o) V_2O_5] was studied at 440°C in argon, by using cyclic voltammetry on a gold electrode. The effect of the addition of sulfate and lithium ions on the electrochemical processes in the molten potassium pyrosulfate was also investigated. The potential window for pure $K_2S_2O_7$ was estimated as 2.1 V, being limited by the $S_2O_7^{2-}$ oxidation and reduction. The oxidation of SO_4^{2-} to oxygen is reversible in the basic melt. It is found that V(V) electroreduction proceeds in two steps. The first reduction stage [V(V) → V(IV)], starting at 0.7-0.8 V vs. Ag⁺/Ag, is reversible for V_2O_5 concentrations lower than 5 m/o and at potential scan rates less than 200 mV/s. For all studied compositions, the first reduction stage is a one-electron reaction. The second reduction stage [V(IV) → V(III)], starting at 0.1-0.2 V, is irreversible and under ohmic control at all studied V_2O_5 concentrations. The presence of Li_2SO_4 causes a noticeable depolarization effect on the V(V) reduction and the V(IV) oxidation.

Introduction

The molten V_2O_5-$M_2S_2O_7$ system (M is an alkali metal) is used as a catalytic medium for sulfur dioxide oxidation with oxygen or air, and this has been a subject of numerous publications for the last fifty years.[1-5] However, the mechanism of this catalytical process is not clearly understood, the following problems remaining unsolved: (*i*) The number of the catalytical reaction steps involved has not been defined; two-step,[1,6] three-step,[2] and four-step[4] mechanisms have been proposed. (*ii*) The structure of catalytically active V(V) species has to be elucidated. Neither proposed monomeric,[6] nor dimeric[4,5,7] structure of the dioxovanadium complexes has been convincingly determined. (*iii*) The first unsolved problem also leads to a question concerning the possibility of the V(V) two-stage reduction (both to V(IV) and V(III) species). The precipitation of solid

V(III) compounds in the liquid-gas $M_2S_2O_7$/V_2O_5-SO_2/O_2/SO_3/N_2 system (where M is Na, K, or Cs), has been proven by chemical and x-ray analysis.[4] Electrochemical investigations in the V_2O_5-$K_2S_2O_7$ melt could neither prove nor disprove the V(IV) → V(III) reduction reaction.[6,9,12] (*iv*) The nature of the promoting effect of alkali ions on the catalytic activity of the V_2O_5-$K_2S_2O_7$ melt is unknown. It was found in practice that the efficiency increased with the alkali atomic number (or ionic radius) and the presence of sodium cations had a promotive effect at low temperatures (close to the point of catalyst deactivation, *i.e.,* 440°C[2]); and that cesium ions decreased the temperature of deactivation.[4,10-13]

Therefore, investigations of the mechanism of catalytical reactions in the molten V_2O_5-$M_2S_2O_7$ system are still of great significance. By using electrochemical techniques, the oxidation and the reduction parts of the complex chemical reaction can be separated; moreover, some oxidation

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and reduction agents (such as O_2, SO_2, and SO_3) can be excluded, thus simplifying the investigation. As a result, useful information for the mechanism could be obtained.

The electrochemical behavior of molten potassium pyrosulfate and its mixtures with potassium sulfate and vanadium pentoxide was studied by Durand et al.,[6,15] Comtat et al.,[14] Frank and Winnick,[7] Scott et al.,[8] and Dojcinovic et al.[9] in different gas atmospheres. From these references, large disagreements can be seen between the experimental data, and the conclusions on the width of the potential window and the nature of the electrochemical processes involved. According to Durand et al.,[15] the potential window of the gold electrode in molten potassium pyrosulfate at 430°C was 0.41 V wide for the acidic melt and 0.51 V wide for the basic melt, with a difference as high as 0.52 V between acidic and basic cathodic limits. The anodic limit was ascribed to gold electrodissolution in the acidic melt, and in the basic melt to the $S_2O_7^{2-}$ ion oxidation with oxygen evolution. The cathodic limit was ascribed to a reduction of $S_2O_7^{2-}$ (or SO_3).[6] These explanations have not been tested experimentally, and the difference in the potential windows of the acidic and basic $K_2S_2O_7$ melts seems questionable being compared with the results obtained by Comtat et al.,[14] Frank and Winnick,[7] and Dojcinovic et al.[9] Thus Comtat et al.[14] observed the same anodic limit for the basic electrolyte at a platinum and a gold electrode. Frank and Winnick[7] also obtained an approximately 0.6 V wide potential window at a gold electrode in N_2, air, SO_2/air, SO_2/O_2/N_2 atmospheres, in both acidic and basic molten potassium pyrosulfate. Oxidation of SO_4^{2-} was observed at an anodic limit of 0.8-0.9 V vs. Ag/Ag$^+$, whereas $S_2O_7^{2-}$ reduction was seen as the cathodic limiting reaction at 0.25 V. However the experiments of Frank and Winnick[7] were done at 370-400°C, i.e., at temperatures lower than the melting point of dry $K_2S_2O_7$ (i.e., 418.52°C[16]). This indicates the presence of water in the molten potassium pyrosulfate, and therefore a possible water effect on the results of the experiments should be taken into account. These considerations could also explain the 1.0 V difference between the potentials of the cathodic limiting reactions for the pyrosulfate melts given by Frank and Winnick[7] and Dojcinovic et al.[9]

Taking into account that SO_4^{2-} ions are present in potassium pyrosulfate melt owing to the dissociation reaction (where the former SO_3 dissolves in molten potassium pyrosulfate through the formation of $S_3O_{10}^{2-}$ solvate complexes[17])

$$2S_2O_7^{2-} \leftrightarrow S_3O_{10}^{2-} + SO_4^{2-} \qquad [1]$$
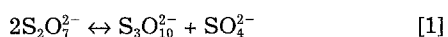
the electrochemical characteristics of molten alkali sulfates are also of interest. Alkali sulfates have been studied more extensively and carefully than the pyrosulfates.[18-22]

The electrochemical behavior of solutions of V_2O_5 and $VOSO_4 \cdot 3.5H_2O$ [0.25-1.0 mole percent (m/o)] in molten potassium pyrosulfate was investigated by Durand et al.[6] by using gold electrodes. Frank and Winnick[7] have studied the electrochemistry of V_2O_5 solutions [1-5 weight percent (w/o)] in basic and acidic $K_2S_2O_7$ in N_2, O_2, SO_2/N_2, and SO_2/O_2/N_2 atmospheres.

Durand et al.[6] have concluded that in the studied concentration range, the V(V) ↔ V(IV) electrochemical conversion involves a reversible one-electron reaction. They assumed that V(V) and V(IV) species were monomeric in both acidic and basic melts, with V(IV) existing in the form of $VOSO_4$ and $VO(SO_4)_2^{4-}$, and with V(V) in the form of $VO_2SO_4^-$ and $VO_2(SO_4)_2^{3-}$, in the acidic and basic electrolytes, respectively. These considerations are in agreement with spectrophotometric, cryoscopic, and potentiometric results for dilute V_2O_5 solutions in molten $K_2S_2O_7$-K_2SO_4,[16] which showed that monomeric $VO_2SO_4^-$ and $VO_2SO_4S_2O_7^{3-}$ were the most probable complexes.

Frank and Winnick[7] supposed that the reaction V(V) ↔ V(IV) was reversible in the concentration range of 1-5 w/o of V_2O_5. The calculated number of electrons (n) for the reaction varied from one to two. The authors believed that a two-electron reaction was most likely, and hence the vana-

dium species dissolved in the $K_2S_2O_7$ melt were in the form of the dimeric structures.

On the basis of the calorimetric, density, and conductivity measurements of V_2O_5 solutions (molar fraction of V_2O_5 = 0-0.5266) in molten $K_2S_2O_7$, Fehrmann et al.[23] and Hatem et al.[24] have proposed that the complex formation should occur at the compositions of $2K_2S_2O_7$:$1V_2O_5$ and $1K_2S_2O_7$:$1V_2O_5$. That means the existence of dimeric $(VO_2)_2(SO_4)_2S_2O_7^{4-}$ and polymeric $(VO_2SO_4)_n^{n-}$ species in the concentrated V_2O_5 solutions.

There is further information which might be used to help unravel "monomeric" and "polymeric" theories: a monomeric salt, $K_3VO_2SO_4S_2O_7$, was isolated from the $K_2S_2O_7$-V_2O_5 system,[25] and a dimeric compound, $Cs_4(VO)_2O(SO_4)_4$, was found in the $Cs_2S_2O_7$-V_2O_5 system.[26] Karydis et al.[27] also have obtained a phase diagram with a distectic composition of $3M_2S_2O_7$:$1V_2O_5$ and "no sign of the formation of dimeric V(V) compounds" in the molten V_2O_5-$M_2S_2O_7$ (M = 80% K + 20% Na) system.

In the case of V(IV), both monomeric and polymeric structures seem to exist, although in dilute systems the existence of only monomeric vanadyl complexes was shown.[5] These results are in agreement with the electrochemical data of Durand et al.[6] At high concentrations of V(IV) compounds in the pyrosulfate melts polymeric V(IV) species seem predominant.[28]

The disagreements concerning the V(IV) → V(III) reaction stage,[6,9,12] may be explained on the basis of different contents of water in the melts. The potential window could, depending on the level of moisture, be too narrow to obtain the second vanadium reduction wave (the difference between V(V) → V(IV) and V(IV) → V(III) potentials can exceed 0.68 V[28]).

In short, additional electrochemical measurements should be made under dry conditions and in an inert gas atmosphere (to exclude possible oxygen effect on the potential window of molten potassium pyrosulfate). The present study was conducted to provide useful electrochemical kinetic data for molten potassium pyrosulfate solutions with a wide concentration range of V_2O_5, and to have a good understanding of the catalytic mechanism.

Experimental

Pure and dry $K_2S_2O_7$ was obtained by thermal decomposition of $K_2S_2O_8$ (Merck, Pro Analysi, maximum 0.001%N) as described earlier.[16] K_2SO_4 (Merck, Suprapur) and Li_2SO_4 (Sigma, 99%) were dried at 500°C overnight. V_2O_5 from Cerac (99.9% pure) and Ag_2SO_4 from Heraeus (99.9% pure) were used without further purification. All sample preparation and handling were performed in an argon-filled glove box (Vacuum Atmospheres Inc.), with a measured oxygen and water concentration less than 10 ppm.

Cyclic voltammetry measurements were performed in a hermetically closed three-electrode quartz cell with an epoxy resin-joined and water-cooled stainless steel head (Fig. 1). The reference electrode was a silver wire placed in a Pyrex cylindric chamber with a Pyrex frit bottom. A melt of potassium pyrosulfate saturated with silver and potassium sulfates was used as the electrolyte in the reference silver electrode chamber. This reference system has been proven to have a stable potential in the studied temperature range.[14]

A gold wire sealed in a Pyrex tube served as the working electrode. A gold-wire spiral served as counter-electrode. It has been shown that gold is stable in both acidic and basic $K_2S_2O_7$ melts, and therefore gold was used as the electrode material in previous electrochemical investigations.[16]

After the cell was filled with electrolyte and hermetically closed in an argon glove box, it was placed in a vertical aluminum-block furnace, with temperature regulation to within ±0.1°C.[29] The components of the melt could be mixed by automatic rocking of the furnace. The temperature of the melt was measured by a calibrated Chromel-Alumel thermocouple in a Pyrex case placed inside the electrochemical cell.

Voltammetric measurements were carried out with a Schlumberger Model SI1286 electrochemical interface, and a Graphtec Model WX3000-1 X-Y Recorder.

Results and Discussion

Voltammetric Measurements in the $K_2S_2O_7$ and $K_2S_2O_7$-K_2SO_4 Melts at 440°C

A characteristic cyclic voltammogram obtained at a gold electrode in molten $K_2S_2O_7$ in argon is shown in Fig. 2. From Fig. 2, it can be seen that the potential window of the potassium pyrosulfate is limited by a gradual reduction at −1.1 V and a steep oxidation at 1.0 V. In addition, four minor waves can be seen inside the electrochemical window: three reduction waves (A, B, and D) and one oxidation wave (C). The processes corresponding to the minor waves could affect the potential window of molten potassium pyrosulfate, and therefore their identification is important.

The dependence of the A, C, and D peak parameters on the potential scan rate (V_E) is shown in Fig. 3-5. All the peak currents depend linearly on the square root of the potential scan rate, and all the peak potentials are linearly dependent on the logarithm of the potential scan rate. It should be noticed that wave A becomes suppressed during cycling (Fig. 6).

The effect of melt acidity was also studied, by adding potassium sulfate to the potassium pyrosulfate. A comparison of the voltammetric characteristics of molten $K_2S_2O_7$ and $K_2S_2O_7$-K_2SO_4 systems (saturated with K_2SO_4 according to the data of Ref. 21) is made in Fig. 7. It is seen that in
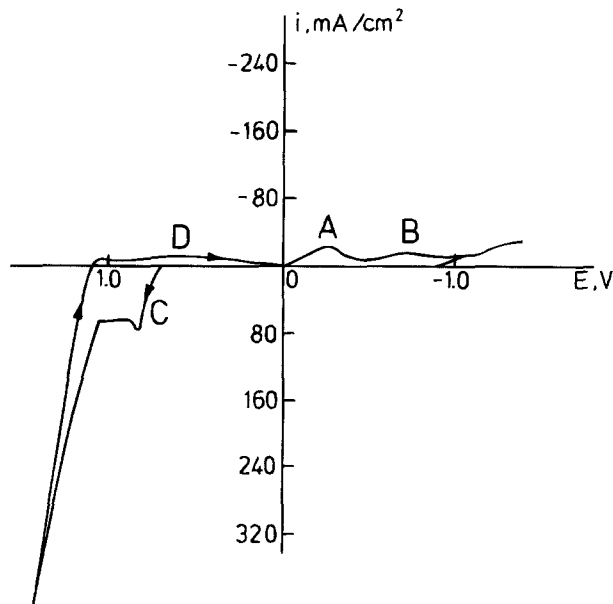
Fig. 2. Cyclic voltammogram measured with gold electrodes in molten $K_2S_2O_7$ at 50 mV/s and 440°C.
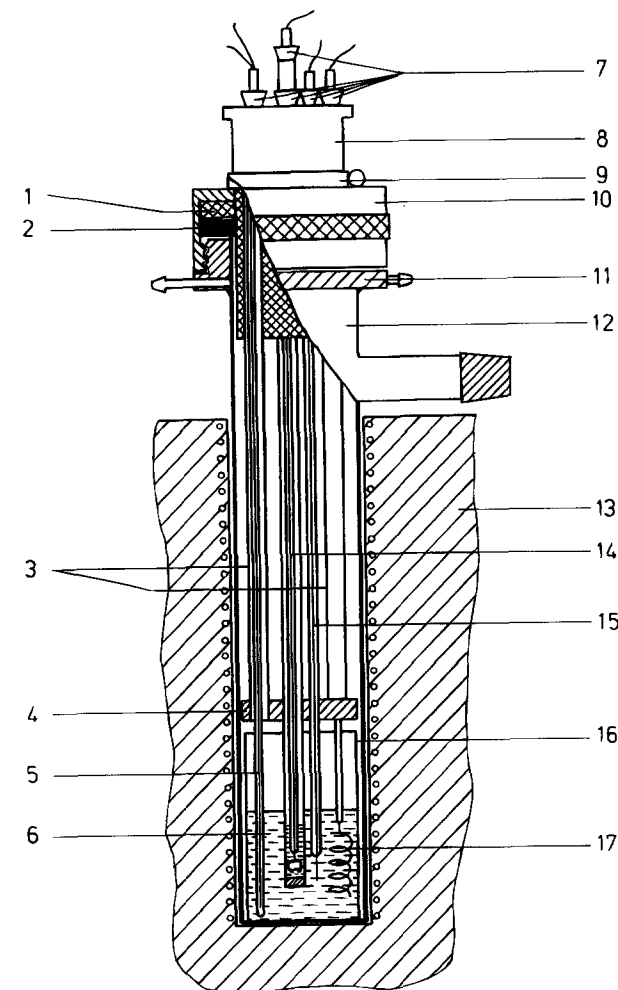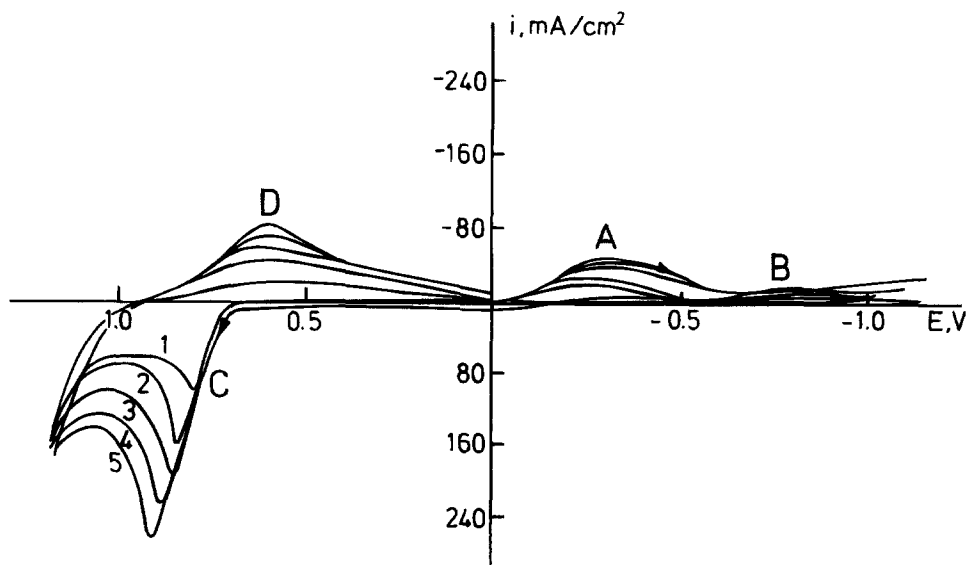
Fig. 1. The electrochemical cell: 1, Teflon ring; 2, vacuum rubber ring; 3, ceramic tubes; 4, ceramic screen; 5, thermocouple; 6, electrolyte; 7, rubber stoppers; 8, Teflon lid; 9, fixation ring; 10, stainless steel cover; 11, stainless steel lid; 12, quartz tube; 13, oven; 14, reference electrode; 15, working electrode; 16, Pyrex glass; 17, counterelectrode.

basic (SO_4^{2-}-rich) melts, the peak potential of reaction C moves in the positive direction and becomes less sharp. A new anodic reaction (E) appears at approximately 0.9 V. For the reactions C, D, and E in the basic melt, peak currents depend linearly on the square root of the potential scan rate, and peak potentials are independent of the potential scan rate in the 25-200 mV/s region (for E at the 50-100 mV/s region) (Fig. 8 and 9). For reaction A, the peak current and peak potential are linearly dependent on the square root and logarithm of the potential scan rate, respectively (Fig. 8 and 9).

According to Nicholson and Shain,[30] Eq. 2 describes the dependence of the peak potential of the irreversible process on the potential scan rate

$$E_p = E^0 - \frac{RT}{\alpha n_\alpha F}\left[0.78 - \ln k_s + 1/2 \ln \frac{D\alpha n_\alpha F V_E}{RT}\right] \quad [2]$$

where E_p is the peak potential, E_o is the standard potential, k_s is the specific rate constant, α is the transfer coefficient; n_α is the number of electrons taking part in the irreversible electrochemical reaction; D is the diffusion coefficient; R is the gas constant; F is the Faraday constant; T is absolute temperature.

The linear dependence of the peak potential on the logarithm of the potential scan rate is an indication of irreversibility of the electron transfer stage of the electrochemical reaction. In the case of a reversible reaction, the peak potential should be independent of the potential scan rate.[31] It is seen from Fig. 4-6 that the electrochemical reactions A, C, and D are irreversible. Therefore we can use the Nicholson and Shain[30] equation (Eq. 3), to calculate the value of αn_α for the studied electrochemical reactions

$$E_p - E_{p/2} = -1.857\frac{RT}{\alpha n_\alpha}F \quad [3]$$

(E_p and $E_{p/2}$ are peak and half-peak potentials, respectively).

The αn_α values obtained for A, C, and D peaks using Eq. 3 at different potential scan rates are given in Table I. By assuming as usual[31] that α equals 0.5, the numbers of electrons participating in A, C, and D processes are estimated to be 3 (the calculated n_α are 3.27, 2.70, 2.70, and 2.76 at 200, 300, 400, and 500 mV/s, respectively), 3 (3.27, 3.27, 2.87, and 2.87) and 2 (2.08, 1.91, 1.76, and 1.76), respectively.

The number of electrons participating in the reversible electrochemical reaction can be calculated[31] using Eq. 4
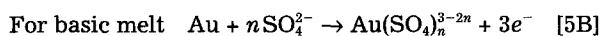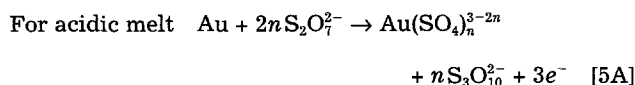
Fig. 3. Cyclic voltammograms measured with gold electrodes in molten $K_2S_2O_7$ at 440°C and curve 1, 100; curve 2, 200; curve 3, 300; curve 4, 400; curve 5, 500 mV/s.

$$E_p - E_{p/2} = -2.20 \frac{RT}{nF} \qquad [4]$$

The n values for the reversible (at least at low potential scan rates) electrochemical reactions, C and E, are given in Table I. For reaction C, these data are in agreement with a three-electron process obtained in the acidic melt ($n = 3.04$, 3.43, and 3.04 at 50, 75, and 100 mV/s, respectively). Process E is evidently a two-electron reaction ($n = 2.28$ and 2.36 for 50 and 100 mV/s, respectively).

In the investigated electrolyte system a three-electron process is possible only when gold participates in the reaction. Therefore, from our data and the results of Durand et al.,[15] wave C can be ascribed to the electro-oxidation of gold according to reactions Eq. 5A and 5B

For acidic melt $Au + 2nS_2O_7^{2-} \rightarrow Au(SO_4)_n^{3-2n}$

$$+ nS_3O_{10}^{2-} + 3e^- \qquad [5A]$$

For basic melt $Au + nSO_4^{2-} \rightarrow Au(SO_4)_n^{3-2n} + 3e^- \qquad [5B]$

The kinetics of oxidation is probably dependent on the chemical reaction forming the gold sulfate complex (so-called EC-mechanism). According to the theoretical inves-
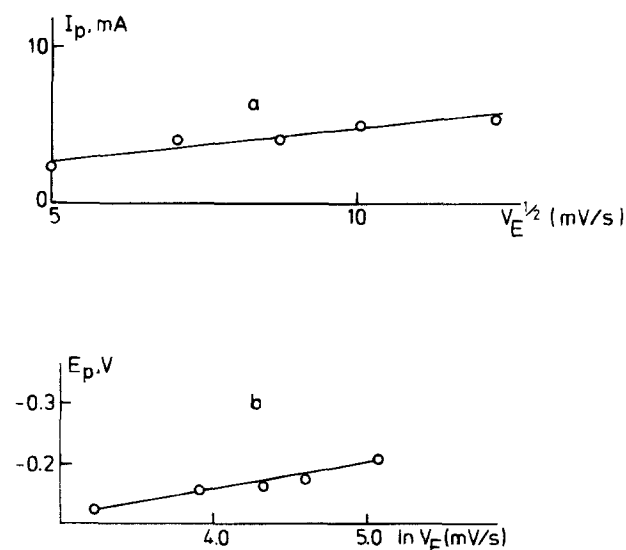
tigation of Nicholson and Shain,[30] the following slow chemical reaction will be able to overrule the reversible (i.e., quick) electrochemical reaction from the oxidation-reduction equilibrium. In the case of a fast following chemical reaction an anodic voltammogram for the reversible electrochemical reaction will usually be obtained but without the opposite cathodic process. However, even in this case, we still might observe a voltammetric picture of an EC-mechanism with slow chemical reaction at high potential scan rates. In fact, as seen in Fig. 7 and 9, the electrochemical reaction C is irreversible in the acidic melt (Eq. 5A) and reversible in the basic melt, where the concentration of SO_4^{2-} ions is sufficiently high (Eq. 5B). The related cathodic wave is absent for 5B, and at the potential scan rates higher than 100 V/s this process becomes irreversible.
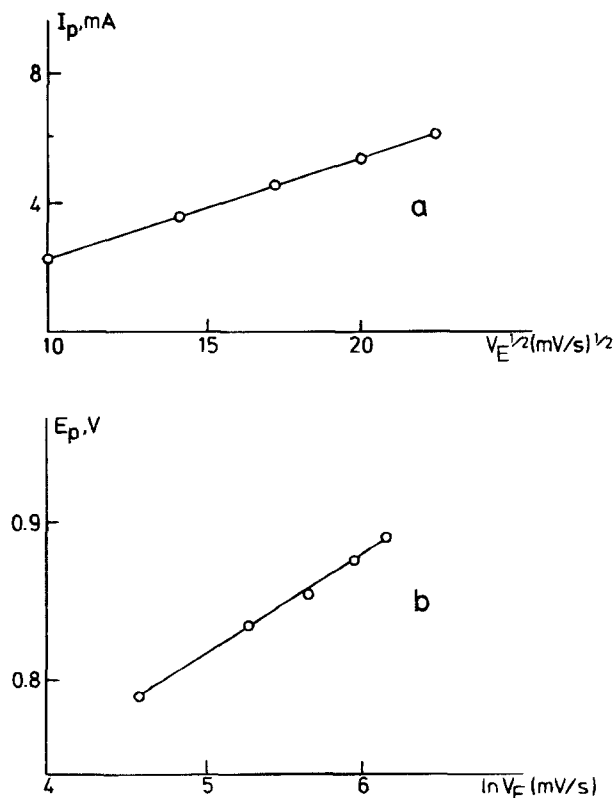

Fig. 4. Peak current (a) and peak potential (b) of wave A as function of potential scan rate obtained with Au electrodes in $K_2S_2O_7$ at 440°C.

Fig. 5. Peak current (a) and peak potential (b) of wave C vs. potential scan rate obtained in molten $K_2S_2O_7$ with Au electrodes at 440°C.
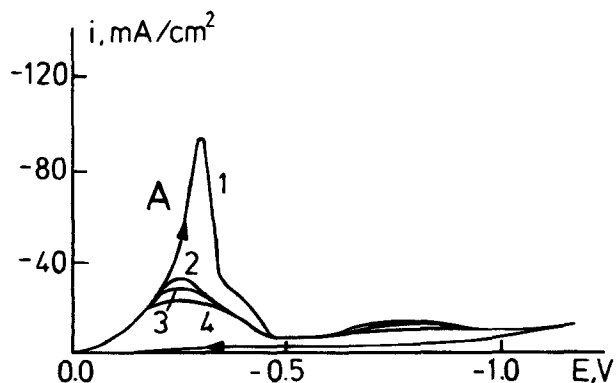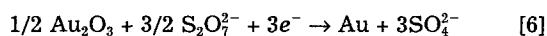
Fig. 6. Cyclic voltammograms measured with a gold electrode in molten $K_2S_2O_7$ at 440°C and 100 mV/s.

The reaction related to wave A, corresponding to gold participation, is eliminated during cycling. Evidently it is a surface gold-oxide reduction, which can be described by the following equation

$$1/2 \ Au_2O_3 + 3/2 \ S_2O_7^{2-} + 3e^- \rightarrow Au + 3SO_4^{2-} \qquad [6]$$

The voltammetric wave E appears only in basic melts (containing an excess of sulfate). Wave E is caused by a quasi-reversible two-electron reaction (the reversibility depends on the potential scan rate). It is known[18] that sulfate participates in both the anodic and the cathodic limiting processes in the (Li, K)$_2$SO$_4$ eutectic melt at 625°C. The anodic limiting process was the oxidation of the sulfate-ion to sulfur trioxide and oxygen gas. The cathodic limiting process was the reduction of sulfate to sulfite, possibly followed by additional steps leading to the formation of sulfur, sulfide, or both, depending on the conditions of electrolysis. Equilibrium potentials were obtained for the anodic limiting processes, which occur at about +0.9 V *vs.* Ag/Ag$^+$.[19] This is in agreement with Frank and Winnick's data for molten $K_2S_2O_7$.[7] For the platinum electrode, the rest potential of the $O^{2-}/O_2(g)$ couple was between +0.046 and +0.025 V *vs.* Ag/Ag$^+$, depending on the treatment of platinum. Burrows and Hills[20] have shown that the potential-determining reaction involves one or more types of oxides of platinum. Apparently no proper oxygen/oxide electrode has been achieved in this melt. Salzano and Newman[21] have ascertained that sulfur dioxide and trioxide were electrochemically active in the alkali sulfate melts. Boxall and Johnson[22] observed a Nernstian behavior of the reaction (Eq. 7)
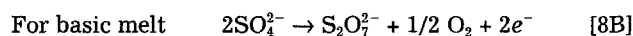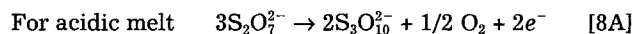
$$SO_3(g) + 1/2 \ O_2(g) + 2e^- \leftrightarrow SO_4^{2-} \qquad [7]$$
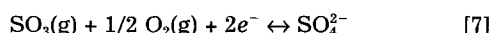
with a standard potential of +0.774 V *vs.* Ag/Ag$^+$. In a voltammetric study in the molten (Li, K)$_2$SO$_4$ at 625°C, Burrows and Hills[20] have found a SO$_3$ (or $S_2O_7^{2-}$) electroreduction wave at about −0.7 V (which is approximately 1.0 V more negative than in Ref. 7), a SO$_2$ electroreduction wave at *ca.* −1.5 V and a SO$_2$ electro-oxidation peak at −0.3 V *vs.* Ag/Ag$^+$.

Combining our information with the data of Rahmel,[19] and Salzano and Newman[21] on the reversible SO$_4^{2-}$ oxidation at a potential of 0.9 V in the sulfate melt, we ascribe wave E to an equation of the same kind as Eq. 7. Process D is a two-electron electrochemical reaction and proceeds at the potential corresponding to the reduction of the O$_2$/SO$_3$ gaseous mixture in the sulfate melt.[22] Therefore we could also suppose O$_2$/SO$_3$ reduction for wave D in the pyrosulfate melt. The absence of the additional reduction wave corresponding to the sulfate-ion oxidation can be explained as due to the same products of the $S_2O_7^{2-}$ and SO$_4^{2-}$ oxidation.

Therefore the oxidation limiting reaction of molten potassium pyrosulfate (1.0 V *vs.* Ag/Ag$^+$) can be described

by the following reactions (Eq. 8A and 8B) taking into account that free SO$_3$ cannot exist in molten pyrosulfates[17]

For acidic melt $\quad 3S_2O_7^{2-} \rightarrow 2S_3O_{10}^{2-} + 1/2 \ O_2 + 2e^- \quad$ [8A]

For basic melt $\quad 2SO_4^{2-} \rightarrow S_2O_7^{2-} + 1/2 \ O_2 + 2e^- \quad$ [8B]

The reduction wave B starts at the same potential as the SO$_3$ reduction in the sulfate melt,[20] *i.e.*, −0.5 V *vs.* Ag/Ag$^+$. The shape (of almost limiting current type) of the wave in the acidic melt is typical for the preceding slow chemical reaction mechanism.[30] Therefore, wave B can be ascribed to the electrochemical reduction of solvated SO$_3$,[14] according to Eq. 9

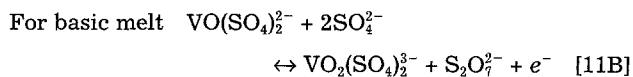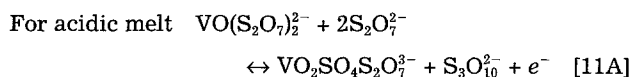$$3S_3O_{10}^{2-} + 2e^- \rightarrow SO_2 + 4S_2O_7^{2-} \qquad [9]$$
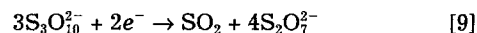
The electroreduction stability limit (−1.1 V) of the potassium pyrosulfate melt should be the reduction of the pyrosulfate anion, probably according to Eq. 10

$$2S_2O_7^{2-} + 2e^- \rightarrow SO_2 + 3SO_4^{2-} \qquad [10]$$
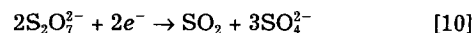
The Electrochemical Behavior of V_2O_5 in Molten $K_2S_2O_7$

The electrochemical behavior of V$_2$O$_5$ in molten potassium pyrosulfate at a gold electrode was studied in a wide concentration range. The voltammetric curve obtained for 2 m/o of V$_2$O$_5$ is shown in Fig. 10. It is seen that two new cathodic waves (F and G) and one anodic wave (H, which obviously is an oxidation of the first reduction product) appear in the presence of V$_2$O$_5$. The dependence of the F, G, and H wave-parameters on the potential scan rate is shown in Fig. 11. The F and H peak currents depend linearly on the square root of the potential scan rate, and the peak potentials are virtually independent on the potential scan rate (Fig. 15 and 16). For a melt with 2 m/o V$_2$O$_5$, the ratio of the first reduction (F) and the oxidation (H) peak currents is close to unity (Table II). The voltammetric characteristics of the K$_2$S$_2$O$_7$-V$_2$O$_5$ system of formal V$_2$O$_5$ concentrations up to 20 m/o are shown in Fig. 12-16 and in Table II. The F peak current is linearly dependent on the formal V$_2$O$_5$ concentration. Starting from 5 m/o of V$_2$O$_5$ the F and H peak potentials depend linearly on the logarithm of the potential scan rate. The ratio between F and H peak currents decreases with the concentration of V$_2$O$_5$, having a minimum at 5 m/o. The reduction wave G, instead of a peak, shows a linear current-potential dependence for high potential scan rates. A new oxidation wave, I, corresponding to the reduction wave G, becomes noticeable at 10 m/o of V$_2$O$_5$.

Hence, the first reduction-oxidation process (waves F and H) seems to be reversible below 5 m/o of V$_2$O$_5$ but irreversible at higher concentrations. It can be seen from Table II that at all studied concentrations both peaks F and H are one-electron reactions. It means that these waves are caused by the V(V) → (IV) and V(IV) → V(V) reactions, and that only one vanadium atom participates in these processes. They may be described by Eq. 11

For acidic melt $\quad VO(S_2O_7)_2^{2-} + 2S_2O_7^{2-}$

$\qquad\qquad \leftrightarrow VO_2S_2O_4S_2O_7^{3-} + S_3O_{10}^{2-} + e^- \quad$ [11A]

For basic melt $\quad VO(SO_4)_2^{2-} + 2SO_4^{2-}$

$\qquad\qquad \leftrightarrow VO_2(SO_4)_2^{3-} + S_2O_7^{2-} + e^- \quad$ [11B]

The change in kinetics of the reaction given by Eq. 11 at V$_2$O$_5$ concentrations higher than 5 m/o could be explained by an increase in degree of dimerization or of polymerization of the V(IV) species, proceeding via a mechanism of electrochemical desorption, in which a slow charge-transfer step is usually involved.[31]

Assuming (*i*) the potential difference between F and G reactions,[28] (*ii*) the electrochemical behavior of the V(IV) cathodic materials,[32] and (*iii*) the chemical identification of V(III) species as the products of the reduction of V(V) under the conditions of commercial sulfuric acid production,[4] we propose a V(IV) → V(III) reduction as an explanation for wave G. The shape of the voltammetric curve can be explained by the low solubility of the V(IV) and V(III) com-

Fig. 7. Cyclic voltammograms measured with gold electrodes at 440°C and 100 mV/s in $K_2S_2O_7$ (1) and $K_2S_2O_7$ saturated with K_2SO_4 (2) melts.
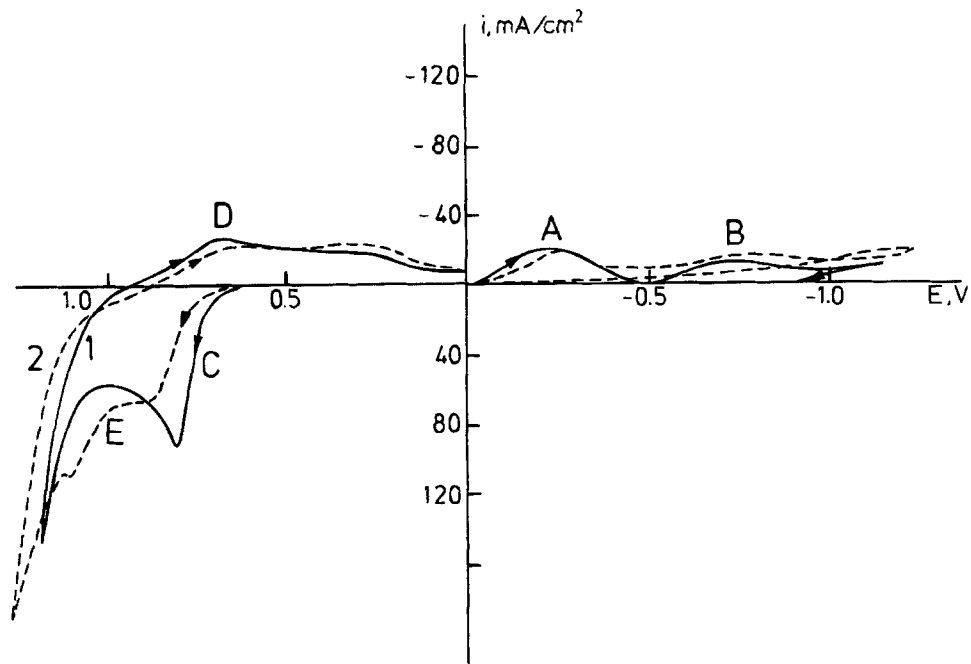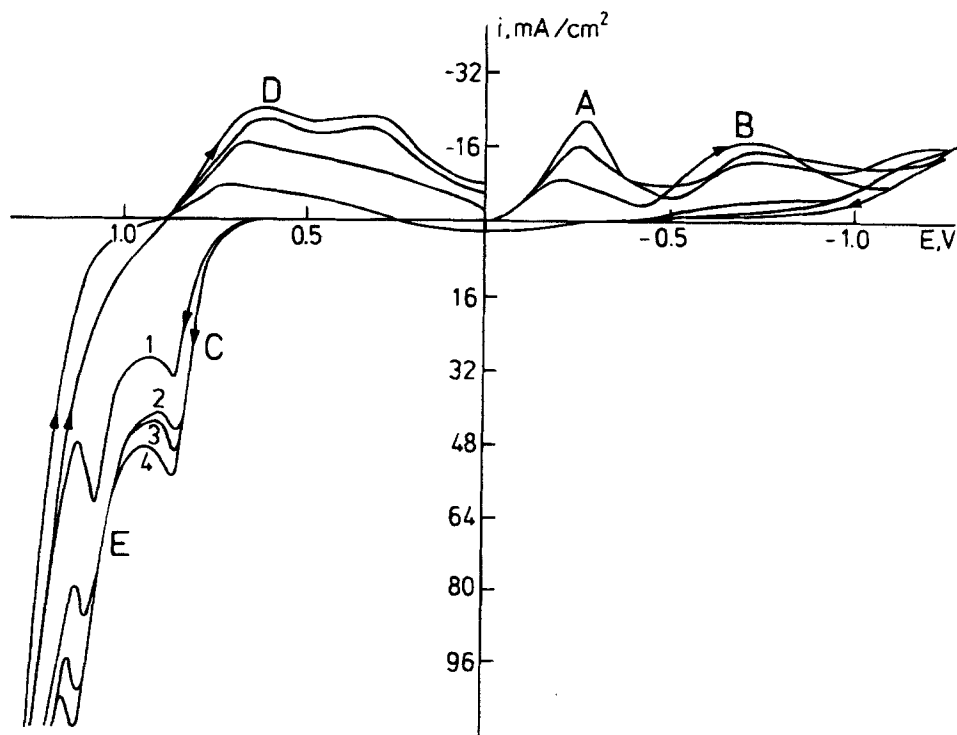

Fig. 8. Cyclic voltammograms measured with gold electrodes in molten $K_2S_2O_7$ saturated with K_2SO_4 at 440°C and curve 1, 25; curve 2, 50; curve 3, 75; curve 4, 100 mV/s.

pounds at 440°C,[4] and therefore one has an ohmic control of reaction G.

Starting from 10 m/o of V_2O_5, a new oxidation wave (wave I) appears on the voltammetric curves. This wave can be related to a V(III) → V(IV) reaction considering the reversible performance of the VO_2 secondary battery cathodes.[32]

Figures 14-16 (and Table II) demonstrate the voltammetric effect of adding 5.5 m/o Li_2SO_4 to a 10 m/o V_2O_5 solution in a potassium pyrosulfate melt. After addition of lithium sulfate, a white precipitate appeared in the melt. Taking into account the higher solubility of Li_2SO_4 than K_2SO_4 (which is 4.64 m/o at 440°C [21]) in molten $K_2S_2O_7$ and a possible exchange equilibrium (Eq. 12), in the reciprocal system

$$Li_2SO_4 + K_2S_2O_7 \rightarrow Li_2S_2O_7 + K_2SO_4 \qquad [12]$$
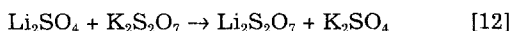
we assume that all the added lithium sulfate is practically present in the form of lithium pyrosulfate in the $K_2S_2O_7$ melt.

It can be seen that the Li^+ ion has a promoting effect on both oxidation and reduction processes, with the depolarization being almost three times higher for the V(V) → V(IV) reduction than for the V(IV) → V(V) oxidation. The ratio between the anodic and the cathodic peak currents is closer to unity in the presence of Li_2SO_4 in the studied electrolytes. It should also be noted that saturation of a $K_2S_2O_7$ melt by potassium sulfate has only a marginal effect on the V(V) ↔ V(IV) process.

The thermodynamical characteristics of the electrochemical reactions of Eq. 11A and 11B obviously depend on the alkali cation nature: the smaller the cation radius the higher its polarization effect on the complex vanadium par-
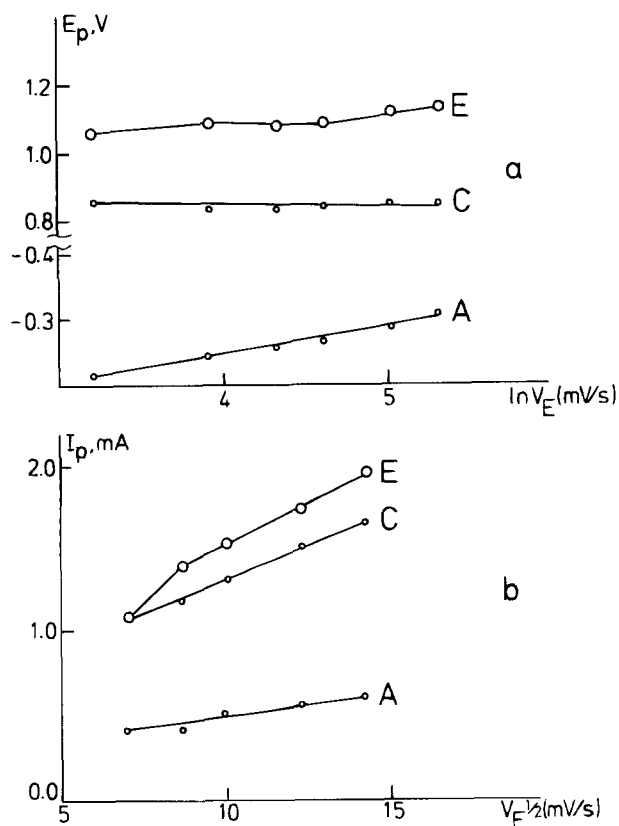
Fig. 9. Peak potential (a) and peak current (b) of waves A, C, and E as function of potential scan rate obtained in molten $K_2S_2O_7$ saturated with K_2SO_4 with gold electrodes and at 440°C.
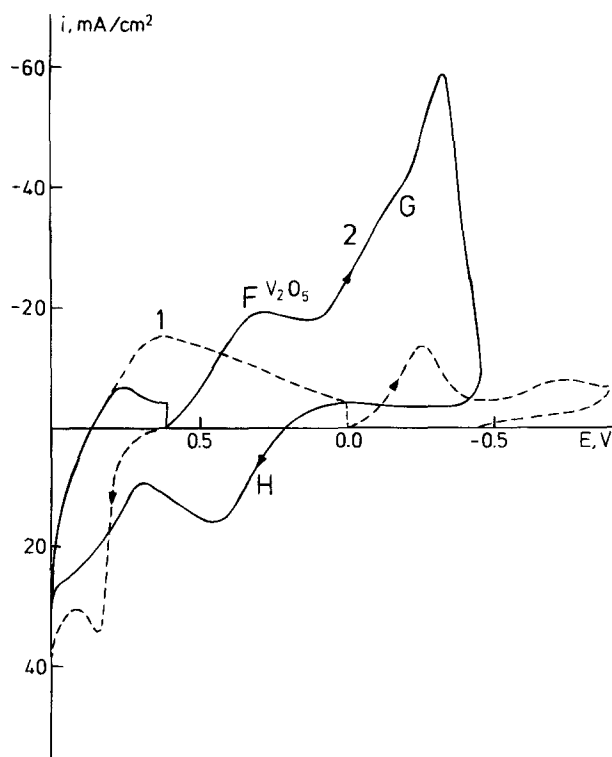

Fig. 10. Cyclic voltammograms measured with gold electrodes in (1) molten $K_2S_2O_7$ and (2) molten $K_2S_2O_7$ + 2 m/o V_2O_5 at 440°C and 100 mV/s.

ticles. This could cause the weakening of the V-O bond and facilitate the vanadium reduction.

The alkali-ion activation effect could qualitatively be divided into two types: "large amount additive" activation when the additive considerably changes the physicochemical properties of the bulk melt (*i.e.*, Cs+); and "small amount additive" [25] activation when the bulk physicochemical properties are not significantly changed (Na+, Li+).

For understanding of the "large amount" promoting effect, at least two factors should be taken into account.

1. Most cesium salts have supercooling and glass-forming tendencies, which are more pronounced for their near-eutectic mixtures with strongly polarizing cation salts (lithium, sodium, or small alkali-earth ions): the more diversity and number of particles in a multicomponent system, the higher the glassforming tendency[33] (so-called confusion principle). Moreover, the solubility of the vanadium species will be higher in the pyrosulfates with weakly polarizing cations, VO_2^+ and VO^{2+} are strong polarizing
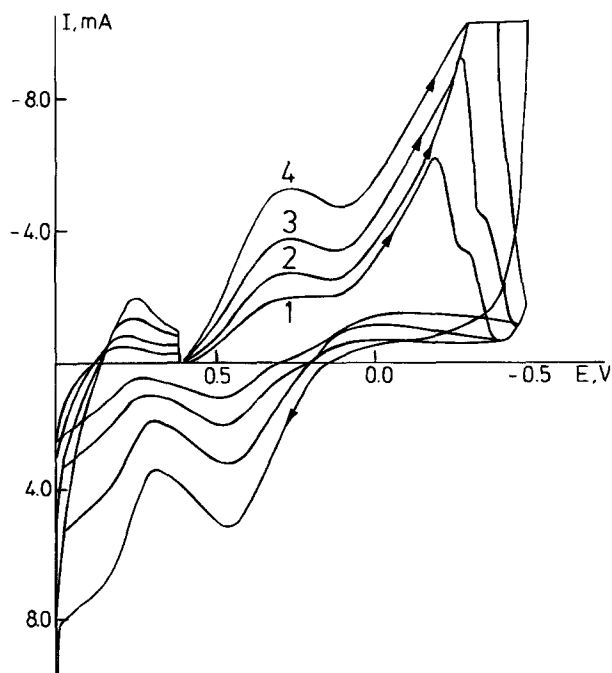
Table I. Peak and half-peak potential difference, $E_p - E_{p/2}$, αn_α [a] for the irreversible A, C, and D reactions and the number of participating electrons, n, for the reversible C and E reactions obtained in molten $K_2S_2O_7$ and $K_2S_2O_7$-K_2SO_4 systems at 440°C.

Electrochemical reaction	Potential scan rate, V/s	$E_p - E_{p/2}$, V	αn_α	n_α, n
A	0.200	0.070	1.637	3.27
	0.300	0.085	1.348	2.70
	0.400	0.085	1.348	2.70
	0.500	0.083	1.380	2.76
C	0.200	0.070	1.637	3.27
	0.300	0.070	1.637	3.27
	0.400	0.080	1.433	2.87
	0.500	0.080	1.433	2.87
D	0.100	0.110	1.042	2.08
	0.200	0.120	0.955	1.91
	0.300	0.130	0.878	1.76
	0.400	0.130	0.878	1.76
C	0.050	0.045		3.04
	0.075	0.040		3.43
	0.100	0.045		3.04
E	0.050	0.060		2.28
	0.100	0.058		2.36

[a] αn_α is the product of the transfer coefficient and the number of electrons participating in the irreversible A, C, D reactions.

Fig. 11. Cyclic voltammograms measured with gold electrodes in molten $K_2S_2O_7$ + 2 m/o V_2O_5 at 440°C and curve 1, 25; curve 2, 50; curve 3, 100; curve 4, 200 mV/s.

Table II. αn_α [a] for the irreversible and the number of participating electrons, n, for the reversible V(V) $\leftrightarrow$ V(IV) reaction as well as I_p^c/I_p^c in the molten $K_2S_2O_7$-V_2O_5 system at 440°C and 100 mV/S.

m/o V_2O_5	Reaction	n	αn_α	I_p [a]$/I_p$ [c]
2	Anodic	0.90		
	Cathodic	0.75		0.90
3	Anodic	0.67		
	Cathodic	0.71		0.90
5	Anodic		0.76	
	Cathodic		0.53	0.55
10	Anodic		0.71	
	Cathodic		0.45	0.60
20	Anodic		0.55	
	Cathodic		0.38	0.68
10	Anodic		0.55	
5.5 m/o	Cathodic		0.38	0.79
Li_2SO_4				

[a] αn_α is the product of the transfer coefficient and the number of electrons participating in the irreversible reaction.

Fig. 13. V(V) → V(IV) reduction peak current vs. V_2O_5 concentration obtained in $K_2S_2O_7$-V_2O_5 melts with gold electrodes at 400 mV/s and 440°C.

cations, and tend to form complexes with the solvent. Therefore, the less competition for the solvent anions, the higher solubility of the vanadium compounds.

2. The electroconductivity of the vanadium-containing pyrosulfate melts should have noticeable effect on their catalytical activity. Large alkali cations have less tendency to form clusters. They could have a mobility equal to that for small cations (lithium or sodium), the so called Chemla effect.[34] Moreover, for molten salts with easily polarizable molecular anions, the electroconductivity of cesium or potassium salts increases in the presence of small amounts
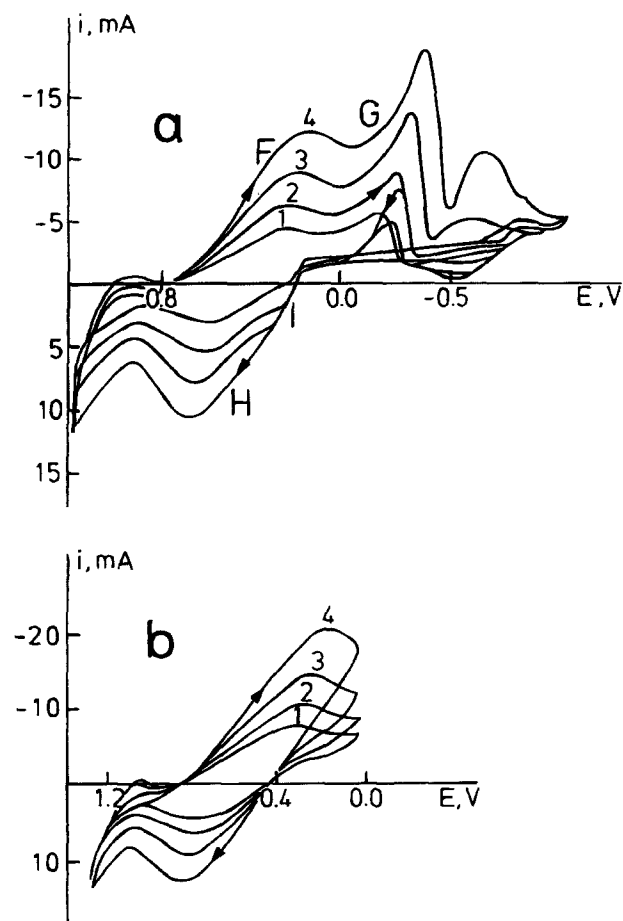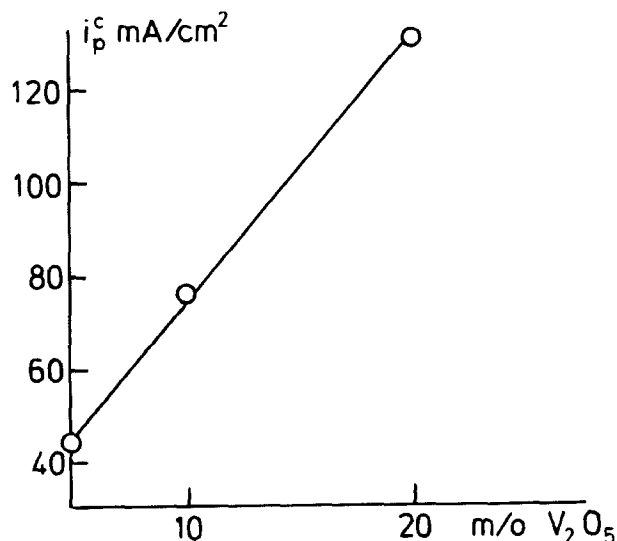
of lithium (or sodium) salts.[35] This can be explained by the weakening of the Cs^+-anion bonding in the presence of highly polarizing cations.

In industrial catalysis, the activation effect of small amounts of sodium sulfate is well known.[36,37] This effect can be explained as a change in the parameters of the catalytical reaction by highly polarizing Na^+ ions in the catalytically active vanadium complexes.

There is no indication in the literature that there would be a beneficial effect of the addition small amounts of Li^+ (sulfate or pyrosulfate). Large amounts of lithium pyrosulfate has shown no or a negative promoting effect in a series of alkali metal pyrosulfates.[38] If our explanation of the Na^+
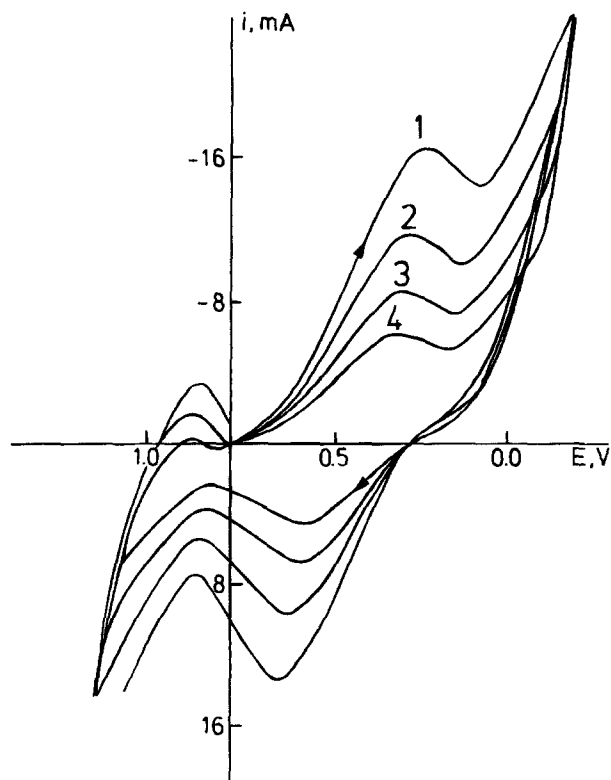

Fig. 12. Cyclic voltammograms measured with gold electrodes in molten $K_2S_2O_7$ + 10 m/o V_2O_5 (a) and molten $K_2S_2O_7$ + 20 m/o V_2O_5 (b) at 440°C and curve 1, 50; curve 2, 100; curve 3, 200; curve 4, 400 mV/s.

Fig. 14. Cyclic voltammograms measured with gold electrodes in the $K_2S_2O_7$-10 m/o V_2O_5-Li_2SO_4 (sat.) at 440°C and curve 1, 400; curve 2, 200; curve 3, 100; curve 4, 50 mV/s.
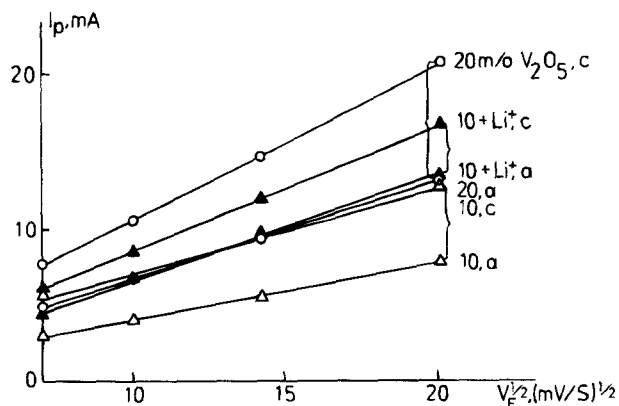
Fig. 15. V(V) → V(IV) and V(IV) → V(V) peak currents as function of potential scan rate obtained in molten $K_2S_2O_7$-V_2O_5 and $K_2S_2O_7$-V_2O_5-Li_2SO_4 systems with gold electrodes at 440°C. c, Cathodic; a, anodic.
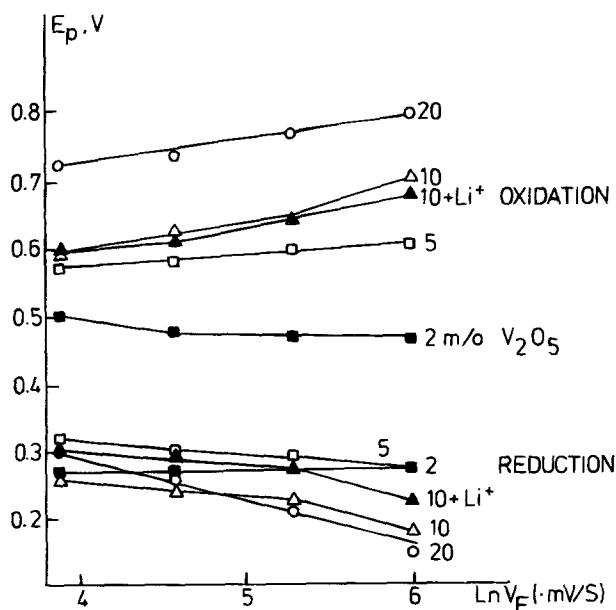
Fig. 16. V(V) → V(IV) and V(IV) → V(V) peak potentials *vs.* potential scan rate obtained in molten $K_2S_2O_7$-V_2O_5 and $K_2S_2O_7$-V_2O_5-Li_2SO_4 systems with gold electrodes at 440°C.

promoting effect is correct, and the Li^+ activation effect on the electrochemical V(V) ↔ V(IV) processes is taken into account, we would expect a promoting effect for diluted Li^+ solutions, also for industrial catalysts.

Conclusions

The potential window of pure molten $K_2S_2O_7$ was determined to be 2.1 V, being limited by $S_2O_7^{2-}$ oxidation and reduction. The formation of oxygen in basic melts proceeds reversibly at more negative potentials than in acidic melts where the process is irreversible.

The V_2O_5 reduction process includes two stages: V(V) → V(IV) and V(IV) → V(III). The first stage is reversible up to a fraction of 5 m/o of V_2O_5 and is a one-electron reaction at all studied concentrations (*i.e.*, up to 20 m/o). Hence, only one vanadium atom is involved in the reaction.

The presence of Li^+ ions causes a noticeable acceleration of the V(V) electroreduction.

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