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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 V₂O₅-MₓS₂O₇ (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 electrocatalytic oxidation of SO₂ in the V₂O₅-MₓS₂O₇ system and the effect of these alkali cations on the electrochemical behavior of V₂O₅ in the alkali pyrosulfate melts. It has been shown that Na⁺ ions had a promoting effect on the V(IV) → V(V) 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 the catalytic activity of the alkali cation on the V(IV) → V(V) oxidation. The peak current of the V(IV) → V(V) oxidation waves vs. Na₃S₂O₆ concentration plots had maximums at ca. 8.5 mol % of Na₃S₂O₆ in air atmosphere for all the studied potential scan rates. In the Cs₂S₂O₇-K₂S₂O₇ (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 V₂O₅-Na₃S₂O₆-K₂S₂O₇ system. The V(IV) → V(V) oxidation peak currents were approximately 1.5 times higher than in the V₂O₅-K₂S₂O₇ 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 SO₂ 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 V₂O₅-MₓS₂O₇) for sulfuric acid production.

Introduction

The present work is a continuation of our investigation of the electrochemistry of the molten V₂O₅-MₓS₂O₇ system (M is an alkali metal). 1-3 This melt is found to be a realistic model of the V₂O₅-MₓS₂O₇ catalyst for sulfur dioxide oxidation with air in sulfuric acid production and in SO₂ removal from flue gases.

In the industrial catalytic SO₂ 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). 4-7 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 promoting effect. This fact was explained on the basis of the increasing ability of the alkali sulfates to react with SO₂ and therefore increasing the stability of the alkali pyrosulfates in the series from Li₂S₂O₇ to Cs₂S₂O₇.

It was also found that the activity and thermal stability of the V₂O₅ catalysts promoted only by sodium salts were much lower than those based on potassium salts. 8,9 However small amounts (up to 20 mol %) of sodium salts appeared to increase the activity of the potassium vanadium sulfate catalysts, 10 especially in the lower part of the working temperature range. This effect was explained as a result of the formation of potassium-sodium oxosulfovanadates (+ V). 11 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 SO₂ catalytic oxidation. The mechanism of this catalytic process has been the subject of numerous publications at least for 50 years. 2-21 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 SO₂ oxidation believe that the V(IV) oxidation with oxygen is the rate-determining stage. 4,5,11,13 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(IV) + SO₂ → V(V) + SO₃⁻.

2X + SO₂ ↔ 2Y

[2]

The latter depends very much on the SO₂ partial pressure and at low SO₂ pressures it can become the rate-determining stage. 6 Many researchers 8-13 have also shown for K/V catalysts that oxygen diffusion affects the rate-determining stage of the SO₂ oxidation. However, there is still a strong disagreement about the number and nature of the stages in the catalytic SO₂ oxidation. Thus Mars and Maessen 14 suggested a two-step mechanism almost 30 years ago for both K/V and K,Na/V catalysts. According to them the SO₂ oxidation proceeds through the fast establishment of the equilibrium

SO₂ + 2V⁺ + O₂⁻ ↔ SO₃²⁻ + 2V⁴⁺ [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 SO₂ 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 SO₃. Mars and Maessen thought that these oxosulfo groups can enclose and stabilize the V⁴⁺ ion.

The same considerations were behind the three-step mechanism for the 330-380°C temperature range introduced by Glueck and Kenney. 7 They assumed that a melt containing V⁴⁺ will absorb SO₂ without liberation of the equivalent amount of SO₃ and therefore two types of the V⁴⁺ particles will be present in the molten catalyst at low temperatures: (VOSO₄)₂ and V₂O₅SO₂. 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. 9 They assumed the following mechanism
V$_3$O$_5$ concentration range in Ar, air, and S$_3$O$_2$/air atmospheres was studied by Bjerrum et al. It was shown that molten potassium pyrosulfate at 440°C in the 1-20 mol % V(III) compounds would probably lead to higher solubility of the V(IV) and a mixture of alkali ions, such as Na, K, or Na, K, and Cs, decreased vanadium concentration in the catalyst. Eriksen et al. suggested that a mixture of alkali cations on the electrochemical behavior of V$_2$O$_5$ in alkali pyrosulfate melts.

Experimental

Pure and dry K$_2$S$_3$O$_7$ and Na$_3$S$_3$O$_7$ were prepared by thermal decomposition of K$_2$S$_3$O$_7$ and Na$_3$S$_3$O$_7$ (Merck, Pro Analysis, maximum 0.001% by weight N) as described earlier. Cesium pyrosulfate was synthesized from CsH$_2$O$_3$ (Aldrich, Cs$_2$CO$_3 <$ 5%), and (NH$_4$)$_2$S$_3$O$_7$ (Merck, >98%). After filtration, the CsOH and (NH$_4$)$_2$S$_3$O$_7$ aqueous solutions were mixed and left in an ice bath for 3 h. The resulting precipitate, long white needle-shaped Cs$_3$S$_3$O$_7$ 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$_3$S$_3$O$_7$ crystals were dried overnight in a desiccator and then heated to 300°C in nitrogen atmosphere to form Cs$_3$S$_3$O$_7$ according to the reaction

$$\text{Cs}_3\text{S}_3\text{O}_7 \xrightarrow{\text{heat}} \text{Cs}_3\text{S}_3\text{O}_7 + 1/2 \text{O}_2$$

V$_2$O$_5$ from Cerac (99.9% by weight pure) and Ag$_2$SO$_4$ from Heraeus (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. The reference electrode was a silver wire placed in a Pyrex cylindrical chamber with a thin-walled
spherical bottom. A melt of K$_2$S$_2$O$_7$ saturated with Ag$_2$SO$_4$ 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. 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 CV~1A (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.\(^{35}\)

**Results and Discussion**

**Cyclic voltammetry of the molten V$_2$O$_5$-Na$_2$S$_2$O$_7$-K$_2$S$_2$O$_7$ system.** The effect of Na$^+$ ions on the electrochemical behavior of V$_2$O$_5$ in molten K$_2$S$_2$O$_7$ was studied in the 2-10 mol % Na$_2$S$_2$O$_7$ 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$_2$O$_5$ (5 mol %) solution in molten K$_2$S$_2$O$_7$ and in molten K$_2$S$_2$O$_7$ containing 7.6 mol % of Na$_2$S$_2$O$_7$ in air atmosphere at 440°C is shown in Fig. 1. It has been already proved\(^{36}\) that the reduction wave Red$_1$ (Fig. 1) is a one-electron electro-reduction 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$_1$) and the V(IV) oxidation (Fig. 1, wave Ox$_1$). 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 electro-reduction. Moreover, it can be seen that when Na$^+$ ions were added to the molten V$_2$O$_5$-K$_2$S$_2$O$_7$ system the peak currents of both the V(IV) reduction and the V(V) oxidation waves increased $\pm 25\%$. This means that both reactions were accelerated by the Na$_2$S$_2$O$_7$ addition.

The study on the electrochemical kinetics in the V$_2$O$_5$-Na$_2$S$_2$O$_7$-K$_2$S$_2$O$_7$ melt has been made only for the V(IV) $\to$ V(V) oxidation because of the importance of this state in the mechanism of the catalytic oxidation of SO$_2$. As usual in cyclic voltammetry, the potential scan rate ($V$) variation has been used.\(^{37}\) Plots of peak current ($I_p$) and peak potential ($E_{p}$) for the wave Ox$_1$ (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 $I_p$ vs. $V^{1/2}$ plots in Fig. 2 indicate that the process is limited by the diffusion of vanadium complexes. It can

**Table I.** The V(IV) $\to$ V(V) oxidation for 5.0 mol % V$_2$O$_5$ in a solvent of 93.5 mol % K$_2$S$_2$O$_7$ and 6.5 mol % Na$_2$S$_2$O$_7$ in air at 440°C. Peak current, peak potential, and half-peak potential of wave Ox$_1$ vs. potential scan rate.

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>Peak current (mA)</th>
<th>Peak potential (V)</th>
<th>Half-peak potential $E_{p1/2}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5.88 $^a$</td>
<td>0.44</td>
<td>0.25</td>
</tr>
<tr>
<td>0.9</td>
<td>5.71</td>
<td>0.45</td>
<td>0.25</td>
</tr>
<tr>
<td>0.8</td>
<td>5.43</td>
<td>0.44</td>
<td>0.25</td>
</tr>
<tr>
<td>0.7</td>
<td>5.27</td>
<td>0.44</td>
<td>0.25</td>
</tr>
<tr>
<td>0.6</td>
<td>5.01</td>
<td>0.43</td>
<td>0.25</td>
</tr>
<tr>
<td>0.5</td>
<td>4.85</td>
<td>0.43</td>
<td>0.25</td>
</tr>
<tr>
<td>0.4</td>
<td>4.01</td>
<td>0.44</td>
<td>0.25</td>
</tr>
</tbody>
</table>

$^a$ Subscripts indicate less reliable figures.

**Table II.** The V(IV) $\to$ V(V) oxidation for 5.0 mol % V$_2$O$_5$ in a solvent of 92.4 mol % K$_2$S$_2$O$_7$ and 7.6 mol % Na$_2$S$_2$O$_7$ in air at 440°C. Peak current, peak potential, and half-peak potential of wave Ox$_1$ vs. potential scan rate.

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>Peak current (mA)</th>
<th>Peak potential (V)</th>
<th>Half-peak potential $E_{p1/2}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>6.58</td>
<td>0.47</td>
<td>0.24</td>
</tr>
<tr>
<td>0.9</td>
<td>6.47</td>
<td>0.45</td>
<td>0.24</td>
</tr>
<tr>
<td>0.8</td>
<td>6.11</td>
<td>0.46</td>
<td>0.24</td>
</tr>
<tr>
<td>0.7</td>
<td>5.87</td>
<td>0.46</td>
<td>0.24</td>
</tr>
<tr>
<td>0.6</td>
<td>5.57</td>
<td>0.45</td>
<td>0.25</td>
</tr>
<tr>
<td>0.5</td>
<td>5.29</td>
<td>0.46</td>
<td>0.24</td>
</tr>
</tbody>
</table>

$^a$ Subscripts indicate less reliable figures.

**Fig. 1.** Cyclic voltammograms obtained at a gold electrode in a 5 mol % solution of V$_2$O$_5$ in (1) a K$_2$S$_2$O$_7$ melt, and (2) a K$_2$S$_2$O$_7$-Na$_2$S$_2$O$_7$ [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$_1$ obtained in a 5 mol % solution of V$_2$O$_5$, in (1), a K$_2$S$_2$O$_7$-Na$_2$S$_2$O$_7$ [Na/K = 6.5/93.5] melt and (2), a K$_2$S$_2$O$_7$-Na$_2$S$_2$O$_7$ [Na/K = 7.6/92.4] melt at 440°C in a dry air atmosphere.
also be seen that even small increases in the Na₅S₂O₇ concentration (from 6.5 to 7.6 mol %) cause significant promotion of the V(IV) reduction and the V(IV) oxidation. However, the \( I_p - V^\text{2/2} \) linearity does not give more definite information on the mechanism of the studied electrochemical reactions.¹⁵

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 \( \ln(V) \), and one at fast scan rates where \( E_p \) is linearly dependent of \( \ln(V^2) \). 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 stage at high potential scan rates.¹⁵ The voltammetric reversible (where \( E_p \) is independent of \( \ln(V) \)) and irreversible (where \( E_p \) is linearly dependent of \( \ln(V) \)) 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 Na₅S₂O₇ the V(IV) oxidation becomes irreversible 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 V₂O₅-K₂S₂O₇ 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:

- **Irreversible**: \( E_p = 2.2(RT/\eta F) \)  
- **Reversible**: \( E_p = 1.857(RT/\eta F) \)

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

\( n \) was calculated for the irreversible condition by assuming as usual¹⁵ that \( \alpha \) 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 % Na₅S₂O₇ and (100-\( x \)) mol % K₂S₂O₇ with 5 mol % V₂O₅ 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 % Na₅S₂O₇ and 91.5 mol % K₂S₂O₇.

The results of the investigation of the Na+ effect on the V(IV) electro-reduction and V(IV) electro-oxidation in a solvent of \( x \) mol % Na₅S₂O₇ and (100-\( x \)) mol % K₂S₂O₇ with 10 mol % V₂O₅ added and \( x = 5, 10, 15 \) in argon atmosphere are given in Fig. 6. It can be seen that sodium ions affect both current and potentials for the electrochemical V(IV) → V(V) reduction and the V(IV) → V(IV) oxidation in the same way as in an air atmosphere and the optimum concentration of the Na₅S₂O₇ 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(IV) → V(V) reduction and the V(IV) → V(IV) oxidation.

It is a common opinion that the V(IV) → V(IV) oxidation with oxygen is the rate-determining stage of the catalytic SO₂ oxidation,⁶,¹⁵ 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

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### Table III. The V(IV) → V(V) oxidation for 5.0 mol % V₂O₅ in a solvent of 93.5 mol % K₂S₂O₇ and 6.5 mol % Na₅S₂O₇ in air at 440°C. Type of the kinetics and number of the electrons participating in the oxidation.

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>Kinetics</th>
<th>Number of electrons, ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>Irreversible</td>
<td>1.15</td>
</tr>
<tr>
<td>0.8</td>
<td>Irreversible</td>
<td>1.22</td>
</tr>
<tr>
<td>0.7</td>
<td>Quasi-reversible</td>
<td>—</td>
</tr>
<tr>
<td>0.6</td>
<td>Quasi-reversible</td>
<td>—</td>
</tr>
<tr>
<td>0.5</td>
<td>Reversible</td>
<td>0.74</td>
</tr>
<tr>
<td>0.4</td>
<td>Reversible</td>
<td>0.72</td>
</tr>
</tbody>
</table>

### Table IV. The V(IV) → V(V) oxidation for 5.0 mol % V₂O₅ in a solvent of 92.4 mol % K₂S₂O₇ and 7.6 mol % Na₅S₂O₇ in air at 440°C.

<table>
<thead>
<tr>
<th>Scan rate (V/s)</th>
<th>Kinetics</th>
<th>Number of electrons, ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>Quasi-reversible</td>
<td>—</td>
</tr>
<tr>
<td>0.9</td>
<td>Quasi-reversible</td>
<td>—</td>
</tr>
<tr>
<td>0.8</td>
<td>Reversible</td>
<td>0.63</td>
</tr>
<tr>
<td>0.7</td>
<td>Reversible</td>
<td>0.63</td>
</tr>
<tr>
<td>0.6</td>
<td>Reversible</td>
<td>0.63</td>
</tr>
<tr>
<td>0.5</td>
<td>Reversible</td>
<td>0.64</td>
</tr>
</tbody>
</table>
V₂O₅-K₂S₂O₇ and V₂O₅-Na₂S₂O₇ melts are very similar. It has been shown in the present paper that the addition of Na₂S₂O₇ changes the mechanism of the V(IV) oxidation. Therefore, the voltammetric technique reflects the kinetic changes in the rate-determining step of the catalytic SO₂ 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 V₂O₅ catalyst. Moreover, if there is a direct connection between the Na⁺ promotion of the catalytic SO₂ oxidation and the electrochemical V(V) → V(IV) reaction, it is then possible that the electrochemically defined optimum Na₂S₂O₇ 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 Na₂S₂O₇ concentration for the vanadium catalyst.

As discussed above, the change of the V(V) electroreduction and V(IV) electro-oxidation from reversible behavior at V₂O₅ 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 V₂O₅-Na₂S₂O₇-K₂S₂O₇ 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 V₂O₅ in the molten K₂S₂O₇-Cs₂S₃O₇ system.—The results of a voltammetric investigation of a 5 mol % V₂O₅ in a K₂S₂O₇-Cs₂S₃O₇ (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 V₂O₅-K₂S₂O₇ 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 V₂O₅-Na₂S₂O₇-K₂S₂O₇ 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(IV) → V(IV) reduction; however, instead of the peak shape, the cathodic vanadium reduction wave Red₂ (Fig. 7) is more similar to a polarographic wave with a limiting current.

As in the case of the V₂O₅-Na₂S₂O₇-K₂S₂O₇ system, the kinetics of the V(IV) → V(IV) electro-oxidation were analyzed. The results of this study are given in Fig. 8 and 9 and in Table V. It can be seen that the ratio I₁/V₁² 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 Ox₂ 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, E₂ moves in the negative direction with increase in the potential scan rate. These are clear diagnostic criteria of a mechanism with slow chemical reaction
ions accelerate the \( V(V) \rightarrow V(IV) \) reaction, and especially the \( V(IV) \rightarrow V(V) \) oxidation, restoring the electrochemical equilibrium. The high currents during the \( V(V) \rightarrow V(IV) \) reduction and \( V(IV) \rightarrow V(V) \) oxidation are obviously not caused by the higher conductivity of the \( V_2O_5-Cs_2S_2O_7-K_2S_2O_7 \) system. Rather, it means that the formation of \( Cs^+ \) containing catalysts\(^{26} \) can provide 

\[ \Delta E_{pa} = \frac{RT}{nF} \ln(10) \text{ mV} \]  
and if the increase in the potential scan rate was not 

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

where \( X \) is a constant.

It can be seen from Table V that the maximum increase 

\[ \ln(10) \approx -mV \]  

per hundredfold increase of \( V \) in 

\[ \ln(10) \approx -mV \]  

With Eq. 10 we can calculate \( n \) for the \( V(IV) \rightarrow V(IV) \) oxidation. 

\[ n \approx \frac{8314.713}{9015} = 9.24 \]  

Using Eq. 10, we can calculate \( n \) for the \( V(IV) \rightarrow V(IV) \) oxidation. 

\[ \ln(10) \approx -\frac{157}{n} \text{ mV} \]  

![Fig. 8. Peak current vs. square root of the potential scan rate for wave \( O_3 \) obtained for a 5 mol % solution of \( V_2O_5 \) in a \( Cs_2S_2O_7-K_2S_2O_7 \) melt at 440°C in a dry air atmosphere.](image)

![Fig. 9. Peak potential vs. logarithm of the potential scan rate of wave \( O_3 \) obtained for a 5 mol % solution of \( V_2O_5 \) in a \( Cs_2S_2O_7-K_2S_2O_7 \) melt at 440°C in a dry air atmosphere.](image)

Conclusions

The effect of \( Na^+ \) and \( Cs^+ \) ions on the electrochemical 

\[ V(IV) \rightarrow V(IV) \]  

and \( V(IV) \rightarrow V(V) \) oxidation was
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) \to 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 CsS_2O increased the peak current density considerably compared to the V_2O_5-K_2S_2O system (\sim 58\%).

Addition of Na_2S_2O_7 to the V_2O_5-Cs_2S_2O-K_2S_2O 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-K_2S_2O melt. Na$^+$ ions also affect the preceding chemical reaction without changing 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(IV) \to V(IV) reaction in the sulfuric acid catalyst.

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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 → R-R + 2CO2 + 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 (Pacetic = 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 an alkyl carboxylic acid RCOOH to yield a dimer R-R

2RCOOH → R-R + 2CO2 + 2e− + 2H+

[1]

is an important step in the production of sebacic acid from monomethyl adipate and is commonly carried out in a parallel-plate reactor. However, present parallel-plate reactor technology has several limitations: (i) salt electrolytes, organic solvents, and organic cosolvents are required to improve ionic conductivity and dissolve the reactant; (ii) the platinum anode is oxidized 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 avoids 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 by oxidation of the anode, remains confined within the PEM. Because (i) the Kolbe oxidation of liquid acetic acid is well documented 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 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. The first investigations were by Ogumi et al. on the hydrogenation of maleic acid and olefins and the reduction of p-benzoquinone to 1,4-dihydroxybenzene, and by Sarrazin et al. on the reduction of methyl 1,2-dibromo-1,2-cyclobutane carboxylate to methyl 1,2-cyclobutanedicarboxylate. In these studies...