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Petrushina, Irina; Bjerrum, Niels; Berg, Rolf W.; Cappeln, Frederik Vilhelm

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Electrochemical Behavior of Molten V$_2$O$_5$-K$_2$S$_2$O$_7$-KHSO$_4$ Systems

I. M. Patrushina,* N. J. Bjerrum,* R. W. Berg, and F. Coppens

Materials Science Group, Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

ABSTRACT

The electrochemical behavior of K$_2$S$_2$O$_7$-V$_2$O$_5$, K$_2$S$_2$O$_7$-V$_2$O$_5$, and K$_2$S$_2$O$_7$-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 K$_2$S$_2$O$_7$-KHSO$_4$ were investigated by voltammetry performed with Au and Pt electrodes in an argon atmosphere. It was shown that H$^+$ 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($V$)$\rightarrow$V($IV$) and V($IV$)$\rightarrow$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 explained by protonic 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 V$_2$O$_5$-M$_2$S$_2$O$_7$ system (M is an alkali metal). This melt has proved to be a realistic model of the V$_2$O$_5$-M$_2$O catalyst for sulfur dioxide oxidation with oxygen or air in sulfuric acid production and SO$_2$ removal from flue gases. Flue gases can contain a significant amount of water (ca. 7% by volume). It is known that water dissolves in molten alkali pyrosulfates with formation of hydrogen sulfates

$$\text{H}_2\text{O} + \text{S}_2\text{O}_7^{2-} \rightarrow 2\text{HSO}_4^- \quad [1]$$

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.

* Electrochemical Society Active Member.

It has been shown$^{1,2}$ that electrochemical measurements can provide valuable information about the type of vanadium complexes formed in the K$_2$S$_2$O$_7$-V$_2$O$_5$ molten system and knowledge concerning the reaction mechanism during catalysis. Therefore the electrochemistry of K$_2$S$_2$O$_7$-V$_2$O$_5$ melts was studied in an attempt to understand the effect of water.

Previously, neither the electrochemistry of V$_2$O$_5$ in the molten K$_2$S$_2$O$_7$-KHSO$_4$ mixtures, nor the electrochemical behavior of K$_2$S$_2$O$_7$-KHSO$_4$ melts have been studied.

Hadjid et al.$^1$ investigated the electrochemistry of V$_2$O$_5$ in molten NH$_4$HSO$_4$ up to 0.5 mol V$_2$O$_5$/kg, i.e., 0.4 mole percent (m/o) at 200°C using Pt electrode. It was concluded that vanadium existed only in oxidation states five (V($V$) in acidic media and VO$_2$SO$_4$ in basic media) and four (VOSO$_4$ in acidic media and VO(SO$_4$)$_2$ in basic media), VOSO$_4$ being slightly soluble in the neutral melt. The standard potential of the V($V$)/V($IV$) electrochemical system was estimated as 0.677 V vs. an Ag/Ag$_2$SO$_4$ reference electrode. The electrochemical V($V$)$\rightarrow$V($IV$) reaction was shown to be a reversible one-electron process at 200°C.

REFERENCES

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.3,4,11 Thus, the electrochemical reduction of V(V) in aqueous solutions can proceed in two stages forming (V(III)) by the following reactions:

\[ \text{H}_2\text{O} + \text{M}_2\text{SO}_4 + \text{SO}_3 = 2\text{MHSO}_4 \]  

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/Ag’ at 100 and 500 mV/s, respectively. Almost all electrochemical data for K_2S_2O_7 and V_2O_5-K_2S_2O_7 melts were obtained at Au electrodes using the Ag/Ag’ 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_2S_2O_7 melts up to 550°C and therefore, seems to be the most suitable material for the electrochemical investigations in KHSO_4-K_2S_2O_7 containing electrolytes. As a result an additional electrochemical investigation in KHSO_4 and KHSO_4-K_2S_2O_7 melts using an Au working electrode vs. Ag/Ag’ is required. Such data are provided here to help distinguish the voltammetric characteristics of the molten KHSO_4-K_2S_2O_7 solvent and also with added vanadium compounds.

Experimental

Pure and dry K_2S_2O_7 was obtained by thermal decomposition of K_2SO_4 (Merck, Pro Analysis, maximum 0.01% by weight N) as described earlier.3 KHSO_4 (Merck, p.a.) was dried at 120°C for 24 h and then stored in a dry box. K_2S_2O_7 (Merck, Suprapur) was dried at 500°C overnight. V_2O_5 from Cerac (99.9% by weight pure) and Ag_2SO_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.1 The reference electrode was a silver wire placed in a Pyrex cylindrical chamber with a thin-walled sphere bottom. A melt of KHSO_4 saturated with Ag_2SO_4 was used as the electrolyte for the reference electrode for the experiments with molten K_2S_2O_7-KHSO_4 or molten K_2S_2O_7-KHSO_4-V_2O_5. A melt of 3 weight percent (w/o) solution of Ag_2SO_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_2O_5.

Gold and platinum wires sealed in Pyrex tubes served as working electrodes. In most cases, the working electrode area was 0.236 cm². 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_3 (10 v/o), O_2 (26 v/o), and N_2 (64 v/o), bubbling the gas through the Pyrex tube immersed in the molten electrolyte. Commercial gases were used: SO_3 (99.9% by volume), O_2 (99.8% by volume, 0.2 v/o N_2, and Ar), and N_2 (≤40 ppm of O_2). The SO_3-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 CVIA (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 GPE5 (Eco Chemie) software packages. The data were corrected for IR drops using current interruption technique.24

Results and Discussion

Voltammetric measurements on Pt and Au electrodes in melts of KHSO_4 and K_2S_2O_7-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. 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. 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 that wave R$_1$ is due to the reduction of the gold oxide through the following reaction

\[
\frac{1}{2}Au_2O_3 + \frac{1}{2}S_2O_3 + 3e^- \rightarrow Au + 3SO_2^{2-}
\]  

Wave Ox$_1$, according to Ref. 1,6 is the electrochemical dissolution of the gold electrode which can be described by the following equation

\[Au + 2n \cdot S_3O_2^{2-} \rightarrow Au(SO_4)^{2n-} + nS_2O_3^{2-} + 3e^-\]

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

\[3S_2O_2^{2-} \rightarrow 2S_2O_3^{2-} + \frac{1}{2}O_2 + 2e^-\]

and wave R$_4$ is the electrochemical reduction of solvated SO$_3$ mixed with oxygen. Wave R$_1$ appears only at high potential scan rates and can be ascribed to electrochemical reaction of gold complexes because it is decreasing simultaneously with wave Ox$_1$ after the additions of KHSO$_4$. Wave R$_1$ 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$_5$ 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. hydrogen reduction is the cathodic limiting reaction in molten alkali hydrogen sulfates. Reaction Ox$_5$ can be identified with Eq. 6.17 This conclusion is in agreement with the results of anodic galvanostatic transient measurements made by Gilroy, 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., the residual EMF, after electrolysis of the molten potassium hydrogenosulfate, was 0.602 V at 269°C. This EMF was identified with the poten-

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**Fig. 1.** Voltammetric curves obtained with a gold electrode in molten K$_2$S$_2$O$_7$ (1); and K$_2$S$_2$O$_7$ + 7.5 m/o KHSO$_4$ (2) at 800 mV/s and 440°C in Ar atmosphere.

**Fig. 2.** Voltammetric curve obtained with a gold electrode in molten K$_2$S$_2$O$_7$ - 10 m/o KHSO$_4$ at 1000 mV/s and 440°C in Ar atmosphere.

**Fig. 3.** Comparison of voltammetric curves for different electrode materials, platinum (Pt) and gold (Au) in molten KHSO$_4$ at 300 mV/s and 265°C in Ar atmosphere.
tional 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 Ox₁ 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 0.6 V vs. the hydrogen electrode), and (iii) the experimental data obtained by Gilroy²⁷ (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 R₁) and a 0.96 V anodic limit (wave Ox₁) at 300 mV/s (Fig. 3, solid line). The cathodic wave R₁ is obviously the electrochemical reduction of the gold compound formed in the reaction Ox₁.

Experimental data on the electrochemical behavior of gold in KHSO₄ melts and comparison of the voltammograms obtained in molten K₂S₂O₇ and KHSO₄ electrolytes at 440°C (Fig. 5) show that the cathodic wave R₁ on the K₂S₂O₇-KHSO₄ voltammogram (Fig. 1) can be ascribed to proton reduction and the anodic wave Ox₁ 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-KHSO₄-V₂O₅ and K₂S₂O₇-KHSO₄-V₂O₅ systems at 440°C in argon atmosphere. Electrochemical behavior of vanadium tetroxide (V₂O₅) in molten K₂S₂O₇ and K₂S₂O₇-KHSO₄.—We have found previously that in the molten system containing vanadium pentoxide, K₂S₂O₇-V₂O₅, the electrochemical reduction of V₂O₅ 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 (R₁, Fig. 6). Corresponding V(III) → V(IV) oxidation wave (wave Ox₁) preceded the V(IV) → V(III) reduction (wave Ox₁). In K₂S₂O₇-V₂O₅ melts, the V(IV) → V(III) reduction stage (wave R₁) was observed after the first cycle, i.e., after V(IV) species have been produced electrochemically.

The results of the voltammetric measurements in K₂S₂O₇-V₂O₅ (sat.)-KHSO₄ (10 mole percent (m/o) melt are given in Fig. 7 and 8. It can be seen that a new reduction wave (R₃) appears between V(IV) → V(III) (R₁) and V(IV) → V(II) (R₂) reduction waves. Wave R₂ (Fig. 7, 8) and wave R₃ (Fig. 2) are situated in the same potential region. Therefore we can ascribe wave R₃ to H⁺ (or HSO₄⁻) reduction. The fact that hydrogen formation (wave R₂) proceeds at more positive potentials than V(IV) → V(III) reduction, (wave R₁) helps us to understand the reason for the absence of the second vanadium electroreduction stage in the published experimental data for K₂S₂O₇-V₂O₅ melts containing water.²⁴²⁵

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.

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) (solid curve) at 1000 mV/s and 440°C in Ar atmosphere.

The 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 (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.

Therefore the Nicholson and Shain equation, Eq. 13, can be used to calculate the number of electrons (n$_e$) participating in the rate defining stages

\[ E_p - E_{1/2} = -1.857 \frac{RT}{n_eF} \]

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. Calculated numbers of electrons are given in Table I. Similar to the “dry” K$_2$S$_2$O$_7$-V$_2$O$_5$ melt, 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. 8. Voltammetric curve obtained with a gold electrode in molten K$_2$S$_2$O$_7$-KHSO$_4$ (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.
The more positive peak potentials of V(IV) oxidation in K₂S₂O₇-KHSO₄-V₂O₅ (than in K₂S₂O₇-V₂O₅) is a result of a change in the kinetics of this reaction. This change can be caused by the formation of stable VO₅SO₄·3H₂O 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 K₂S₂O₇-V₂O₅ and K₂S₂O₇-KHSO₄-V₂O₅ melts under SO₂/air atmosphere—The liquid-gas M₂S₂O₇-V₂O₅/SO₂-N₂ 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 K₂S₂O₇-V₂O₅ and K₂S₂O₇-KHSO₄-V₂O₅, melts under a SO₂/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 SO₂/O₂ 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 KHSO₄) 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 SO₂/air atmosphere than in argon atmosphere.

The V(IV) → V(V) oxidation kinetics in the “dry” K₂S₂O₇-V₂O₅ changes from slow charge-transfer stage in argon to slow preceding chemical reaction in SO₂/O₂ atmosphere (Fig. 14). Figure 14 (A) demonstrates the well-known voltammetric criterion for the slow preceding chemical reaction mechanism: oxidation peak potential moves in the negative direction with growth of the potential scan rate. After the addition of water (or KHSO₄) the V(IV) → V(V) oxidation kinetics, like in the argon atmosphere, becomes a slow charge-transfer kinetics (Fig. 14B). Therefore it is easier to detect the inhibiting water effect on the V(IV) → V(V) oxidation in the SO₂/O₂ atmosphere than in argon atmosphere. Neither the SO₂/O₂ atmosphere nor the water change type of the kinetics of the V(V) → V(IV) reduction (Fig. 12, 14). However there is a small positive change of V(V) → V(IV) peak potential after KHSO₄.

Table 1. Potential difference between peak and “half-peak” potentials, \( E_p - E_{1/2} \), and the number of participating electrons, \( n \), for the V(V) → V(IV) and V(IV) → V(V), obtained in molten K₂S₂O₇ containing KHSO₄ (10 m/o) and V₂O₅ (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 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_{10} )</td>
<td>0.7</td>
<td>0.23, 0.99</td>
<td></td>
</tr>
<tr>
<td>( R_{10} )</td>
<td>0.7</td>
<td>0.20, 1.14</td>
<td></td>
</tr>
<tr>
<td>( O_{19} )</td>
<td>0.5</td>
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</tr>
<tr>
<td>( R_{19} )</td>
<td>0.5</td>
<td>0.17, 1.30</td>
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</tr>
<tr>
<td>( O_{10} )</td>
<td>0.2</td>
<td>0.23, 0.99</td>
<td></td>
</tr>
<tr>
<td>( R_{10} )</td>
<td>0.2</td>
<td>0.16, 1.28</td>
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</tr>
<tr>
<td>( O_{10} )</td>
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<td>0.22, 1.02</td>
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<tr>
<td>( R_{10} )</td>
<td>0.1</td>
<td>0.20, 1.10</td>
<td></td>
</tr>
</tbody>
</table>
addition in the SO₂/O₂ 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 V₂O₅ was studied in K₂S₂O₇-KHSO₄-V₂O₅ and K₂S₂O₇-V₂O₅ melts in argon and SO₂/air atmospheres.

Fig. 13. Voltammetric curves obtained with a gold electrode in molten K₂S₂O₇-10 m/o V₂O₅ (solid line) and molten K₂S₂O₇-10 m/o V₂O₅-10 m/o KHSO₄ (dashed line) at 500 mV/s and 440°C in SO₂/air atmosphere.

Fig. 14. Peak potentials of the V(V) → V(IV) reduction and V(IV) → V(V) oxidation voltammetric waves in dependence on the logarithm of the potential scan rate obtained in molten K₂S₂O₇-10 m/o V₂O₅ (A) and molten K₂S₂O₇-10 m/o V₂O₅-10 m/o KHSO₄ (B) at 440°C in SO₂/air atmosphere.

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

Kohjiro Hara* and Tadayoshi Sakata

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

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) 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 La₈SrₓCuO₄. 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 (H²⁻) 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 propane, which are hardly formed at 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 CO₂ 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 electrolyte (the reverse arrangement)), methane was produced at a partial current density of 900 mA cm⁻². 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.

* Electrochemical Society Student Member.