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Electrochemical Study on the Cationic Promotion of the Catalytic SO₂ Oxidation in Pyrosulfate Melts

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ABSTRACT

The electrochemical behavior of the molten V_2O_5-$M_2S_2O_7$ (M = K, Cs, or Na) system was studied using a gold working electrode at 440°C in argon and air atmosphere. The aim of the present investigation was to find a possible correlation between the promoting effect of Cs^+ and Na^+ ions on the catalytic oxidation of SO_2 in the V_2O_5-$M_2S_2O_7$ system and the effect of these alkali cations on the electrochemical behavior of V_2O_5 in the alkali pyrosulfate melts. It has been shown that Na^+ ions had a promoting effect on the V(V) ⇄ V(IV) electrochemical reaction. Sodium ions accelerate both the V(V) reduction and the V(IV) oxidation, the effect being more pronounced in the case of the V(IV) oxidation. Sodium ions also had a significant (almost 0.2 V) depolarization effect on the V(IV) → V(V) oxidation. The peak current of the V(IV) → V(V) oxidation waves vs. $Na_2S_2O_7$ concentration plots had maximums at ca. 8.5 mol % of $Na_2S_2O_7$ in air atmosphere for all the studied potential scan rates. In the $Cs_2S_2O_7$-$K_2S_2O_7$ (1:1) melt the V(IV) → V(V) oxidation was affected by Cs^+ ions with a depolarization effect of 0.2 V and an even more significant acceleration than the in molten V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$ system. The V(IV) → V(V) oxidation peak currents were approximately 1.5 times higher than in the V_2O_5-$K_2S_2O_7$ system at all studied potential scan rates. No correlation has been found between the described effects and the electric conductivity of the systems. The rate-determining stage in the catalytic SO_2 oxidation most likely is the oxidation of V(IV) to V(V) and the Na^+ and Cs^+ promoting effect is based on the acceleration of this stage. It has also been proposed that voltammetric measurements can be used for fast optimization of the composition of the vanadium catalyst (which is approximately V_2O_5-$M_2S_2O_7$) for sulfuric acid production.

Introduction

The present work is a continuation of our investigation of the electrochemistry of the molten V_2O_5-$M_2S_2O_7$ system (M is an alkali metal).[1-3] This melt is found to be a realistic model of the V_2O_5-$M_2S_2O_7$ catalyst for sulfur dioxide oxidation with air in sulfuric acid production and in SO_2 removal from flue gases.

In the industrial catalytic SO_2 oxidation the promoting effect of alkali metal ions is well known and widely used. However, the knowledge about the nature of the promotion effect is not comprehensive. The promoters used in modern catalyst for the industrial sulfuric acid production are potassium, cesium, and sodium sulfates (or pyrosulfates).[4-19] It was found in practice that the efficiency of the alkali promoters increases with the alkali atomic number (or ionic radius) and therefore Cs^+ ions have the strongest promotion effect. This fact was explained on the basis of the increasing ability of the alkali sulfates to react with SO_3 and therefore increasing the stability of the alkali pyrosulfates in the series from $Li_2S_2O_7$ to $Cs_2S_2O_7$.

It was also found that the activity and thermal stability of the V_2O_5 catalysts promoted only by sodium salts were much lower than those based on potassium salts.[4,5,16] However small amounts (up to 20 mol %) of sodium salts appeared to increase the activity of the potassium vanadium sulfate catalysts,[16] especially in the lower part of the working temperature range. This effect was explained as a result of the formation of potassium-sodium oxosulfatovanadates (+V).[16] Nevertheless there is no clear explanation of why such different cations as Cs^+ and Na^+ have a similar promotive effect on the catalytic activity.

Understanding of the nature of the alkali ion promotion certainly should be based on the mechanism of the SO_2 catalytic oxidation. The mechanism of this catalytic process, has been a subject of numerous publications at least for 50 years.[4-22] However the following problems remain unsolved.

The number of catalytic reaction steps involved and the rate-determining stage.—Numerous researchers in the field of the catalytic SO_2 oxidation believe that the V(IV) oxidation with oxygen is the rate-determining stage.[5-15,17,18] It was also found that the V(IV) concentration in the catalyst is a function of temperature, thickness of the catalyst layer on the support, and the equilibrium V(V) + SO_2 →

SO_3-V(IV).[7,8] The latter depends very much on the SO_2 partial pressure and at low SO_2 pressures it can become the rate-determining stage.[6] Many researchers[5-13] have also shown for K/V catalysts that oxygen diffusion affects the rate-determining stage of the SO_2 oxidation. However, there is still a strong disagreement about the number and nature of the stages in the catalytic SO_2 oxidation. Thus Mars and Maessen[5] suggested a two-step mechanism almost 30 years ago for both K/V and K,Na/V catalysts. According to them the SO_2 oxidation proceeds through the fast establishment of the equilibrium

$$SO_2 + 2V^{5+} + O^{2-} \rightleftarrows SO_3 + 2V^{4+} \quad [1]$$
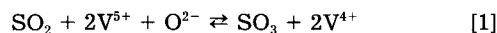
and the rate-determining step is V(IV) oxidation with oxygen. Mars and Maessen also suggested that at temperatures close to an observed sudden decrease of the catalytic activity with temperature the SO_3 solubility in the molten catalyst becomes high enough to slow down the reaction (Eq. 1).

However, the same researchers did not reject the possibility that this break in the Arrhenius plots can be explained by the formation of oxosulfovanadates caused by high concentrations of dissolved SO_3. Mars and Maessen thought that these oxosulfo groups can enclose and stabilize the V^{4+} ion.

The same considerations were behind the three-step mechanism for the 330-380°C temperature range introduced by Glueck and Kenney.[6] They assumed that a melt containing V^{5+} will absorb SO_2 without liberation of the equivalent amount of SO_3 and therefore two types of V^{4+} particles will be present in the molten catalyst at low temperatures: $(VOSO_4)_2$ and $V_2O_4 \cdot SO_3$. Glueck and Kenney argued against the conception of the V(IV) oxidation as a rate-determining step, at least in connection with low operating temperatures: they found no dependence of the catalyst activity on the oxygen pressure in the 330-380°C temperature range. Therefore Glueck and Kenney could not rule out the possibility that Eq. 1 could be far from equilibrium and become a rate-determining stage in the low temperature range.

The idea about a three-step mechanism and two types of V(IV) particles present in the vanadium catalyst at the operating temperatures below 430°C was further developed by Villadsen and Livbjerg.[7] They assumed the following mechanism

$$2X + SO_2 \rightleftarrows 2Y \quad [2]$$

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$$2Y \rightleftarrows 2Z + SO_3 \qquad [3]$$

$$2Z + \tfrac{1}{2} O_2 \rightleftarrows 2X \qquad [4]$$

where X are V(V) species and Y and Z are V(IV) species. Equation 4 was assumed to be far from equilibrium in thin films and in equilibrium in thick films. The authors[7,12] also suggested that the V(IV) oxidation is a rate-limiting step due to the low solubility of oxygen in the molten catalyst. Villadsen and Livbjerg[7] stated that the precipitation of V(IV) complexes is a reason for the drop in the catalytic activity at low operating temperatures because when the V(IV) precipitation was taken into account in the model, the break in the Arrhenius plots disappeared.

The mechanism assumed by Villadsen and Livbjerg[7] was later supported with experimental data obtained by Doering and Berkel[17] for the K/V and Cs/V sulfuric acid catalysts. These researchers agreed with the idea that irreversibility of the stage depicted by Eq. 2 at low temperatures can cause high $Y \cdot SO_3$ concentrations and a drop in the catalytic activity. It was also suggested[17] that molten cesium pyrosulfate decreases the formation of the inactive V(IV) complex compared to the K/V catalyst. It was found[17] that the concentration of the V(IV) complex is very dependent on the SO_2 partial pressure and temperature but slightly dependent on the O_2 partial pressure. However Doering and Berkel still insisted on the kinetic model with V(IV) oxidation as a rate-limiting step.[17]

Boreskov et al.[14] and Balzhinimaev et al.[15] assumed that an associative reaction mechanism, which did not change the valence state of vanadium was possible. They proposed a six-step mechanism that actually consisted of two types of mechanisms: associative (without changes in the vanadium valence state), or reduction-oxidation [with V(IV) → V(IV) changes].

During the last 10 years, important progress has been made in the investigation of the structure of the solid vanadium compounds that can be separated from the liquid catalysts at temperatures lower than the point of the activity drop.[16,19-22] Moreover it has been shown that at low operating temperatures V(III) species can be formed[19] by reduction with SO_2.

The $Na_2VO(SO_4)_2$, $Na_3(VO)_2(SO_4)_4$, $K_4(VO)_3(SO_4)_5$, $K_3(VO)_2(SO_4)_4$, $Cs_2(VO)_2(SO_4)_3$, β-$VOSO_4$, $VOSO_4(SO_2SO_3)_x$ [V(IV) and V(V) deposits] and $NaV(SO_4)_2$, $Na_3V(SO_4)_3$, $KV(SO_4)_2$, $CsV(SO_4)_2$ [V(III) deposits] were assumed to be responsible for the catalyst deactivation.[22] It is also believed[22] that the catalytic activity can be increased by increasing the atomic number of the alkali promoter, mixing of alkali promoters, and decreased vanadium concentration in the catalyst. Eriksen et al.[22] suggested that a mixture of alkali ions, such as Na^+ and K^+ or Na^+, K^+, and Cs^+, would probably lead to higher solubility of the V(IV) and V(III) compounds.

The electrochemical behavior of the V_2O_5 solutions in molten potassium pyrosulfate at 440°C in the 1-20 mol % V_2O_5 concentration range in Ar, air, and SO_2/air atmospheres was studied by Bjerrum et al.[1-3] It was shown that for all studied conditions the V(V) → V(IV) reduction and the V(IV) → V(V) oxidation were one-electron reactions which means that V(V) and V(IV) particles should be monomeric or alternatively the vanadium atoms could be separated by an oxygen atom[20] or SO_4^{2-} anions[21] in the polymeric chains. It was found that the V(V) → V(IV) reduction and the V(IV) → V(V) oxidation were reversible electrochemical reactions up to 5 mol % of V_2O_5 in molten $K_2S_2O_7$. At higher concentrations, these reactions became electrochemically irreversible (i.e., slower). Formation of polymeric V(V) and V(IV) particles at high V_2O_5 concentrations was suggested as a possible reason for this concentration behavior. It was found that the V(V) electroreduction proceeds in two steps with V(V) → V(IV) as the first reduction stage and V(IV) → V(III) as the second reduction stage. It was also shown that the presence of water in the V_2O_5-$K_2S_2O_7$ molten mixture made the second stage more pronounced.

The reason for the sudden drop of the catalytic activity at 380-430°C.—Most researchers ascribe this activity drop to the precipitation of insoluble V(IV) or V(III) oxosulfo complexes and a subsequent reduction in the concentration of the V(V) active complexes in the molten catalyst. However there is some disagreement concerning V_2O_5-$Cs_2S_2O_7$ melts. According to Boghosian et al.[19,22] the reason is the same as for other alkali cations containing vanadium catalysts, i.e., precipitation of the V(IV) and V(III) compounds in this case as $Cs_2(VO)_2(SO_4)_3$, $CsV(SO_4)_2$. Still, Doering et al.[17,18] claimed the absence of V(IV) precipitation in the cesium system down to 300°C, which was much lower than the point of the activity drop, i.e., 400°C. In this case the drop in activity was explained on the basis of the reduced availability of V(V) because of the increased V_2O_4-SO_3 concentrations at the low operating temperatures.

Almost 30 years ago, Glueck and Kenney[6] gave a very sharp characterization of the state of the art in the study on the mechanism of the SO_2 catalytic oxidation. We would like to mention it in the present paper because it also describes the present situation, "It is clear that almost any kinetics can be fitted by choosing appropriate values of the different rate constants and it is obviously desirable, if possible to study the individual reaction steps separately."

By using electrochemical techniques, the oxidation and the reduction parts of the complex chemical reaction can be separated; moreover, some oxidation 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 can be obtained. It has been shown[1-3] that electrochemical measurements can provide important information about the vanadium complexes formed in the $K_2S_2O_7$-V_2O_5 or $K_2S_2O_7$-$KHSO_4$-V_2O_5 molten systems and give some knowledge concerning the reaction mechanism during catalysis.

In the present paper, the electrochemical behavior of molten V_2O_5-$M_2S_2O_7$ (M = K, Cs, or Na) was studied by using a gold working electrode at 440°C in argon and air atmospheres. The aim of the present investigation was to find possible correlations between the promoting effect of Na^+ and Cs^+ ions on the catalytic oxidation of SO_2 and the effect of these alkali cations on the electrochemical behavior of V_2O_5 in alkali pyrosulfate melts.

Experimental

Pure and dry $K_2S_2O_7$ and $Na_2S_2O_7$ were prepared by thermal decomposition of $K_2S_2O_8$ and $Na_2S_2O_8$ (Merk, Pro Analysi, maximum 0.001% by weight N) as described earlier.[23] Cesium pyrosulfate was synthesized from $CsOH \cdot H_2O$ (Aldrich, $Cs_2CO_3 < 5\%$), and $(NH_4)_2S_2O_8$ (Merck, >98%). After filtration, the CsOH and $(NH_4)_2S_2O_8$ aqueous solutions were mixed and left in an ice bath for 3 h. The resulting precipitate, long white needle-shaped $Cs_2S_2O_8$ crystals, was washed with ice-cooled water, ethanol, and ether. The crystals were then dissolved in the minimal amount of preheated (54°C) water in order to accomplish a further purification. The solution was then left in an ice bath for 3 h and the crystals were washed twice with ice-cooled water, ethanol, and ether. Finally the $Cs_2S_2O_8$ crystals were dried overnight in an desiccator and were then heated to 300°C in nitrogen atmosphere to form $Cs_2S_2O_7$ according to the reaction

$$Cs_2S_2O_8 \xrightarrow{\text{heat}} Cs_2S_2O_7 + 1/2\, O_2 \qquad [5]$$
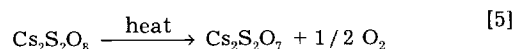
V_2O_5 from Cerac (99.9% by weight pure) and Ag_2SO_4 from Heraues (99.9% by weight pure) were used without further purification. All sample preparation and handling was performed in an argon-filled glove box (Vacuum Atmospheres Inc.) with a measured oxygen and water concentration less than 10 ppm or in a dry air box with water concentration less than 16 ppm.

Cyclic voltammetry measurements were performed in a hermetically closed three-electrode quartz cell previously described.[1,2] The reference electrode was a silver wire placed in a Pyrex cylindrical chamber with a thin-walled

spherical bottom. A melt of $K_2S_2O_7$ saturated with Ag_2SO_4 was used as the electrolyte for the reference electrode in all the experiments. Gold wires sealed in Pyrex tubes served as working electrodes. In most cases the working electrode area was 0.1 cm^2. A gold wire spiral served as a counter electrode. The cell was filled with electrolyte and hermetically closed in a dry glove box, and placed in a vertical copper-aluminum-block furnace with temperature regulation to within ±1°C.[24] 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 pocket placed inside the electrochemical cell.

The voltammetric measurements were carried out with the THJ Instrument potentiostat (Denmark) controlled by CV1A (THJ Instrument) and Easy Plot 2.02 (MIT and Spiral Software) software packages and with a potentiostat/galvanostat (Autolab-PGSTAT 20, Eco Chemie, The Netherlands) controlled by GPES (Eco Chemie) software packages. The data were corrected for IR drops by using the current interruption technique.[25]

Results and Discussion

Cyclic voltammetry of the molten V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$ system.—The effect of Na^+ ions on the electrochemical behavior of V_2O_5 in molten $K_2S_2O_7$ was studied in the 2-10 mol % $Na_2S_2O_7$ concentration range at 440°C in air and in an Ar atmosphere. The results obtained are given in Fig. 1-5 and Tables I-IV.

A comparison of the voltammetric behavior of V_2O_5 (5 mol %) solution in molten $K_2S_2O_7$ and in molten $K_2S_2O_7$ containing 7.6 mol % of $Na_2S_2O_7$ in air atmosphere at 440°C is shown in Fig. 1. It has been already proved[1] that the reduction wave Red_1 (Fig. 1) is a one-electron electroreduction of V(V) to V(IV) and the oxidation wave Ox_1 (Fig. 1) is a one-electron electro-oxidation of V(IV) to V(V). It can be seen from Fig. 1 [curve (2)] that sodium ions noticeably affect both the V(V) reduction (Fig. 1, wave Red_2) and the V(IV) oxidation (Fig. 1, wave Ox_2). The initial potentials of both reactions move in the negative direction: for example, at a potential scan rate of 0.8 V/s (Fig. 1) there was a ~ −0.26 V shift for the V(IV) oxidation and a ~ −0.17 V shift for the V(V) reduction. A potential shift in the negative direction means a depolarization of the electro-oxidation and polarization of the electroreduction. Moreover, it can be seen that
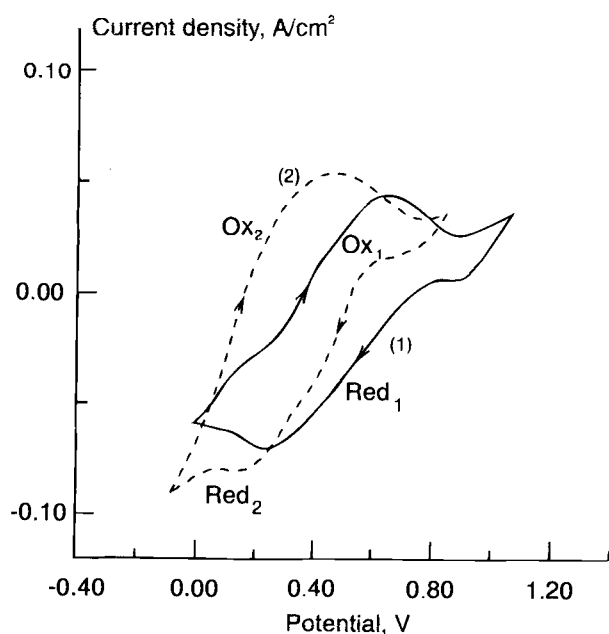
Table I. The V(IV) → V(V) oxidation for 5.0 mol % V_2O_5 in a solvent of 93.5 mol % $K_2S_2O_7$ and 6.5 mol % $Na_2S_2O_7$ in air at 440°C. Peak current, peak potential, and half-peak potential of wave Ox_2 vs. potential scan rate.

Scan rate (V/s)	Peak current (mA)	Peak potential (V)	Half-peak potential $E_{p/2}$ (V)
1.0	5.89$_5$ [a]	0.44$_5$	0.25$_9$
0.9	5.71$_1$	0.45$_5$	0.25$_7$
0.8	5.43$_6$	0.44$_4$	0.25$_7$
0.7	5.27$_1$	0.44$_1$	0.26$_1$
0.6	4.81$_0$	0.43$_8$	0.25$_2$
0.5	4.38$_9$	0.43$_7$	0.25$_4$
0.4	3.91$_8$	0.44$_0$	0.25$_1$

[a] Subscripts indicate less reliable figures.

Table II. The V(IV) → V(V) oxidation for 5.0 mol % V_2O_5 in a solvent of 92.4 mol % $K_2S_2O_7$ and 7.6 mol % $Na_2S_2O_7$ in air at 440°C. Peak current, peak potential, and half-peak potential of wave Ox_2 vs. potential scan rate.

Scan rate (V/s)	Peak current (mA)	Peak potential (V)	Half-peak potential $E_{p/2}$ (V)
1.0	6.58$_6$	0.47$_2$	0.24$_3$
0.9	6.47$_6$	0.45$_2$	0.24$_8$
0.8	6.11$_9$	0.46$_2$	0.24$_6$
0.7	5.87$_7$	0.46$_2$	0.24$_9$
0.6	5.57$_8$	0.46$_4$	0.25$_0$
0.5	5.29$_7$	0.46$_1$	0.24$_9$

when Na^+ ions were added to the molten V_2O_5-$K_2S_2O_7$ system the peak currents of both the V(V) reduction and the V(IV) oxidation waves increased ≥25%. This means that both reactions were accelerated by the $Na_2S_2O_7$ addition.

The study on the electrochemical kinetics in the V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$ melt has been made only for the V(IV) → V(V) oxidation because of the importance of this state in the mechanism of the catalytic oxidation of SO_2.[5-15,17,18] As usual in cyclic voltammetry, the potential scan rate ($V_E^{1/2}$) variation has been used.[25] Plots of peak current (I_P) and peak potential (E_p) for the wave Ox_2 (Fig. 1) vs. the square root and logarithm of the potential scan rate, respectively, are given in the Fig. 2-4 and Tables I-IV.

The linear $I_p - V_E^{1/2}$ plots in Fig. 2 indicate that the process is limited by the diffusion of vanadium complexes. It can
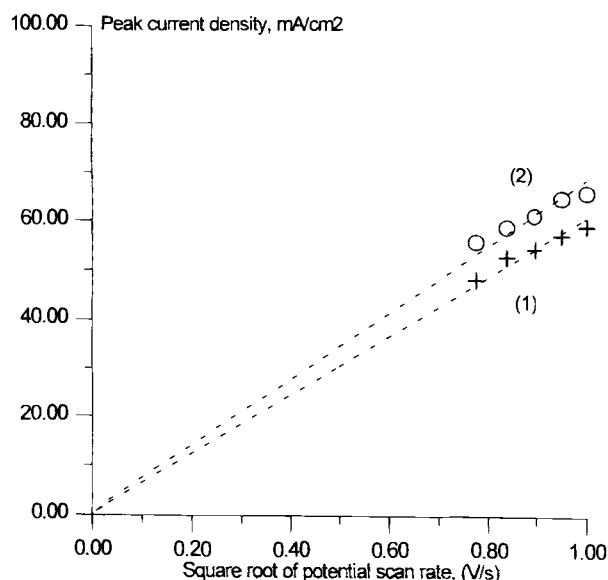

Fig. 1. Cyclic voltammograms obtained at a gold electrode in a 5 mol % solution of V_2O_5 in (1) a $K_2S_2O_7$ melt, and (2) a $K_2S_2O_7$-$Na_2S_2O_2$ (Na/K = 7.6/91.5) melt at 440°C in dry air atmosphere. The potential scan rate was 0.8 V/s.

Fig. 2. Peak current vs. square root of the potential scan rate for wave Ox_2 obtained in a 5 mol % solution of V_2O_5 in (1), a $K_2S_2O_7$-$Na_2S_2O_2$ (Na/K = 6.5/93.5) melt and (2), a $K_2S_2O_7$-$Na_2S_2O_2$ (Na/K = 7.6/92.4) melt at 440°C in a dry air atmosphere.

also be seen that even small increases in the $Na_2S_2O_7$ concentration (from 6.5 to 7.6 mol %) cause significant promotion of the V(V) reduction and the V(IV) oxidation. However, the $I_P - V_E^{1/2}$ linearity does not give more definite information on the mechanism of the studied electrochemical reactions.[25]

Figure 3 shows a plot of the anodic peak potential vs. the logarithm of the potential scan rate for a Na:K ratio of 6.5:93.5. The results fall in two groups; one at slow scan rates where E_p is independent of $\ln(V_E)$, and one at fast scan rates where E_p is linearly dependent of $\ln(V_E^{1/2})$. These are the diagnostic criteria for a typical kinetic behavior for most types of electrochemical reactions: from a reversible charge-transfer stage at low potential scan rates through a quasi-reversible region to an irreversible charge-transfer stage at high potential scan rates.[25] The voltammetric reversible [where E_p is independent of $\ln(V_E)$] and irreversible [where E_p is linearly dependent of $\ln(V_E)$] regions can be mathematically simulated and can therefore be used in the kinetic study. It can also be seen from Fig. 4 that in the case of 7.6 mol % of $Na_2S_2O_7$ the V(IV) oxidation becomes reversible for almost all studied potential scan rates. It means that with increased concentration of Na^+ ions the charge-transfer stage of the V(IV) oxidation was accelerated (compared to the molten V_2O_5-$K_2S_2O_7$ system).

Depending on the reversibility of the charge-transfer stage, the following equations were used for determination of the number of electrons participating in the rate-determining step

Reversible $E_{p/2} - E_p = 2.2(RT/nF)$ [6]

Irreversible $E_{p/2} - E_p = 1.857(RT/\alpha n_a F)$ [7]

where E_p is the peak potential; $E_{p/2}$ is the half-peak potential (when $I = I_p/2$); R is the gas constant; F is the Faraday constant; n is the number of electrons; α is the transfer coefficient; T is the absolute temperature.

n was calculated for the irreversible condition by assuming as usual[25] that α equals 0.5. The results of the calculation are given in Tables III and IV. It can be seen that the number of electrons participating in the V(IV) oxidation was one under all conditions studied. It means that the number of the participating electrons did not change despite the change in the mechanism of the V(IV) oxidation.

In electrochemistry, current is proportional to the rate of the electrochemical reaction. Therefore, if the addition of Na^+ ions increased the current, it means that the electrochemical reaction was accelerated. In this connection, it was also important to study the promoting effect vs. the concentration of the promoter. The concentration dependence of the Na^+ promoting effect on the V(IV) electro-oxidation was studied in a solvent consisting of x mol % $Na_2S_2O_7$ and (100-x) mol % $K_2S_2O_7$ with 5 mol % V_2O_5 added and with x in the 2.5-10 concentration range. The results are given in Fig. 5. It can be seen that the maximum anodic peak current is found at a solvent composition of 8.5 mol % $Na_2S_2O_7$ and 91.5 mol % $K_2S_2O_7$.

The results of the investigation of the Na^+ effect on the V(V) electroreduction and V(IV) electro-oxidation in a solvent of x mol % $Na_2S_2O_7$ and (100-x) mol % $K_2S_2O_7$ with 10 mol % V_2O_5 added and x = 5, 10, 15 in an argon atmosphere are given in Fig. 6. It can be seen that sodium ions affect both current and potentials for the electrochemical V(V) → V(IV) reduction and the V(IV) → V(V) oxidation in the same way as in an air atmosphere and the optimum concentration of the $Na_2S_2O_7$ promoter is close to what has been found for air atmosphere. On the basis of the results obtained in argon and air atmospheres, one can conclude that oxygen does not change the effect of Na^+ on the V(V) → V(IV) reduction and the V(IV) → V(V) oxidation.

It is a common opinion that the V(IV) → V(V) oxidation with oxygen is the rate-determining stage of the catalytic SO_2 oxidation,[5-15,17,18] and it is obvious that the electrochemical data reflects the acceleration (i.e., current increase) of the V(IV) oxidation. This increase of current surely was not caused by a difference in the conductivity because it has been found that the conductivities of the
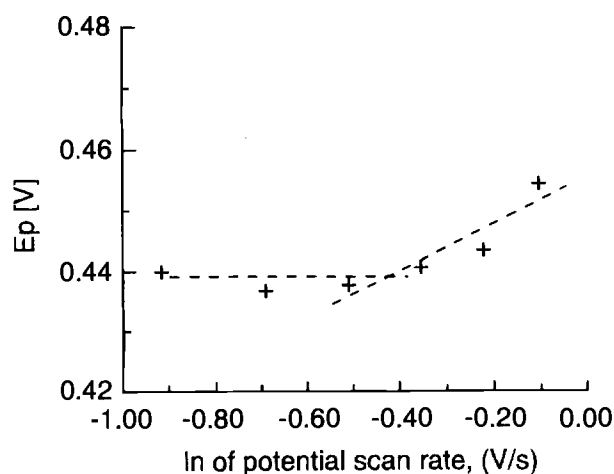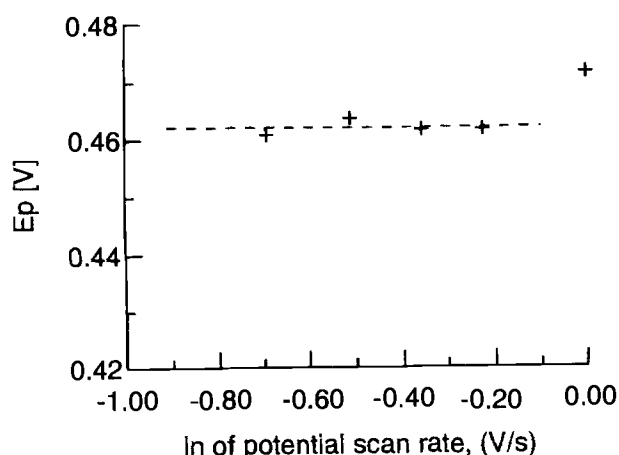
Fig. 3. Peak potential vs. logarithm of the potential scan rate for wave Ox_2 obtained in a 5 mol % solution of V_2O_5 in the $K_2S_2O_7$-$Na_2S_2O_2$ (Na/K = 6.5/93.5) melt at 440°C in dry air atmosphere.

Fig. 4. Peak potential vs. logarithm of the potential scan rate for wave Ox_2 obtained in 5 mol % solution of V_2O_5 in the $K_2S_2O_7$-$Na_2S_2O_2$ (Na/K = 7.6/92.4) melt at 440°C in a dry air atmosphere.

Table III. The V(IV) → V(V) oxidation for 5.0 mol % V_2O_5 in a solvent of 93.5 mol % $K_2S_2O_7$ and 6.5 mol % $Na_2S_2O_7$ in air at 440°C. Type of the kinetics and number of the electrons participating in the oxidation.

Scan rate (V/s)	Kinetics	Number of electrons, n
0.9	Irreversible	1.15
0.8	Irreversible	1.22
0.7	Quasi-reversible	—
0.6	Quasi-reversible	—
0.5	Reversible	0.74
0.4	Reversible	0.72

Table IV. The V(IV) → V(V) oxidation for 5.0 mol % V_2O_5 in a solvent of 92.4 mol % $K_2S_2O_7$ and 7.6 mol % $Na_2S_2O_7$ in air at 440°C.

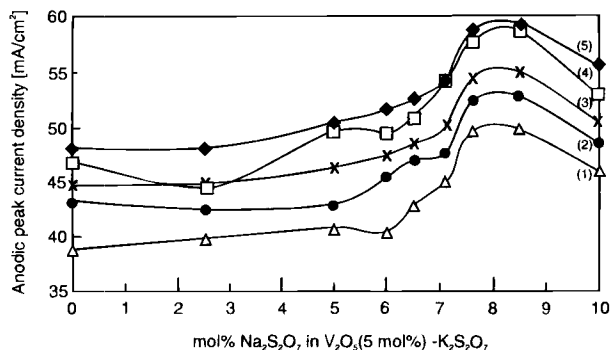| Scan rate (V/s)	Kinetics	Number of electrons, n
1.0	Quasi-reversible	—
0.9	Quasi-reversible	—
0.8	Reversible	0.63
0.7	Reversible	0.63
0.6	Reversible	0.63
0.5	Reversible	0.64

Fig. 5. Dependence of the peak current of wave Ox_2 on the $Na_2S_2O_7$ content in a V_2O_5-$Na_2S_2O_2$-$K_2S_2O_7$ (5 mol % V_2O_5) melt in dry air atmosphere at 440°C and (1) 0.6, (2) 0.7, (3) 0.8, (4) 0.9, and (5) 1.0 V/s, respectively.

V_2O_5-$K_2S_2O_7$ and V_2O_5-$Na_2S_2O_7$ melts are very similar.[26] It has been shown in the present paper that the addition of $Na_2S_2O_7$ changes the mechanism of the V(IV) oxidation. Therefore the voltammetric technique reflects the kinetic changes in the rate-determining step of the catalytic SO_2 oxidation in the presence of the alkali promoter. We can conclude that cyclic voltammetry can be used as a technique for the investigation of the nature of the cationic promotion of the V_2O_5 catalyst. Moreover, if there is a direct connection between the Na^+ promotion of the catalytic SO_2 oxidation and the electrochemical V(V) ⇌ V(IV) reaction, it is then possible that the electrochemically defined optimum $Na_2S_2O_7$ concentration [i.e., the concentration at which the highest peak currents of the V(V) electroreduction and V(IV) electro-oxidation were obtained] can also be the optimum $Na_2S_2O_7$ concentration for the vanadium catalyst.

As discussed above, the change of the V(V) electroreduction and V(IV) electro-oxidation from reversible behavior at V_2O_5 concentrations lower than 5 mol % to an irreversible behavior at higher concentrations was explained by an increase in the degree of dimerization/polymerization of the V(V) or V(IV) species. If this idea is right, then the restoration of the equilibrium (i.e., to reversible conditions) in the presence of Na^+ ions may mean that these ions

destroy the V(V) or V(IV) dimeric/polymeric structures. Moreover, the higher polarization of the V(V) reduction and lower polarization of the V(IV) oxidation in the presence of the highly polarizing Na^+ ions means that in V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$ melts the V(IV) complexes should not interfere with Na^+ ions in contrast to the behavior of the V(V) complexes.

The fact that Na^+ ions can promote the V(V) → V(IV) reaction itself (i.e., in the absence of oxygen) indicates that during the catalytic process the V(IV) oxidation with oxygen is a rate-determining stage not because of slow diffusion of oxygen but because of the slow electron transfer kinetics of the V(IV) oxidation.

Cyclic voltammetry of a 5 mol % solution of V_2O_5 in the molten $K_2S_2O_7$-$Cs_2S_2O_7$ system.—The results of a voltammetric investigation of 5 mol % V_2O_5 in a $K_2S_2O_7$:$Cs_2S_2O_7$ (1:1) melt in the air atmosphere at 440°C are given in Fig. 7-9. The peak parameters for the anodic wave are given in Table V.

It can be seen that in the presence of Cs^+ ions the kinetics of the V(V) → V(IV) reduction and the V(IV) → V(V) oxidation have visible changes, especially in the case of the oxidation. The increase in the anodic peak current (i.e., acceleration) is approximately 58% compared to the V_2O_5-$K_2S_2O_7$ system. This means that the acceleration effect caused by Cs^+ ions is more than twice as strong as the acceleration effect caused by Na^+ ions. As in the case of the V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$ melt, the V(IV) → V(V) oxidation proceeds with depolarization in the presence of Cs^+ ions. There is no significant change in the initial potential of the V(V) → V(IV) reduction; however, instead of the peak shape, the cathodic vanadium reduction wave Red_3 (Fig. 7) is more similar to a polarographic wave with a limiting current.

As in the case of the V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$ system, the kinetics of the V(IV) → V(V) electro-oxidation was analyzed. The results of this study are given in Fig. 8 and 9 and in Table V. It can be seen that the ratio $I_p/V_E^{1/2}$ is linearly dependent on the square root of the potential scan rate and decreases with increasing potential scan rate (Fig. 8). The peak potential of wave Ox_3 is linearly dependent on the logarithm of the potential scan rate but, unlike what it would be in the case of an irreversible electrochemical reaction, E_p moves in the negative direction with increase in the potential scan rate. These are clear diagnostic criteria of a mechanism with slow chemical reaction
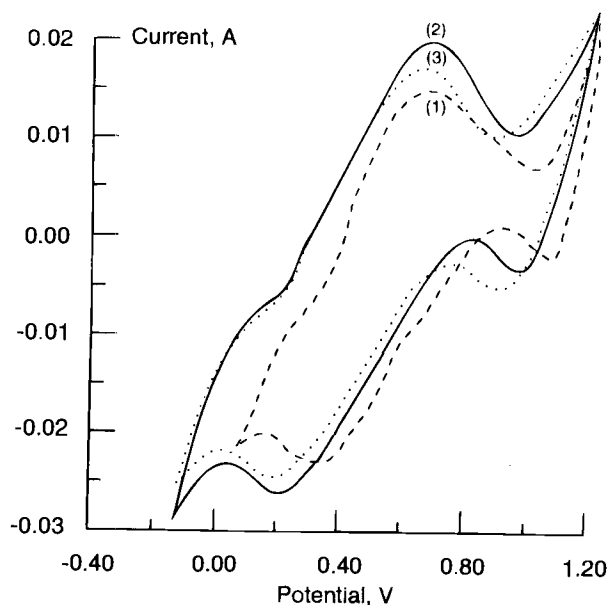

Fig. 6. Cyclic voltammograms obtained at a gold electrode in a V_2O_5 (10 mol %)-(x mol % $Na_2S_2O_7$-(90-x) mol % $K_2S_2O_7$ system in argon atmosphere for x = (1) 5, (2) 10, and (3) 15 at 500 V/s and 440°C.
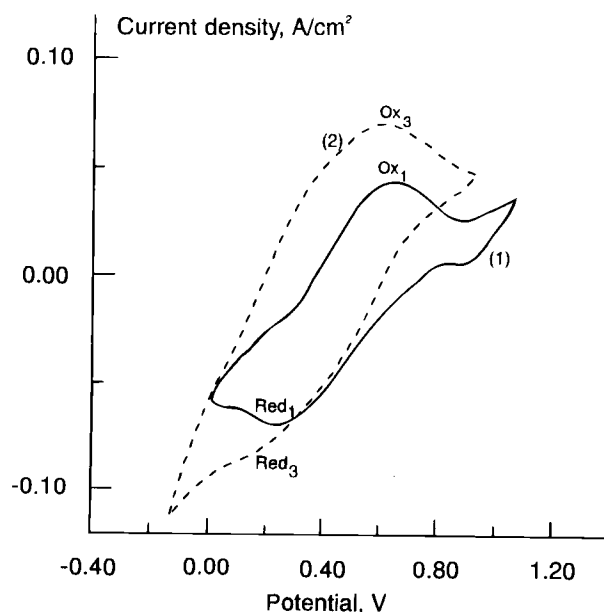

Fig. 7. Cyclic voltammograms obtained at a gold electrode in a 5 mol % solution of V_2O_5 in (1) a $K_2S_2O_7$ melt, and (2) a $Cs_2S_2O_7$-$K_2S_2O_7$ (Cs/K = 1/1) melt, both at 440°C in a dry air atmosphere. The potential scan rate was 0.8 V/s.

Table V. The V(IV) → V(V) oxidation for 5.0 mol % V_2O_5 in a solvent of 50.0 mol % $K_2S_2O_7$ and 50.0 mol % $Cs_2S_2O_7$ in air at 440°C. Peak current, peak potential of wave Ox_3 vs. potential scan rate.

Scan rate (V/s)	Peak current (mA)	Peak potential (V)
1.0	9.31_9	0.59_6
0.9	9.13_4	0.60_6
0.8	8.70_5	0.60_4
0.7	8.35_6	0.60_8
0.6	7.82_5	0.61_6

preceding a reversible electrochemical reaction.[25] It has been found[25] that this negative shift for the anodic peak potential (ΔE_{pa}) equals ca. $60/n$ mV per hundredfold increase in V_E for a reversible reaction at 25°C, i.e.

$$\Delta E_{pa} = \frac{RT}{nF} \ln(10) \text{ mV} \quad \text{per hundredfold increase of } V_E$$
[8]

and if the increase in the potential scan rate was not hundredfold, then

$$\Delta E_{pa} = \frac{1}{X} \cdot \frac{RT}{nF} \ln(10) \text{ mV}$$

$$\text{per hundredfold}^{1/X} \text{ increase of } V_E \quad [9]$$

where X is a constant.

It can be seen from Table V that the maximum increase in scan rate in the present study was from 1.0 to 0.6 V/s, or 1.67. X can then be found by using Eq. 9: $1.67 = 100^{1/X} \rightarrow X = 9.015$. Therefore at 440°C and for a potential scan rate increase of 1.67 times.

$$\Delta E_{pa} = \frac{1}{9.015} \cdot \frac{8.314 \cdot 713}{n \cdot 96485} \cdot \ln(10) = \frac{15.7}{n} \text{ mV} \quad [10]$$

Using Eq. 10 we can calculate n for the V(IV) → V(V) oxidation. An n value of 0.78 was obtained, and therefore it is very unlikely that the number of electrons is higher than one.

We can conclude that the presence of the Cs^+ ions does not change the number of V(V) and V(IV) atoms participating in the V(V) ⇌ V(IV) reaction. However Cs^+ ions significantly change the mechanism of this reaction compared to the V_2O_5-$K_2S_2O_7$ melt. Similar to Na^+ ions, Cs^+
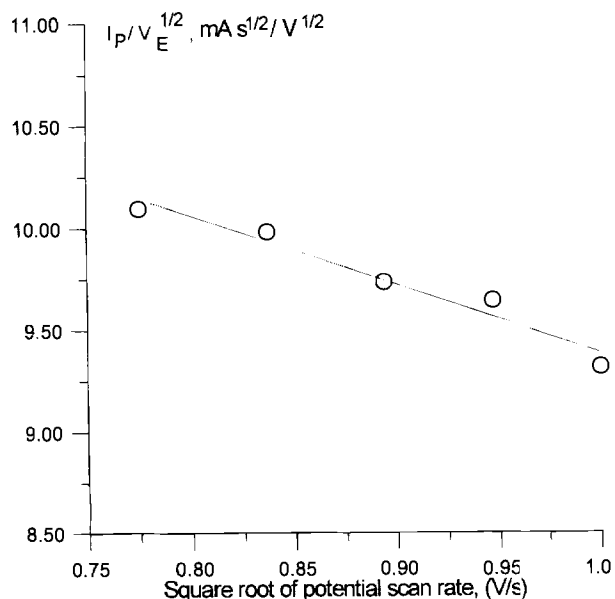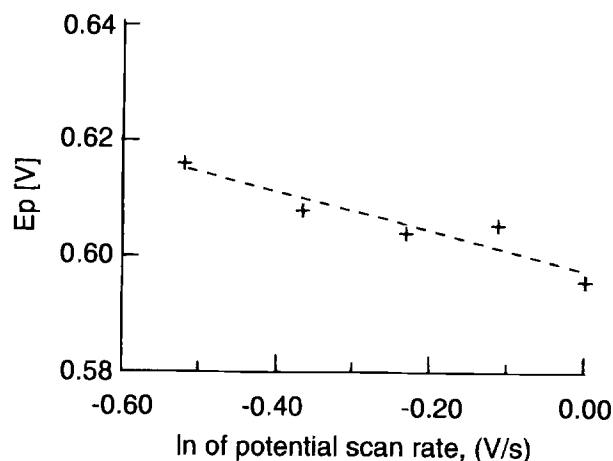
Fig. 9. Peak potential vs. logarithm of the potential scan rate of wave Ox_3 obtained for a 5 mol % solution of V_2O_5 in a $Cs_2S_2O_7$-$K_2S_2O_7$ (Cs/K = 1/1) melt at 440°C in a dry air atmosphere.

ions accelerate the V(V) → V(IV) reaction, and especially the V(IV) → V(V) oxidation, restoring the electrochemical V(V) ⇌ V(IV) equilibrium. The high currents during the V(V) → V(IV) reduction and V(IV) → V(V) oxidation are obviously not caused by the higher conductivity of the V_2O_5-$Cs_2S_2O_7$-$K_2S_2O_7$ system, because it was found that the conductivity of the V_2O_5-$Cs_2S_2O_7$-$K_2S_2O_7$ system is much lower than that of the V_2O_5-$K_2S_2O_7$ or V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$ systems.[26] Rather, it means that the formation of Cs^+ involved V(V) and V(IV) complexes which facilitate the oxidation and reduction reactions. Combining our data about the slow chemical reaction preceding the one-electron V(IV) → V(V) oxidation with the information about the very high solubility of the V(IV) in the Cs^+-containing catalysts[17,18] we can assume stable V(IV) monomeric solvates (oxosulfovanadates) rather than V(IV) polymeric structures. This stable vanadate-sulfate bonding can slow down the desolvation step preceding the charge-transfer step.

Cyclic voltammetry of a 5 mol % solution of V_2O_5 in molten $Na_2S_2O_7$-$K_2S_2O_7$-$Cs_2S_2O_7$ system.—The effect of Na^+ ions on the electrochemical behavior of V_2O_5 in molten $K_2S_2O_7$-$Cs_2S_2O_7$ (1:1) was studied in the 0-7 mol % $Na_2S_2O_7$ concentration range at 440°C in air atmosphere. The results obtained are given in Fig. 10, 11.

It can be seen from Fig. 10 and 11 that small concentrations of Na^+ ions can further accelerate the V(IV) → V(V) oxidation already accelerated by Cs^+ ions. Moreover even small concentrations of Na^+ ions notably change the kinetics of the V(IV) oxidation. $I_p/V_E^{1/2}$ is still linearly dependent on $V_E^{1/2}$ (Fig. 10), i.e., it is still a mechanism with a reversible electrochemical reaction with a slowly preceding chemical reaction, but the slope of the $I_p/V_E^{1/2}$ vs. $V_E^{1/2}$ plots changes significantly after the addition of $Na_2S_2O_7$ to the $K_2S_2O_7$-$Cs_2S_2O_7$ melt. This can mean a change of the type of the preceding chemical reaction or of the type of the V(IV) complexes formed, i.e., Na^+ in one way or another participates in this chemical reaction. It can be seen from Fig. 10 that at small Na^+ concentrations [i.e., 3 mol % of $Na_2S_2O_7$, line (2)] this participation may even cause a slight acceleration of the reaction, however higher $Na_2S_2O_7$ concentrations slow down the V(IV) oxidation (Fig. 10 and 11). We can conclude that the values for the optimum $Na_2S_2O_7$ concentration are different for the V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$ and for the V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$-$Cs_2S_2O_7$ system. These concentration values are possibly defined by the stoichiometry of the active V(V) and V(IV) complexes in the studied melts.

Fig. 8. Peak current vs. square root of the potential scan rate for wave Ox_3 obtained for a 5 mol % solution of V_2O_5 in a $Cs_2S_2O_7$-$K_2S_2O_7$ (Cs/K = 1/1) melt at 440°C in a dry air atmosphere.

Conclusions

The effect of Na^+ and Cs^+ ions on the electrochemical V(V) → V(IV) reduction and V(IV) → V(V) oxidation was
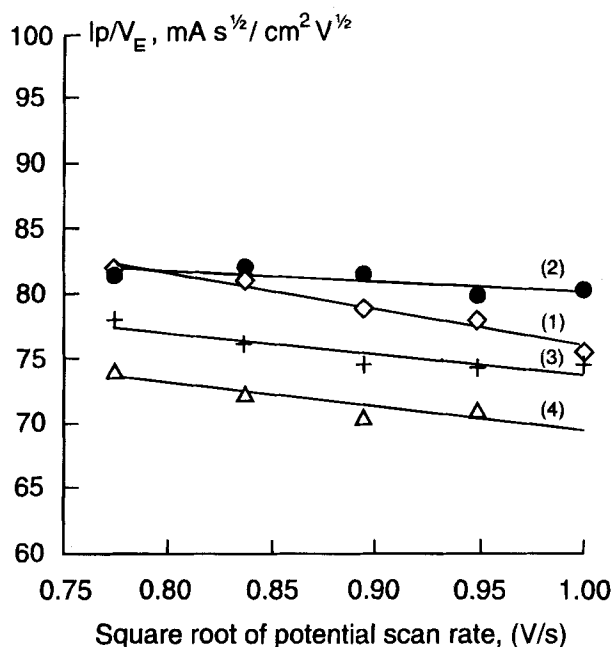
Fig. 10. Peak current vs. square root of the potential scan rate for the V(IV) → V(V) wave obtained in a 5 mol % solution of V_2O_5 in a $Cs_2S_2O_7$-$K_2S_2O_7$ (Cs/K = 1/1) melt containing (1) 0, (2) 3, (3) 5, (4) 7 mol % of $Na_2S_2O_7$ at 440°C in a dry air atmosphere.
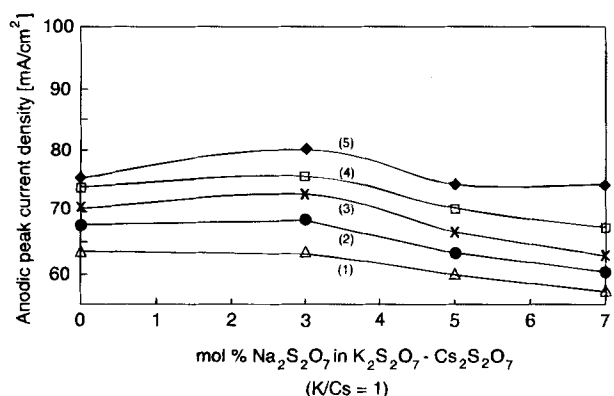

Fig. 11. Dependence of the peak current for the V(IV) → V(V) wave obtained for a 5 mol% solution of V_2O_5 in a $Na_2S_2O_7$-$Cs_2S_2O_7$-$K_2S_2O_7$ melt with different $Na_2S_2O_7$ concentrations at 440°C in a dry air atmosphere. The values for the scan rates were (1) 0.6, (2) 0.7, (3) 0.8, (4) 0.9, (5) 1.0 V/s.

The mechanism of the V(IV) oxidation in V_2O_5-$K_2S_2O_7$-Cs_2S_2O was defined as a mechanism with slow chemical reaction preceding a reversible electrochemical reaction (CE mechanism). The number of electrons participating in the V(IV) → V(V) oxidation process was one. It was assumed that the slow preceding chemical reaction was a destruction of the stable V(IV) solvate complexes. $Cs_2S_2O_7$ increased the peak current density considerably compared to the V_2O_5-$K_2S_2O_7$ system (~58%).

Addition of $Na_2S_2O_7$ to the V_2O_5-Cs_2S_2O-$K_2S_2O_7$ system caused a slight increase (<5%) in the anodic peak current density at $Na_2S_2O_7$ concentrations lower than 3 mol %. At higher $Na_2S_2O_7$ concentrations the Na^+ ions decrease the V(IV) oxidation rate in the V_2O_5-$Cs_2S_2O_7$-$K_2S_2O_7$ melt. Na^+ ions also affect the preceding chemical reaction without changing of the mechanism of this reaction. That may be explained by a change in the mechanism of the preceding chemical reaction or by Na^+ participation in the chemical reaction. We conclude from this investigation that the voltammetric technique can be used to examine the alkali ion promotion effect on the V(V) ⇌ V(IV) reaction in the sulfuric acid catalyst.

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studied in the V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$, V_2O_5-$K_2S_2O_7$-Cs_2S_2O, and V_2O_5-$Na_2S_2O_7$-$K_2S_2O_7$-Cs_2S_2O melts at 440°C in air and argon atmospheres. It was found that both Na^+ and Cs^+ ions help to restore the electrochemical equilibrium in the studied reactions and thus accelerate the V(V) → V(IV) reduction and V(IV) → V(V) oxidation, Cs^+ having a particularly strong effect on the V(IV) oxidation. However the kinetics of the electrochemical reactions under investigation are different in the Na^+ and Cs^+ containing systems. The kinetics changed from a purely irreversible electrochemical reaction at 0.0 mol % $Na_2S_2O_7$ to a purely reversible electrochemical reaction at 7.6 mol % $Na_2S_2O_7$ and greater concentrations.

A maximum of the anodic peak current was found at 8.5 mol % $Na_2S_2O_7$, which is assumed to indicate an optimum concentration for the catalytic activity for the SO_2 oxidation. At 8.5 mol % $Na_2S_2O_7$, the peak current was increased by 25% compared to the pure potassium solvent. This is very close to the result obtained in an argon atmosphere. Thus, it can be concluded that the presence of oxygen does not affect the influence of sodium.

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Kolbe Electrolysis of Acetic Acid in a Polymer Electrolyte Membrane Reactor

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ABSTRACT

A polymer electrolyte membrane (PEM) reactor is described for use in Kolbe electrolysis: the anodic oxidation of an alkyl carboxylic acid with subsequent decarboxylation and coupling to yield a dimer, $2RCOOH \rightarrow R$-$R + 2CO_2 + 2e^- + 2H^+$. Platinized Nafion® 117 is the PEM and functions simultaneously as the electrolyte and separator. Results demonstrating the feasibility of Kolbe electrolysis in a PEM reactor are presented for the oxidation of gaseous acetic acid (in a nitrogen diluent) to ethane and carbon dioxide, with hydrogen evolution at the counter electrode. The investigation includes the following effects on current density, current efficiency, and product selectivity: acetic acid partial pressure ($P_{total} \approx 1$ atm), cell voltage and temperature, phase of the catholyte (liquid water or humidified nitrogen), and the procedure used to prepare the membrane-electrode assembly. Current densities from 0.06 to 0.4 A/cm² with Kolbe current efficiencies of 10 to 90% were obtained for cell voltages ranging from 4 to 10 V. The best results were obtained using PEMs platinized by a nonequilibrium impregnation-reduction method; a 75% current efficiency at 0.3 A/cm² with a cell voltage of 6 V were measured at the following reaction conditions: 42°C reactor, 58 mm Hg acetic acid (50°C acetic acid dew point), and 42°C liquid water to the cathode. These initial results are encouraging for Kolbe electrolysis in a PEM cell; additional work, however, is needed to determine if the PEM strategy may be employed using a liquid-phase reactant. In addition, optimal reaction conditions and downstream mass-transfer separation requirements remain to be determined, both of which are reactant specific.

Introduction

The Kolbe reaction, i.e., the oxidative coupling of a carboxylic acid RCOOH to yield a dimer R-R

$$2RCOOH \rightarrow R - R + 2CO_2 + 2e^- + 2H^+ \qquad [1]$$

is an important step in the production of sebacic acid from monomethyl adipate and is commonly carried out in a parallel-plate reactor.[1,2] However, present parallel-plate reactor technology has several limitations: (i) salt electrolytes, aqueous solvents, and organic cosolvents are required to improve ionic conductivity and dissolve the reactant; (ii) the platinum anode is oxidizd and dissolved in the liquid electrolyte and essentially lost without the burden of additional recovery steps; and (iii) hydrogen evolution is the cathode reaction.

In this work, we describe a reactor that attempts to address the above limitations. The reactor uses a platinized Nafion 117 polymer electrolyte membrane (PEM) simultaneously as the electrolyte and separator, and in this manner eliminates the need for additional electrolyte, aqueous solvent, and organic cosolvent. Because a gas may be fed directly to the anode and/or cathode, solubilized platinum, formed by oxidation of the anode, remains confined within the PEM. Actually, cationic platinum should migrate through the PEM to the cathode and be deposited there for a straightforward recovery. The corrosive loss of anode should also be avoided when using a neat liquid feed that offers no counterion to cationic platinum. Another advantage of the PEM cell is that dioxygen reduction to water may be used as the cathode reaction. In this manner, energy consumption is less than if hydrogen is evolved at the counter electrode, and the product water may be used to hydrate the PEM.

Because (i) the Kolbe oxidation of liquid acetic acid is well documented[3] and (ii) it possesses an appreciable vapor pressure (58 mm Hg at 50°C), it was chosen as the model compound for this study. The oxidation of acetic acid to ethane using a PEM cell is shown schematically in Fig. 1. The anode feed stream consists of acetic acid vapor

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in a nitrogen diluent, and either nitrogen or deionized liquid water is fed to the cathode. Either gas stream may be externally humidified to maintain ionic conductivity in the PEM. Because our focus was on the anode, hydrogen evolution was chosen as the counter electrode reaction. This present work is the initial segment of an ongoing program studying Kolbe synthesis in PEM cells. We chose to investigate first gaseous reactants due, in part, to the successful development of gas-fed PEM fuel cells. In a future communication, we will report the study of PEM cells using liquid feed to the anode, which is an important practical concern since many potential Kolbe reactants have a low vapor pressure (say, < 10 mm Hg at 50°C).

PEM technology has been applied to carry out electroorganic synthesis, as discussed in recent reviews.[4,5] The first investigations were by Ogumi et al.[6] on the hydrogenation of maleic acid and olefins and the reduction of p-benzoquinone to 1,4-dihydroxybenzene, and by Sarrazin et al.[7] on the reduction of methyl 1,2-dibromo-1,2-cyclobutanedicarboxylate to methyl 1,2-cyclobutanedicarboxylate. In these stud-
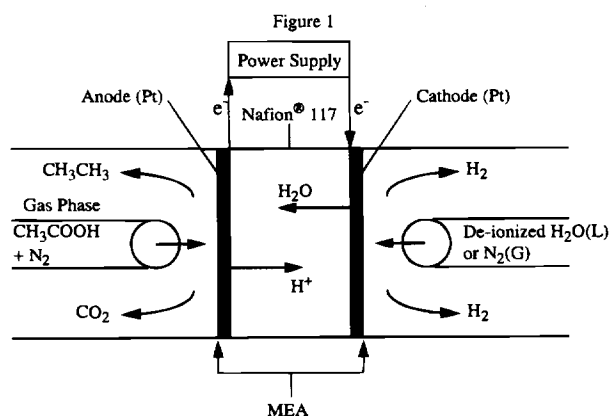

Figure 1

Fig. 1. Schematic diagram of a PEM cell for Kolbe electrolysis of acetic acid vapor and hydrogen evolution as the cathode reaction.