Electrochemical Behavior of Molten V2O5-K2S2O7-KHSO4 Systems

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Electrochemical Behavior of Molten $\text{V}_2\text{O}_5$-$\text{K}_2\text{S}_2\text{O}_7$-$\text{KHSO}_4$

**Systems**

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**ABSTRACT**

The electrochemical behavior of $\text{K}_2\text{S}_2\text{O}_7$-$\text{KHSO}_4$, $\text{K}_2\text{S}_2\text{O}_7$-$\text{V}_2\text{O}_5$, and $\text{K}_2\text{S}_2\text{O}_7$-$\text{V}_2\text{O}_5$-$\text{KHSO}_4$ melts was studied in argon and SO$_2$/air atmospheres using a gold electrode. In order to identify the voltammetric waves due to KHSO$_4$, molten KHSO$_4$ and mixtures of $\text{K}_2\text{S}_2\text{O}_7$-$\text{KHSO}_4$ were investigated by voltammetry performed with Au and Pt electrodes in an argon atmosphere. It was shown that H$_2$O$^+$ reduction took place at 0.26 V vs. an Ag/Ag$_2$SO$_4$ reference electrode, i.e., at a potential in between the V(V) → V(IV) and V(IV) → V(III) reduction stages. The presence of KHSO$_4$ caused an increased concentration of V(III) species in the V$_2$O$_5$ containing molten electrolytes. This effect may be caused either by protonic pro-oxidation of the V(IV) → V(III) reduction with oxygen or air in sulfuric acid production and SO$_2$ catalysis of hydrogen sulfates$^4$,$^5$ by chemical reduction of V(IV) complexes with hydrogen, formed from H$_2$O$^+$ as the product of the electrochemical reduction. Both the V(V) → V(IV) reduction and the V(IV) → V(III) oxidation occurred in a one-electron electrochemical reaction via the OH$^-$ and H$_2$O$_2$ adducts. It has been shown$^1$ that the above mentioned catalytic process of water vaporization proceeds at higher potentials in the water-containing melts in both argon and SO$_2$/air atmospheres. This effect may be explained by participation of the water molecules in the V(IV) active complexes.

**Introduction**

The present work is a continuation of our investigation on the electrochemistry of molten $\text{V}_2\text{O}_5$-$\text{M}_2\text{S}_2\text{O}_7$ systems$^1$ (M is an alkali metal).$^1$ This melt has proved to be a realistic model of the $\text{V}_2\text{O}_5$-$\text{M}_2\text{M}_2\text{O}_7$ catalyst for sulfur dioxide oxidation with oxygen or air in sulfuric acid production and SO$_2$ removal from flue gases.$^2$ Flue gases can contain a significant amount of water (ca. 7% by volume).$^3$ It is known that water dissolves in molten alkali pyrosulfates with formation of hydrogen sulfates$^4$.$^5$

$$\text{H}_2\text{O} + \text{SO}_3^{2-} \rightarrow 2\text{HSO}_4^-$$

Dissolved water (or hydrogen sulfate) may participate in some steps of the above mentioned catalytic process. Obviously the physicochemical properties of the melt and possibly the structure of the catalytically active vanadium species depend on the water activity.

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Experimental data obtained in other electrochemical investigations demonstrate the occurrence of lower stages of vanadium reduction, both in the aqueous electrolytes and in molten salts. Thus, the electrochemical reduction of V(V) in aqueous solutions can proceed in two stages involving V(III) by the following reactions:

\[ \text{VO}_2^+ + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{VO}^2+ + \text{H}_2 \text{O} \quad \text{E}^0 = +1.0 \text{ V} \]
\[ \text{VO}^2+ + 2 \text{H}^+ + \text{e}^- \rightarrow \text{V}^3+ + \text{H}_2 \text{O} \quad \text{E}^0 = +0.34 \text{ V} \]

where \( \text{E}^0 \) is the standard potential vs. a normal hydrogen electrode. The electrochemical reduction of V(III) to V(II) in 2 M aqueous H$_2$SO$_4$ was used as a cathodic process for the redox flow cell. It was shown that V(V) can be chemically reduced to V(III) [in the form of KV(SO$_4$)$_2$] by SO$_4^-$ in molten K$_2$SO$_4$-KHSO$_4$-V$_2$O$_5$, and V$_2$O$_5$-V$_2$O$_3$ systems at 450°C.

In the molten K$_2$SO$_4$-V$_2$O$_5$ systems, catalytically active V(III) complexes (possibly VO$_2$SO$_4$O$_4^-$) were found to react with water forming hydrated complexes by the reaction:

\[ \text{V}_2\text{O}_5\text{SO}_4\text{SO}_4^- + 3\text{H}_2\text{O} \rightarrow \text{VO}_2\text{SO}_4\text{SO}_4^- + 3\text{H}_2\text{O}^- + 2\text{HSO}_4^- \]

In studies on the structure of V(IV) compounds formed in V$_2$O$_5$ solutions in concentrated sulfuric acid, disulfuric acid, and oleum at the ambient temperatures, it was shown that VO(HSO$_4$)$_2$, VO(OH)(HSO$_4$)$_2$, and H$_2$[V(OSO$_4$)$_2$] were the most likely V(IV) compounds. Gillespie et al. have also found evidence for the formation of dimeric H$_2$[V(OSO$_4$)$_2$] species at high V$_2$O$_5$ concentrations.

Until now only the electrochemistry of hydrogen reduction on platinum from molten KHSO$_4$ has been studied. The electroreduction of hydrogen on bright and platinum-plated platinum was studied in molten KHSO$_4$ at 250 to 440°C. Videla et al. suggested hydrogen bonding in the melt. Arvia et al. assumed that the potential window of molten KHSO$_4$ is limited by the following cathodic and anodic electrochemical reactions:

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]
\[ 2\text{HSO}_4^- = \text{H}_2\text{SO}_4 + \text{O}_2 + \frac{1}{2}\text{O}_2 + 2\text{e}^- \]
\[ \text{SO}_2^2- = \text{SO}_4^2- + \frac{1}{2}\text{O}_2 + 2\text{e}^- \]

The residual EMP after the electrolysis of the KHSO$_4$ melt was measured. It was found to be 0.602 V at 269°C and was assumed to be equal to the potential window of this electrolyte. The hydrogen-evolution reaction was studied at a bright Pt electrode at 270 to 430°C. It was shown that the atom-atom combination step at low polarization is rate determining, and at high potentials ion-atom electrochemical desorption is the rate-determining step. These regions are separated by a transition region. By analogy with aqueous H$_2$SO$_4$, it was also shown that PtO$_2$ formation and reduction took place at 0.8 and 0.4 V, respectively, vs. the hydrogen reference electrode.

Equation 5 implies a preceding dissociation of HSO$_4^-$

\[ \text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-} \]

i.e., the presence of more or less "free" protons in molten KHSO$_4$. This assumption is in agreement with the conclusion of Rogers et al. that different particles are responsible for the conductivity and the viscous flow in the molten alkali hydrogen sulfates: the energy barrier for viscosity involves the M$^+$, HSO$_4^-$, and SO$_4^{2-}$ ions (M = alkali metal), while the conductivity involves the H$^+$ ions. A considerably higher electroconductivity of molten KHSO$_4$ after addition of KHSO$_4$ is also in agreement with a proton hopping mechanism of conductivity for molten KHSO$_4$.

White et al. studied the electrochemical behavior of water dissolved in a molten Li$_2$SO$_4$-K$_2$SO$_4$-Na$_2$SO$_4$ eutectic using a gold electrode at 560°C. It was shown that water is solvated in the sulfate melt, occurring in the form of hydrogenosulfate after the reaction:

\[ \text{H}_2\text{O} + \text{M}_2\text{SO}_4 + \text{SO}_4^{2-} = 2\text{MHSO}_4 \]

It was also shown that the reduction of the HSO$_4^-$ ion in molten sulfates proceeds at 0.31 and 0.28 V vs. Ag/AgCl at 100 and 500 mV, respectively.

Almost all electrochemical data for K$_2$SO$_4$ and V$_2$O$_5$-K$_2$SO$_4$ melts were obtained at Au electrodes using the Ag/AgCl reference electrode; and the electrochemical data for molten KHSO$_4$ were obtained at Pt electrodes using primarily the hydrogen reference electrode. However, gold was proven to be corrosion stable both in KHSO$_4$ and in KHSO$_4$-K$_2$SO$_4$ melts up to 550°C and therefore, seems to be the most suitable material for the electrochemical investigations in KHSO$_4$-K$_2$SO$_4$ containing electrolytes.

As a result an additional electrochemical investigation in KHSO$_4$ and KHSO$_4$-K$_2$SO$_4$ melts using an Au working electrode vs. Ag/AgCl is required. Such data are provided here to help distinguish the voltammetric characteristics of the molten KHSO$_4$-K$_2$SO$_4$ solvent and also with added vanadium compounds.

Experimental

Pure and dry K$_2$SO$_4$ was obtained by thermal decomposition of K$_2$SO$_4$ (Merck, Pro Analyse, maximum 0.001% by weight N) as described earlier. KHSO$_4$ (Merck, p.a.) was dried at 120°C for 24 h and then stored in a dry box. K$_2$SO$_4$ (Merck, Suprapur) was dried at 500°C overnight. 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 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 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$_2$SO$_4$ saturated with Ag$_2$SO$_4$ was used as the electrolyte for the reference electrode for the experiments with molten K$_2$SO$_4$-KHSO$_4$ or molten K$_2$SO$_4$-KHSO$_4$-V$_2$O$_5$. A melt of 3 weight percent (w/o) solution of Ag$_2$SO$_4$ in KHSO$_4$ was used as the electrolyte for the reference electrode for the experiments involving molten KHSO$_4$ or molten KHSO$_4$-V$_2$O$_5$.

Gold and platinum wires sealed in Pyrex tubes served as working electrodes. In the most cases the working electrode area was 0.236 cm$^2$. A gold wire spiral served as a counterelectrode. The cell was filled with electrolyte and hermetically closed in the argon 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.

Several voltammetric measurements were done in a mixture of SO$_2$ (10 v/v), O$_2$ (25 v/v), and N$_2$ (64 v/v), bubbling the gas through the Pyrex tube immersed in the molten electrolyte. Commercial gases were used: SO$_2$ (99.9% by volume), O$_2$ (99.8% v/v + 0.2% v/v N$_2$ and Ar), and N$_2$ (<40 ppm of O), the SO$_2$/O$_2$/N$_2$ mixture was supplied from a mixing system based on gas streams monitored by Brooks mass flowmeters. The voltammetric measurements were carried out with a THJ Instrument potentiostat (Denmark) controlled 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 using current interruption technique.

Results and Discussion

Voltammetric measurements on Pt and Au electrodes in melts of KHSO$_4$ and K$_2$SO$_4$-KHSO$_4$ at 265 and 440°C.
Vapor pressure measurements in the K$_2$S$_2$O$_7$-KHSO$_4$ system were performed using the boiling-point-method and the quartz-Bourdon-manometer-method prior to the electrochemical measurements.\textsuperscript{19} The obtained vapor pressure values were lower than 60 Torr for KHSO$_4$ concentrations less than 10 m/o at 440°C. Taking these data into account, we deduce that the K$_2$S$_2$O$_7$-KHSO$_4$ system is sufficiently stable up to 10 m/o KHSO$_4$ at 440°C.

The voltammograms obtained with the gold electrode in the molten K$_2$S$_2$O$_7$, and its mixtures with 7.5 and 10 m/o of KHSO$_4$ at 700 and 1000 mV/s at 440°C are given in Fig. 1 and 2. After addition of KHSO$_4$ to the K$_2$S$_2$O$_7$ melt the reduction wave R$_1$ and the oxidation wave Ox$_1$ appear in the voltammetric curves at the potentials 0.26 and 0.04 V (300 mV/s), respectively. The magnitude of current for the cathodic process (wave R$_1$) depends on the concentration of KHSO$_4$ and the cathodic limit of the potential window moves toward more positive potentials, i.e., the potential window becomes more narrow than for the "dry" K$_2$S$_2$O$_7$ melt.\textsuperscript{1} The oxidation wave Ox$_1$ and the reduction wave R$_1$ are gradually suppressed with the increasing concentration of KHSO$_4$.

It has already been shown\textsuperscript{1} that wave R$_1$ is due to the reduction of the gold oxide through the following reaction

$$\frac{1}{3}Au_2O_3 + \frac{1}{2}S_2O_3 + 3e^- \rightarrow Au + 3SO_4^{2-} \quad [10]$$

Wave Ox$_3$, according to Ref. 1.6 is the electrochemical dissolution of the gold electrode which can be described by the following equation

$$Au + 2n S_2O_3^{2-} \rightarrow Au(SO_4)^{2n+3} + nS_2O_3^{3-} + 3e^- \quad [11]$$

Wave Ox$_3$ is the electrochemical oxidation of S$_2$O$_3^{2-}$

$$3S_2O_3^{2-} + 2O_2 + 3n/2 \rightarrow n/2 S_2O_3 + 3SO_4^{2-} + 2e^- \quad [12]$$

and wave R$_3$ is the electrochemical reduction of solvated SO$_3$ mixed with oxygen.\textsuperscript{1} Wave R$_3$ appears only at high potential scan rates and can be ascribed to electrochemical reduction of gold complexes because it is decreasing simultaneously with wave Ox$_3$ after the additions of KHSO$_4$. Wave R$_3$ is clearly due to KHSO$_4$. To identify the electrochemical process we need information about the electrochemical behavior of molten KHSO$_4$. We compared the electrochemical behavior of the much investigated platinum electrode to the gold electrode under the same conditions.

The voltammogram obtained with a Pt electrode in molten KHSO$_4$ at 265°C and 300 mV/s is given in Fig. 3. Wave R$_1$, at approximately 0.25 V and wave Ox$_1$ at 1.3 V corresponds to the anodic and cathodic limiting reactions, respectively, of the potential window of the KHSO$_4$ melt. According to Arvia et al.\textsuperscript{17} hydrogen reduction is the cathodic limiting reaction in molten alkali hydrogen sulfates. Reaction Ox$_3$ can be identified with Eq. 6.\textsuperscript{17} This conclusion is in agreement with the results of anodic galvanostatic transient measurements made by Gilroy,\textsuperscript{18} the last anodic plateau occurred at 1.0 V vs. the hydrogen reference electrode and the gas evolution took place at this potential.

According to Arvia et al.,\textsuperscript{11} the residual EMF, after electrolysis of the molten potassium hydrogenosulfate, was 0.602 V at 269°C. This EMF was identified with the poten-
tial window of molten KHSO₄, on the basis of the reversibility of the reactions described by Eq. 5 and 6, i.e., it was much lower than in our measurement. However, it is obvious from Fig. 3 that reaction Ox₅ is irreversible. The only "available" cathodic reaction to form an electrochemical couple with hydrogen after KHSO₄ electrolysis is reaction R₆ (Fig. 3). This fact can explain the low values of residual EMF obtained by Arvia et al. Wave R₆ can be ascribed to the reduction of platinum oxide, taking into account the electrochemical behavior of (i) platinum in dilute sulfuric acid (platinum oxide formation and reduction region occurring between 0.4 V and 1.1 V vs. hydrogen electrode), (ii) platinum in concentrated sulfuric acid solutions (platinum oxide formation and reduction region occurring between 0 and 0.6 V vs. the hydrogen electrode), and (iii) the experimental data obtained by Gilroy et al. (platinum oxide reduction in the molten KHSO₄ takes place at 0.4 V vs. the hydrogen electrode).

The gold electrode voltammogram for molten KHSO₄ under Ar atmosphere and at 265°C was characterized by a 0.26 V cathodic limit (wave R₆) and a 0.96 V anodic limit (wave Ox₅) at 300 mV/s (Fig. 3, solid line). The cathodic wave R₆ is obviously the electrochemical reduction of the product of reaction Ox₅.

As the cathodic limiting reaction (and taking into account data obtained with Pt electrode) wave R₆ can be ascribed to H⁺ or HSO₄⁻ reduction on Au (Eq. 5). It was found that the value of the peak current of wave R₆ depends upon the duration of the anodic electrolysis during the corresponding oxidation wave Ox₅. At high potential scan rates it is possible to scan the potential to more positive values to reach (similar to platinum) the anodic electroreduction of the gold compound formed in the reaction Ox₅.

Experimental data on the electrochemical behavior of gold in KHSO₄, melts and comparisons of the voltammograms obtained in molten K₂S₂O₇ and KHSO₄ electrolytes at 440°C (Fig. 5) show that the cathodic wave R₆ on the K₂S₂O₇-KHSO₄ voltammogram (Fig. 1) can be ascribed to proton reduction and the anodic wave Ox₅ to the oxidation of absorbed hydrogen (Eq. 6). It can also be seen from Fig. 5 that the anodic dissolution of gold in molten KHSO₄ proceeds at more positive potentials than in molten K₂S₂O₇, i.e., gold is more stable in the presence of water in K₂S₂O₇ melt than in the "dry" melt.

Voltammetric measurements on a Au electrode in the molten K₂S₂O₇-V₂O₅, K₂S₂O₇-KHSO₄-V₂O₅, and K₂S₂O₇-KHSO₄-V₅O₆ systems at 440°C in argon atmosphere.—Electrochemical behavior of vanadium tetroxide (V₂O₄) in molten K₂S₂O₇ and K₂S₂O₇-KHSO₄.—We have found previously that in the molten system containing vanadium pentoxide, K₂S₂O₇-V₅O₆, the electrochemical reduction of V₅O₆ proceeds in two steps. The first step is a one-electron V(V) —→ V(IV) reduction, starting at 0.7-0.8 V vs. Ag/Ag⁺. The second reduction stage, V(IV) —→ V(III), starting at 0.1-0.2 V, is irreversible and under ohmic control. Similar V(IV) and V(III) electrochemical behaviors were observed in the V(IV) solutions in concentrated H₂SO₄. In the present investigation with vanadium tetroxide added to molten K₂S₂O₇, a V(IV) —→ V(III) reduction wave was also observed (R₆, Fig. 6). Corresponding V(III) —→ V(IV) oxidation wave (wave Ox₅) preceded the V(IV) —→ V(III) reduction (wave Ox₅). In K₂S₂O₇-V₅O₆ melts, the V(IV) —→ V(III) reduction stage (wave R₆) was obtained after the first cycle, i.e., after V(V) species have been produced electrochemically.

The results of the voltammetric measurements in K₂S₂O₇-V₅O₆ (sat.)-KHSO₄ (10 mole percent (m/o) melt are given in Fig. 7 and 8. It can be seen that a new reduction wave (R₈, Fig. 7) appears between V(V) —→ V(IV) (R₆) and V(IV) —→ V(III) (R₆) reduction waves. Wave R₈ (Figs. 7, 8) and wave R₆ (Fig. 2) are situated in the same potential region. Therefore we can ascribe wave R₈ to H⁺ (or HSO₄⁻) reduction. The fact that hydrogen formation (wave R₈) proceeds at more positive potentials than V(IV) —→ V(III) reduction, (wave R₆) helps us to understand the reason for the absence of the second vanadium electroreduction stage in the published experimental data for K₂S₂O₇-V₅O₆ melts containing water.

From Fig. 7 it can be seen that the addition of KHSO₄ causes a higher concentration of V(III). This can be achieved either through the promotion of the V(IV) —→ V(III) electroreduction by protons (Eq. 3) or by a chemi-
Fig. 6. Comparison of voltammetric curves obtained with a gold electrode in molten K$_2$S$_2$O$_7$ (1) and molten K$_2$S$_2$O$_7$-V$_2$O$_5$ (sat.) (2) at 1000 mV/s and 440°C in Ar atmosphere.

Chemical reduction of V(IV) by hydrogen formed during proton electroreduction.

Electrochemical behavior of vanadium pentoxide (V$_2$O$_5$) in molten K$_2$S$_2$O$_7$-KHSO$_4$—The voltammetric data obtained at a gold electrode in a K$_2$S$_2$O$_7$-KHSO$_4$ (10 m/o)-V$_2$O$_5$ (10 m/o) melt are given in Fig. 9 to 12 and in Table I; the voltammogram obtained in a “dry” melt of K$_2$S$_2$O$_7$-V$_2$O$_5$ (10 m/o) is also presented for comparison. It can be seen that the addition of KHSO$_4$ does not affect the V(V) — V(IV) reduction significantly but the peak potential of the V(IV) — V(V) oxidation moves to more positive potentials. For both V(V) — V(IV) and V(IV) — V(V) reactions, peak currents ($I_p$) depend linearly on the square root of the potential scan rate ($V_s$) (Fig. 11). The peak potentials ($E_p$) are linearly dependent on the natural logarithm (ln) of the potential scan rate ($V_s$) (Fig. 12). The linear $E_p$ dependence on the ln $V_s$ (Fig. 12) demonstrates the irreversibility of the charge-transfer stages of both electrochemical reactions.$^{24}$ Therefore the Nicholson and Shain equation, Eq. 13,$^{24}$ can be used to calculate the number of electrons ($n_e$) participating in the rate defining stages

$$E_p - E_{1/2} = -1.857 \frac{RT}{\alpha n_e F}$$

where $E_p$ and $E_{1/2}$ are peak and “half-peak” potentials (i.e., the potentials at $I = I/2$), respectively; $\alpha$ is the transfer coefficient; $n_e$ is the number of electrons taking part in the irreversible electrochemical reaction; $R$ is the gas constant; $F$ is the Faraday constant; and $T$ is the absolute temperature.

It is often assumed that $\alpha$ equals 0.5. $^{24}$ Calculated numbers of electrons are given in Table I. Similar to the “dry” K$_2$S$_2$O$_7$-V$_2$O$_5$ melt,$^1$ V(V) — V(IV) and V(IV) — V(V) in molten K$_2$S$_2$O$_7$-KHSO$_4$-V$_2$O$_5$ are the one-electron reactions. Therefore we can assume that the number of vanadium atoms in the active vanadium complexes does not change upon addition of KHSO$_4$ to the molten K$_2$S$_2$O$_7$-V$_2$O$_5$. 

Fig. 7. Comparison of voltammetric curves obtained with a gold electrode in molten K$_2$S$_2$O$_7$-V$_2$O$_5$ (sat.) (dashed curve) and in molten K$_2$S$_2$O$_7$-KHSO$_4$ (10 m/o)-V$_2$O$_5$ (sat.) (solid curve) at 1000 mV/s and 440°C in Ar atmosphere.

Fig. 8. Voltammetric curve obtained with a gold electrode in molten K$_2$S$_2$O$_7$-V$_2$O$_5$ (10 m/o)-V$_2$O$_5$ (sat.) at 400 mV/s and 440°C in Ar atmosphere.

Fig. 9. Voltammetric curves obtained with a gold electrode in molten K$_2$S$_2$O$_7$-10 m/o V$_2$O$_5$ (solid line) and molten K$_2$S$_2$O$_7$-10 m/o V$_2$O$_5$-10 m/o KHSO$_4$ (dashed line) at 100 mV/s and 440°C in Ar atmosphere.
Fig. 10. Effect of the potential scan rate on the voltammetric curves obtained with a gold electrode in molten K$_2$S$_2$O$_7$-10 m/o V$_2$O$_5$-10 m/o KHSO$_4$: 1, 1000; 2, 700; 3, 500; and 4, 100 mV/s at 440°C in Ar atmosphere.

The more positive peak potentials of V(IV) oxidation in K$_2$S$_2$O$_7$-KHSO$_4$-V$_2$O$_5$ (than in K$_2$S$_2$O$_7$-V$_2$O$_5$) is a result of a change in the kinetics of this reaction. This change can be caused by the formation of stable VOSO$_4\cdot$3H$_2$O complexes in the presence of water in the melt. The water molecules are expected to participate in the electric double-layer formation. As a result they may cause so-called screening of the electrode and subsequent inhibition of V(IV) — V(V) stage. However, in this case they would probably affect both the V(V) reduction and the V(IV) oxidation.

Voltammetry in K$_2$S$_2$O$_7$-V$_2$O$_5$ and K$_2$S$_2$O$_7$-KHSO$_4$-V$_2$O$_5$ melts under SO$_2$/air atmosphere—The liquid-gas M$_2$S$_2$O$_7$-VSOS/SOS-0$_2$-N$_2$ system can be considered to be closer to the catalytic conditions of the industrial sulfuric acid production. Therefore additional voltammetric measurements were made in molten K$_2$S$_2$O$_7$-V$_2$O$_5$ and K$_2$S$_2$O$_7$-KHSO$_4$-V$_2$O$_5$ melts under a SO$_2$/air atmosphere. The experimental results we obtained are given in Fig. 13 and 14. It can be seen that V(IV) → V(V) oxidation in SO$_2$/air atmosphere proceeds at lower polarizations than in argon (compare Fig. 12 and Fig. 14). Similarly to what was found for the Ar atmosphere, the presence of water (or KHSO$_4$) has no significant effect on the V(V) reduction, but it visibly changes the polarization of the V(IV) oxidation, the effect being more pronounced in SO$_2$/air atmosphere than in argon atmosphere.

Table I. Potential difference between peak and “half-peak” potentials, $E_p - E_{1/2}$, and the number of participating electrons, $n_e$, for the V(V) → V(IV) and V(IV) → V(V), obtained in molten K$_2$S$_2$O$_7$, containing KHSO$_4$ (10 m/o) and V$_2$O$_5$ (10 m/o) with Au electrode at 440°C.

<table>
<thead>
<tr>
<th>Electrochemical wave designation</th>
<th>Potential scan rate (V/s)</th>
<th>$E_p - E_{1/2}$ (V)</th>
<th>$n_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox$_{10}$</td>
<td>0.7</td>
<td>0.23</td>
<td>0.99</td>
</tr>
<tr>
<td>R$_{10}$</td>
<td>0.7</td>
<td>0.26</td>
<td>1.14</td>
</tr>
<tr>
<td>Ox$_{10}$</td>
<td>0.5</td>
<td>0.10</td>
<td>1.19</td>
</tr>
<tr>
<td>R$_{10}$</td>
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<td>Ox$_{10}$</td>
<td>0.2</td>
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<tr>
<td>R$_{10}$</td>
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<td>0.16</td>
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<tr>
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<tr>
<td>R$_{10}$</td>
<td>0.1</td>
<td>0.20</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Fig. 11. Peak currents of R$_{10}$ [A] and Ox$_{10}$ [B] waves (Fig. 10) vs. the square root of the potential scan rate.

Fig. 12. Peak potentials of R$_{10}$ [A] and Ox$_{10}$ [B] waves (Fig. 10) vs. logarithm of the potential scan rate.
addition in the SO$_2$/O$_2$ atmosphere (Fig. 14). The effect disappears at high potential scan rates.

Taking into account considerable changes in the mechanism of the V(IV) oxidation and absence of the effect for the V(V) → V(IV) reduction at high potential scan rates, the described water effects are rather caused by change in the structure of the active vanadium complexes in the presence of water, than adsorbed water molecules on the surface of gold electrode.

Conclusions

The effect of water on the electrochemical behavior of V$_2$O$_5$ was studied in K$_2$SO$_4$-KHSO$_4$-V$_2$O$_5$ and K$_2$SO$_4$-V$_2$O$_5$ melts in argon and SO$_2$/air atmospheres with a gold electrode at 440°C. It was shown that water has a promoting effect on the V(IV) → V(III) reduction increasing the concentration of V(III) species in the studied electrolytes.

Both reactions, the V(V) → V(IV) reduction and the V(IV) → V(V) oxidation, remain one-electron electrochemical reactions with increasing concentration of KHSO$_4$ in the molten K$_2$SO$_4$-KHSO$_4$-V$_2$O$_5$ system. Water has no noticeable effect on the kinetics of the V(V) → V(IV) reduction but causes higher polarizations (i.e., inhibition) of the V(IV) → V(IV) oxidation both in the Ar and SO$_2$/air atmospheres.

We conclude that the decreased activity of the V$_2$O$_5$ catalyst in the industrial oxidation of SO$_2$ to sulfuric acid, when the feed gas is moist, is due to the increased concentration of the lower valence vanadium ions, V(III) and V(IV), in the K$_2$SO$_4$ melt when water is present (as KHSO$_4$). Similar conditions exist for the removal of SO$_2$ from industrial flue gases.

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Electrocatalytic Formation of CH₄ from CO₂ on a Pt Gas Diffusion Electrode

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ABSTRACT

Electrochemical reduction of CO₂ under high pressure (<50 atm) on a Pt gas diffusion electrode (Pt-GDE) was studied. When the Pt catalyst layer was directed toward the CO₂ gas phase (the reverse arrangement), methane was produced as the main CO₂ reduction product at high faradaic efficiency and at large partial current density. Ethanol, ethylene, ethane, carbon monoxide, and formic acid were also produced. The effects of the Pt catalyst, electrode arrangement, CO₂ pressure, reaction temperature, and hydrogen pretreatment of the electrode were investigated for this electrocatalytic reaction. Faradaic efficiencies of the formation of CO₂ reduction products such as methane, carbon monoxide, and formic acid depended significantly on the CO₂ pressure and temperature. The yield of CO₂ reduction products was increased by hydrogen pretreatment of the Pt-gas diffusion electrode.

Introduction

In the last decade, electrochemical and electrocatalytic reduction of CO₂ using various metal electrodes under 1 atm in aqueous electrolytes has been extensively studied by many workers. As a result it has been determined that the electrocatalytic activity of the electrode depends strongly on the metal used. For example, on Hg, Pb, In, and Sn, which have large overpotentials for hydrogen formation, formic acid is predominantly formed. Methane, ethylene, and ethanol are preferential reduction products formed on a Cu electrode. However, one of the problems associated with electrochemical reduction of CO₂ in aqueous electrolytes is the low solubility of CO₂ in water (0.033 mol dm⁻³ at 25°C under 1 atm) which leads to mass-transfer limitations for electrolysis at high current density. In order to increase the current density for CO₂ reduction, electrochemical reduction of CO₂ under 1 atm using a gas diffusion electrode (GDE) has been also studied. Mahmood et al. investigated the electrochemical reduction of 1 atm of gaseous CO₂ using GDEs incorporating metal phthalocyanines, Pb, In, and Sn. They reported the formation of formic acid at a faradaic efficiency of 100% on a Pb-GDE at a current density of 115 mA cm⁻². Furuya et al. also reported CO₂ reduction using a GDE containing various metals such as Pb, Zn, Au, Ag, and Cu. Cook et al. and Schwarz et al. reported the electrochemical reduction of 1 atm of CO₂ on GDEs containing Cu and Cu alloys such as Cu-Ag, Cu-Pb, Cu-Zn, and Cu-Cd. Moreover, they showed that ethanol was formed at a faradaic efficiency of 31% at a current density of 180 mA cm⁻² on a GDE containing La₄Sr₂CuO₈. These results show the achievement of CO₂ reduction at a large current density due to gas-phase CO₂ reduction even under 1 atm of CO₂.

We have investigated the electrochemical reduction of CO₂ under high pressure in aqueous electrolytes using various metal electrodes in order to increase the partial current density of the CO₂ reduction. As a result, the partial current density of CO₂ reduction increases with many electrodes with increasing the CO₂ pressure (concentration). Interestingly, it has been found that CO₂ is reduced at high faradaic efficiencies under high pressure on 8 to 10 metal electrodes such as Fe, Ni, Rh, Pt, and Pd which produce predominantly hydrogen by the reduction of water (H⁺) under 1 atm of CO₂. In the cases of Fe and Pt electrodes, formic acid was formed as a preferential product for CO₂ reduction and carbon monoxide was predominantly formed on the Rh electrode. Both formic acid and carbon monoxide were formed at high faradaic efficiencies on Ni and Pd electrodes. Moreover, hydrocarbons such as methane, ethane, ethylene, and propene, which are hardly formed under 1 atm of CO₂, were formed on Fe, Co, and Ni electrodes at high pressure. The selectivity of the reduction product was changed by CO₂ pressure on these electrodes.

Therefore, very large currents for CO₂ reduction and the change in selectivity of reduction products can be expected on the electrochemical reduction of high-pressure CO₂ on GDEs containing 8 to 10 metal electrocatalysts. We have investigated the electrochemical reduction of high-pressure CO₂ on the Pt-GDE for the first time. As a result, CO₂ was reduced with high faradaic efficiency to methane, ethylene, ethanol, carbon monoxide, and formic acid when the Pt catalyst layer was directed toward the gas phase while the gas diffusion layer faced the electrolyte (the reverse arrangement). Methane was produced at a faradaic efficiency of 35% with a partial current density of 313 mA cm⁻² under 20 atm CO₂ at a constant current density of 900 mA cm⁻². Interestingly, when the Pt catalyst layer was directed toward the electrolyte (the normal arrangement, i.e., the gas diffusion layer faced the CO₂ gas phase), CO₂ reduction products were hardly produced and only hydrogen was formed by the reduction of water. In this publication we investigate the effects of CO₂ pressure, reaction temperature, hydrogen pretreatment of the GDE, and the current-potential curves for GDEs under Ar and CO₂ atmospheres in order to study the electrocatalytic activity of the Pt-GDE.

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