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Electrochemical Behavior of Molten V₂O₅-K₂S₂O₇-KHSO₄ Systems

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REFERENCES

- J. R. MacCallum and C. A. Vincent, *Polymer Electrolyte Reviews-2*, Elsevier Applied Science, London (1989).
- B. Scrosati and F. Croce, *Mater. Res. Soc. Symp. Proc.*, **293**, 459 (1993).
- M. Odziemkowski and D. E. Irish, *This Journal*, **139**, 3063 (1992).
- D. Fauteux, *Solid State Ionics*, **17**, 133 (1985).
- F. Bonino, B. Scrosati, A. Selvaggi, and J. Evans, *J. Power Sources*, **18**, 75 (1986).
- P. D. Greene, E. L. Bush, and I. R. Rawlings, Abstract 479, p. 378, The Electrochemical Society Meeting Abstracts, Vol. 5, No. 2, Montreal, PQ, Canada, Oct. 6-11, (1968).
- A. K. Vijh, *J. Mater. Sci.*, **9**, 853 (1974).
- J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, C. F. Luck and J. D. Robertson, *Solid State Ionics*, **53-56**, 647 (1992).
- J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, C. F. Luck, and J. D. Robertson, *J. Power Sources*, **43-44**, 103 (1993).
- J. B. Bates, N. J. Dudney, D. C. Lubben, G. R. Gruzalski, B. S. Kwak, X. Yu, and R. A. Zuhr, *ibid.*, **54**, 58 (1995).
- J. B. Bates, D. Lubben, N. J. Dudney, and F. X. Hart, *This Journal*, **142**, L149 (1995).
- B. Wang, J. B. Bates, F. X. Hart, B. C. Sales, R. A. Zuhr, and J. D. Robertson, *ibid.*, **143**, 3203 (1996).
- L. Boukbir, R. Marchang, Y. Laurent, P. Bacher, and G. Roul, *Ann. Chim. Fr.*, **14**, 475 (1989).
- B. Wang, B. S. Kwak, B. C. Sales, and J. B. Bates, *Non-Cryst. Solids*, **183**, 297 (1995).
- B. Wang, J. B. Bates, B. C. Chakoumakos, B. C. Sales, B. S. Kwak, R. A. Zuhr, and J. D. Robertson, *Mater. Res. Soc. Symp., Proc.*, **369**, 445 (1995).
- J. B. Bates, J. C. Wang, and Y. T. Chu, *J. Non-Cryst. Solids*, **131-133**, 1046 (1991).
- G. E. Jellison and F. A. Modine, *Appl. Opt.*, **29**, 959 (1990).
- C. A. C. Sequeira, J. M. North, and A. Hooper, *Solid State Ionics*, **13**, 175 (1984).
- D. A. G. Bruggeman, *Ann. Phys. (Leipzig)*, **24**, 636 (1935).
- G. E. Jellison, Jr., *Opt. Mater.*, **1**, 41 (1992).
- G. E. Jellison, Jr. and F. A. Modine, *Appl. Phys. Lett.*, **69**, 371 (1996); *ibid.*, **69**, 2137 (1996).
- G. E. Jellison, Jr., *Thin Solid Films*, **234**, 416 (1993).
- J. Tauc, in *The Optical Properties of Solids*, F. Abeles, Editor, p. 277, North-Holland, Amsterdam (1970).
- D. L. Wood and J. Tauc, *Phys. Rev. B*, **5**, 3144 (1972).
- K. Hughes and J. O. Isard, in *Physics of Electrolytes*, Vol. 1, J. Hladik, Editor, p. 351, Academic Press, London (1972).

Electrochemical Behavior of Molten V_2O_5 - $K_2S_2O_7$ - $KHSO_4$ Systems

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ABSTRACT

The electrochemical behavior of $K_2S_2O_7$ - $KHSO_4$ - V_2O_5 , $K_2S_2O_7$ - V_2O_4 , and $K_2S_2O_7$ - $KHSO_4$ - V_2O_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 $K_2S_2O_7$ - $KHSO_4$ 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 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_2O_5 containing molten electrolytes. This effect may be caused either by protonic promotion of the $V(IV) \rightarrow V(III)$ reduction ($VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$) or by chemical reduction of $V(IV)$ complexes with hydrogen, formed from H^+ as the product of the electrochemical reduction. Both the $V(V) \rightarrow V(IV)$ reduction and the $V(IV) \rightarrow V(V)$ oxidation remained one-electron electrochemical reactions after the addition of $KHSO_4$ (or water) to the $H_2S_2O_7$ - V_2O_5 melt. Water had no noticeable effect on the $V(V) \rightarrow V(IV)$ reduction but the $V(IV) \rightarrow V(V)$ oxidation proceeded at higher polarizations 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 V_2O_5 - $M_2S_2O_7$ system (M is an alkali metal).¹ This melt has proved to be a realistic model of the V_2O_5 - M_2O 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}



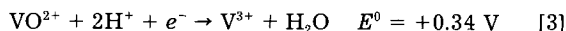
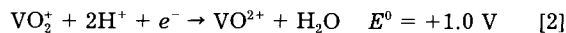
Dissolved water (or hydrogen sulfate) may participate in some steps of the above mentioned catalytical process. Obviously the physicochemical properties of the melt and possibly the structure of the catalytically active vanadium species depend on the water activity.

* Electrochemical Society Active Member.

It has been shown^{1,6} that electrochemical measurements can provide valuable information about the type of vanadium complexes formed in the $K_2S_2O_7$ - V_2O_5 molten system and knowledge concerning the reaction mechanism during catalysis. Therefore the electrochemistry of $K_2S_2O_7$ - $KHSO_4$ - V_2O_5 melts was studied in an attempt to understand the effect of water.

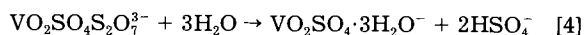
Previously, neither the electrochemistry of V_2O_5 in the molten $K_2S_2O_7$ - $KHSO_4$ mixtures, nor the electrochemical behavior of $K_2S_2O_7$ - $KHSO_4$ melts have been studied. Hadid *et al.*⁷ investigated the electrochemistry of V_2O_5 in molten NH_4HSO_4 [up to 0.5 mol V_2O_5 /kg, i.e., 5.4 mole percent (m/o)] at 200°C using Pt electrode. It was concluded that vanadium existed only in oxidation states five (VO_2^+ in acidic media and $VO_2SO_4^-$ 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_2SO_4 reference electrode. The electrochemical $V(V) \rightarrow V(IV)$ reaction was shown to be a reversible one-electron process at 200°C.

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.⁸⁻¹¹ Thus, the electrochemical reduction of V(V) in aqueous solutions can proceed in two stages forming V(III) by the following reactions⁸



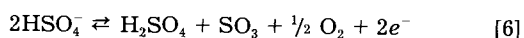
where E^0 is the standard potential *vs.* a normal hydrogen electrode. The electrochemical reduction of V(III) to V(II) in 2 M aqueous H_2SO_4 was used as a cathodic process for the redox flow cell.^{9,10} It was shown that V(V) can be chemically reduced to V(III) [in the form of $\text{KV}(\text{SO}_4)_2$] by SO_2 in molten $\text{K}_2\text{S}_2\text{O}_7$ - KHSO_4 - V_2O_5 and KHSO_4 - V_2O_5 systems at 450°C.¹¹

In the molten $\text{K}_2\text{S}_2\text{O}_7$ - V_2O_5 systems, catalytically active V(V) complexes (possibly $\text{VO}_2\text{SO}_4\text{S}_2\text{O}_7^{3-}$) were found to react with water forming hydrated complexes by the reaction¹²

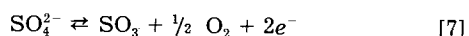


In studies on the structure of V(V) compounds formed in V_2O_5 solutions in concentrated sulfuric acid, disulfuric acid, and oleum at the ambient temperatures, it was shown that $\text{VO}(\text{HSO}_4)_3$, $\text{VO}(\text{OH})(\text{HSO}_4)_2$, and $\text{H}[\text{VO}(\text{HSO}_4)_4]$ were the most likely V(V) compounds.¹³⁻¹⁵ Gillespie *et al.*¹⁴ have also found evidence for the formation of dimeric $\text{H}[\text{V}_2\text{O}_3(\text{HSO}_4)_6]$ species at high V_2O_5 concentrations.

Until now only the electrochemistry of hydrogen reduction on platinum from molten KHSO_4 has been studied.¹⁶⁻¹⁸ The electroreduction of hydrogen on bright and platinized platinum was studied in molten KHSO_4 at 250 to 440°C.^{16,17} Videla *et al.* suggested hydrogen bonding in the melt.¹² Arvia *et al.*¹³ assumed that the potential window of molten KHSO_4 is limited by the following cathodic and anodic electrochemical reactions

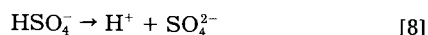


or



The residual EMF after the electrolysis of the KHSO_4 melt was measured.¹⁷ 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 studied¹⁸ 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_2SO_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.¹⁸

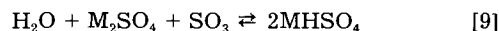
Equation 5 implies a preceding dissociation of HSO_4^-



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.*¹⁹ 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 only H^+ ions. A considerably higher electroconductivity of molten $\text{K}_2\text{S}_2\text{O}_7$ after addition of KHSO_4 ²⁰ is also in agreement with a proton hopping mechanism of conductivity for molten KHSO_4 - $\text{K}_2\text{S}_2\text{O}_7$.

White *et al.*²¹ studied the electrochemical behavior of water dissolved in a molten Li_2SO_4 - K_2SO_4 - Na_2SO_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 hydrogensulfate after the reaction



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 $\text{K}_2\text{S}_2\text{O}_7$ and V_2O_5 - $\text{K}_2\text{S}_2\text{O}_7$ 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 - $\text{K}_2\text{S}_2\text{O}_7$ melts up to 550°C²² and therefore, seems to be the most suitable material for the electrochemical investigations in KHSO_4 - $\text{K}_2\text{S}_2\text{O}_7$ containing electrolytes. As a result an additional electrochemical investigation in KHSO_4 and KHSO_4 - $\text{K}_2\text{S}_2\text{O}_7$ 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 - $\text{K}_2\text{S}_2\text{O}_7$ solvent and also with added vanadium compounds.

Experimental

Pure and dry $\text{K}_2\text{S}_2\text{O}_7$ was obtained by thermal decomposition of $\text{K}_2\text{S}_2\text{O}_8$ (Merck, Pro Analyti, maximum 0.001% by weight N) as described earlier.⁴ KHSO_4 (Merck, p.a.) was dried at 120°C for 24 h and then stored in a dry box. K_2SO_4 (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 $\text{K}_2\text{S}_2\text{O}_7$ saturated with Ag_2SO_4 was used as the electrolyte for the reference electrode for the experiments with molten $\text{K}_2\text{S}_2\text{O}_7$ - KHSO_4 or molten $\text{K}_2\text{S}_2\text{O}_7$ - 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 the 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 $\pm 1^\circ\text{C}$.²³ 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/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_2 (>99.9% by volume), O_2 (99.8 v/o + 0.2 v/o N_2 and Ar), and N_2 (<40 ppm of O_2). The $\text{SO}_2/\text{O}_2/\text{N}_2$ 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.²⁴

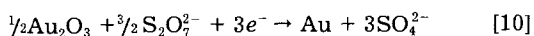
Results and Discussion

Voltammetric measurements on Pt and Au electrodes in melts of KHSO_4 and $\text{K}_2\text{S}_2\text{O}_7$ - KHSO_4 at 265 and 440°C.—

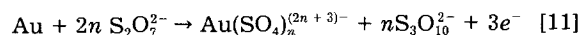
Vapor pressure measurements in the $K_2S_2O_7$ - $KHSO_4$ system were performed using the boiling-point-method and the quartz-Bourdon-manometer-method prior to the electrochemical measurements.²⁵ The obtained vapor pressure values were lower than 60 Torr for $KHSO_4$ concentrations less than 10 m/o at 440°C. Taking these data into account, we deduce that the $K_2S_2O_7$ - $KHSO_4$ system is sufficiently stable up to 10 m/o $KHSO_4$ at 440°C.

The voltammograms obtained with the gold electrode in the molten $K_2S_2O_7$, 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 $K_2S_2O_7$ melt the reduction wave R_1 and the oxidation wave Ox_1 appear in the voltammetric curves at the potentials 0.26₀ and 0.04₅ 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" $K_2S_2O_7$ melt.¹ The oxidation wave Ox_2 and the reduction wave R_4 are gradually suppressed with the increasing concentration of $KHSO_4$.

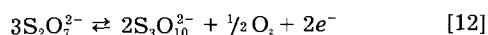
It has already been shown¹ that wave R_2 is due to the reduction of the gold oxide through the following reaction



Wave Ox_2 , according to Ref. 1,6 is the electrochemical dissolution of the gold electrode which can be described by the following equation



Wave Ox_3 is the electrochemical oxidation of $S_2O_7^{2-}$



and wave R_3 is the electrochemical reduction of solvated SO_3 mixed with oxygen.¹ Wave R_4 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_2 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.

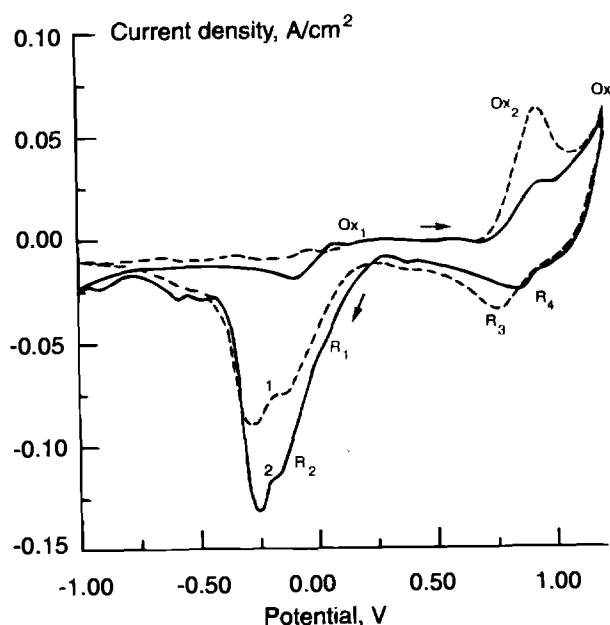


Fig. 1. Voltammograms obtained with a gold electrode in molten $K_2S_2O_7$ (1); and $K_2S_2O_7$ + 7.5 m/o $KHSO_4$ (2) at 800 mV/s and 440°C in Ar atmosphere.

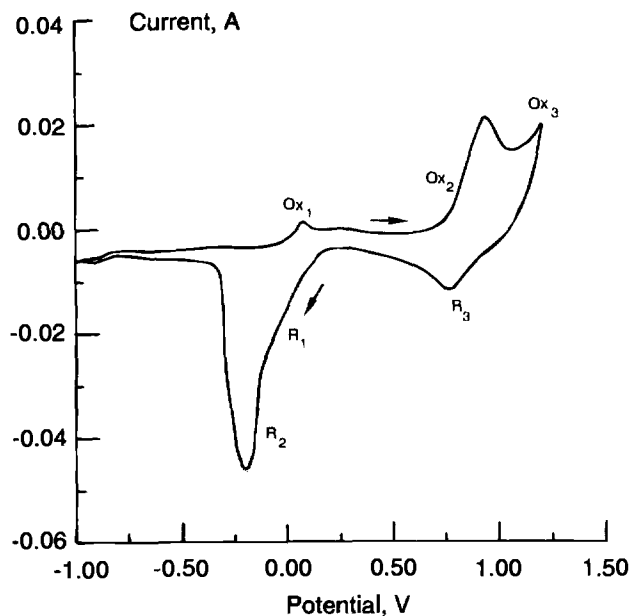


Fig. 2. Voltammogram obtained with a gold electrode in molten $K_2S_2O_7$ + 10 m/o $KHSO_4$ at 1000 mV/s and 440°C in Ar atmosphere.

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.*¹⁷ 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,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.*,¹⁷ the residual EMF, after electrolysis of the molten potassium hydrogenosulfate, was 0.602 V at 269°C. This EMF was identified with the poten-

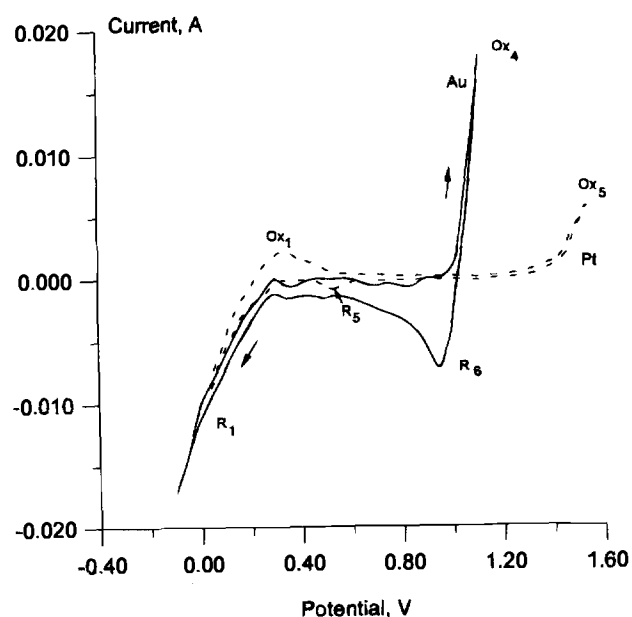


Fig. 3. Comparison of voltammograms for different electrode materials, platinum (Pt) and gold (Au) in molten $KHSO_4$ at 300 mV/s and 265°C in Ar atmosphere.

tial window of molten KHSO_4 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 Ox_5 is irreversible. The only "available" cathodic reaction to form an electrochemical couple with hydrogen after KHSO_4 electrolysis is reaction R_5 (Fig. 3). This fact can explain the low values of residual EMF obtained by Arvia *et al.*¹⁷ Wave R_5 can be ascribed to the reduction of platinum oxide, taking into account the electrochemical behavior of (i) platinum in dilute sulfuric acid²⁶ (platinum oxide formation and reduction region occurring between 0.4 V and 1.1 V *vs.* hydrogen electrode), (ii) platinum in concentrated sulfuric acid solutions²⁷ (platinum oxide formation and reduction region occurring between 0 and 0.6 V *vs.* the hydrogen electrode), and (iii) the experimental data obtained by Gilroy¹⁸ (platinum oxide reduction in the molten KHSO_4 takes place at 0.4 V *vs.* the hydrogen electrode).

The gold electrode voltammogram for molten KHSO_4 under Ar atmosphere and at 265°C was characterized by a 0.26 V cathodic limit (wave R_1) and a 0.96 V anodic limit (wave Ox_5) at 300 mV/s (Fig. 3, solid line). The cathodic wave R_6 is obviously the electrochemical reduction of the product of reaction Ox_4 .

As the cathodic limiting reaction (and taking into account data obtained with Pt electrode) wave R_1 can be ascribed to H^+ or HSO_4^- reduction on Au (Eq. 5). It was found that the value of the peak current of wave R_6 depends upon the duration of the anodic electrolysis during the corresponding oxidation wave Ox_4 . At high potential scan rates it is possible to scan the potential to more positive values to reach (similar to platinum) the anodic oxidation of HSO_4^- ion at 1.45 V, *i.e.*, wave Ox_5 (Fig. 4). We can assume that wave Ox_4 is a passivation peak corresponding to the anodic dissolution of gold in molten KHSO_4 . Therefore wave R_6 can be ascribed to the electroreduction of the gold compound formed in the reaction Ox_4 .

Experimental data on the electrochemical behavior of gold in KHSO_4 melts and comparison of the voltammograms obtained in molten $\text{K}_2\text{S}_2\text{O}_7$ and KHSO_4 electrolytes at 440°C (Fig. 5) show that the cathodic wave R_1 on the $\text{K}_2\text{S}_2\text{O}_7$ - KHSO_4 voltammogram (Fig. 1) can be ascribed to proton reduction and the anodic wave Ox_1 to the oxidation of absorbed hydrogen (Eq. 6). It can also be seen from Fig. 5 that the anodic dissolution of gold in molten KHSO_4 proceeds at more positive potentials than in molten

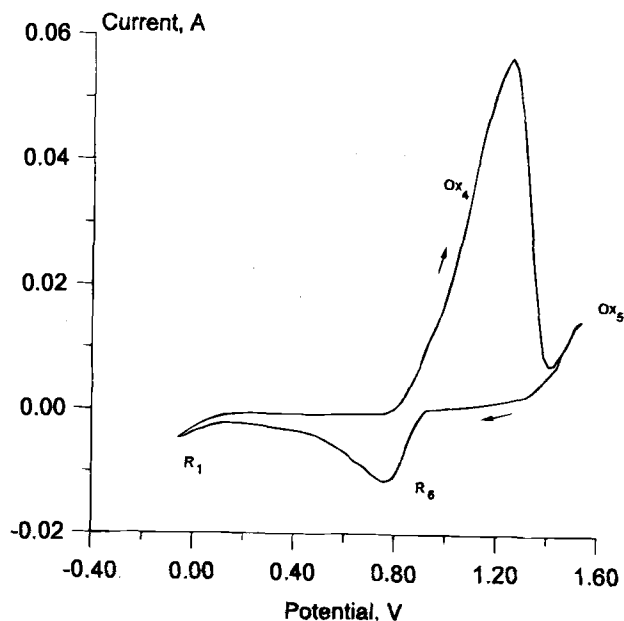


Fig. 4. Voltammetric curves obtained with a gold electrode in molten KHSO_4 at 1000 mV/s and 265°C in Ar atmosphere.

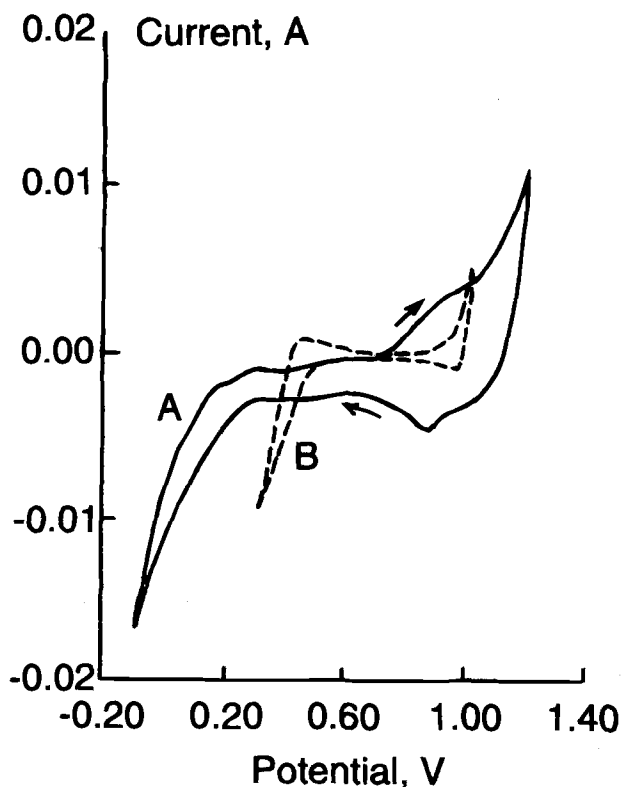


Fig. 5. Comparison of voltammetric curves obtained with a gold electrode in molten $\text{K}_2\text{S}_2\text{O}_7$ (A) and molten KHSO_4 (B) at 1000 mV/s and 440°C in Ar atmosphere.

$\text{K}_2\text{S}_2\text{O}_7$, *i.e.*, gold is more stable in the presence of water in $\text{K}_2\text{S}_2\text{O}_7$ melt than in the "dry" melt.

Voltammetric measurements on a Au electrode in the molten $\text{K}_2\text{S}_2\text{O}_7$ - V_2O_5 , $\text{K}_2\text{S}_2\text{O}_7$ - KHSO_4 - V_2O_5 , and $\text{K}_2\text{S}_2\text{O}_7$ - KHSO_4 - V_2O_5 systems at 440°C in argon atmosphere.—Electrochemical behavior of vanadium tetroxide (V_2O_4) in molten $\text{K}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$ - KHSO_4 .—We have found¹ previously that in the molten system containing vanadium pentoxide, $\text{K}_2\text{S}_2\text{O}_7$ - V_2O_5 , the electrochemical reduction of V_2O_5 proceeds in two steps. The first step is a one-electron $\text{V(V)} \rightarrow \text{V(IV)}$ reduction, starting at 0.7–0.8 V *vs.* Ag/Ag^+ . The second reduction stage, $\text{V(IV)} \rightarrow \text{V(III)}$, 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 H_2SO_4 .¹⁰ In the present investigation with vanadium tetroxide added to molten $\text{K}_2\text{S}_2\text{O}_7$, a $\text{V(IV)} \rightarrow \text{V(III)}$ reduction wave was also observed (R_{11} , Fig. 6). Corresponding $\text{V(III)} \rightarrow \text{V(IV)}$ oxidation wave (wave Ox_9) preceded the $\text{V(IV)} \rightarrow \text{V(V)}$ oxidation (wave Ox_{10}). In $\text{K}_2\text{S}_2\text{O}_7$ - V_2O_5 melts, the $\text{V(V)} \rightarrow \text{V(IV)}$ reduction stage (wave R_{10}) was obtained after the first cycle, *i.e.*, after V(V) species have been produced electrochemically.

The results of the voltammetric measurements in $\text{K}_2\text{S}_2\text{O}_7$ - V_2O_5 (sat.)- KHSO_4 (10 mole percent (m/o)) melt are given in Fig. 7 and 8. It can be seen that a new reduction wave (R_{12}) appears between $\text{V(V)} \rightarrow \text{V(IV)}$ (R_{10}) and $\text{V(IV)} \rightarrow \text{V(III)}$ (R_{11}) reduction waves. Wave R_{12} (Fig. 7, 8) and wave R_1 (Fig. 2) are situated in the same potential region. Therefore we can ascribe wave R_{12} to H^+ (or HSO_4^-) reduction. The fact that hydrogen formation (wave R_{12}) proceeds at more positive potentials than $\text{V(IV)} \rightarrow \text{V(III)}$ reduction, (wave R_{11}) helps us to understand the reason for the absence of the second vanadium electroreduction stage in the published experimental data for $\text{K}_2\text{S}_2\text{O}_7$ - V_2O_5 melts containing water.^{6,28}

From Fig. 7 it can be seen that the addition of KHSO_4 causes a higher concentration of V(III) . This can be achieved either through the promotion of the $\text{V(IV)} \rightarrow \text{V(III)}$ electroreduction by protons (Eq. 3)⁸ or by a chemi-

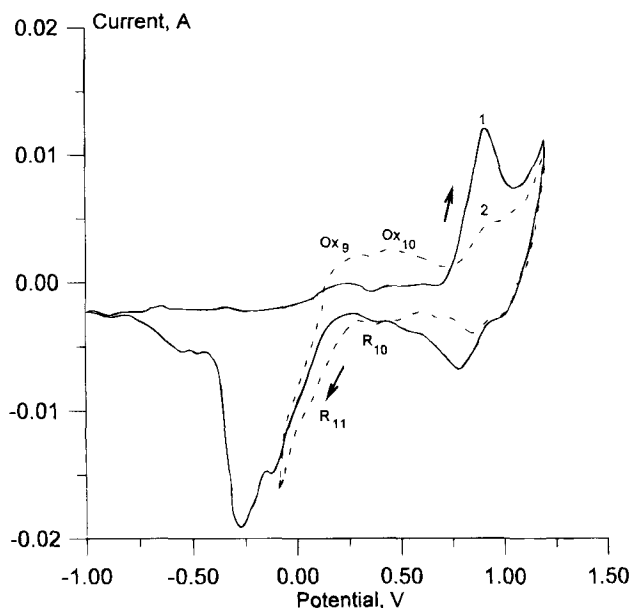


Fig. 6. Comparison of voltammetric curves obtained with a gold electrode in molten $K_2S_2O_7$ (1) and molten $K_2S_2O_7-V_2O_4$ (sat.) (2) at 1000 mV/s and 440°C in Ar atmosphere.

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

Electrochemical behavior of vanadium pentoxide (V_2O_5) in molten $K_2S_2O_7-KHSO_4$.—The voltammetric data obtained at a gold electrode in a $K_2S_2O_7-KHSO_4$ (10 m/o)- V_2O_5 (10 m/o) melt are given in Fig. 9 to 12 and in Table I; the voltammogram obtained in a “dry” melt of $K_2S_2O_7-V_2O_5$ (10 m/o) is also presented for comparison. It can be seen that the addition of $KHSO_4$ does not affect the $V(V) \rightarrow V(IV)$ reduction significantly but the peak potential of the $V(IV) \rightarrow V(V)$ oxidation moves to more positive potentials. For both $V(V) \rightarrow V(IV)$ and $V(IV) \rightarrow V(V)$ 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

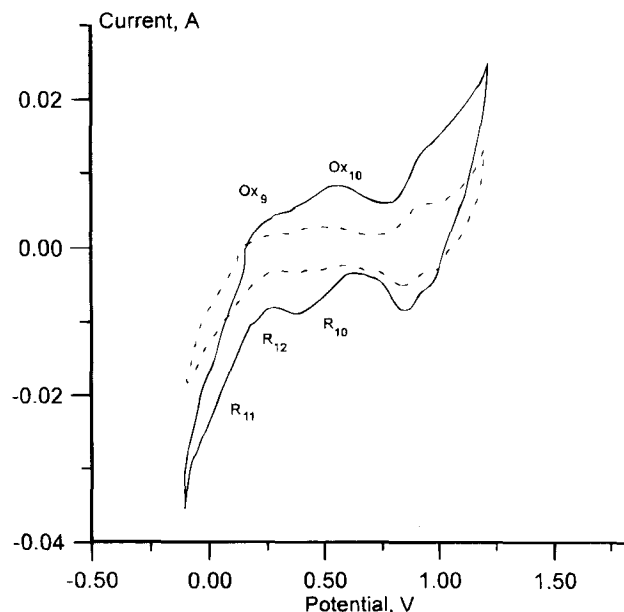


Fig. 7. Comparison of voltammetric curves obtained with a gold electrode in molten $K_2S_2O_7-V_2O_4$ (sat.) (dashed curve) and in molten $K_2S_2O_7-KHSO_4$ (10 m/o)- V_2O_4 (sat.) (solid curve) at 1000 mV/s and 440°C in Ar atmosphere.

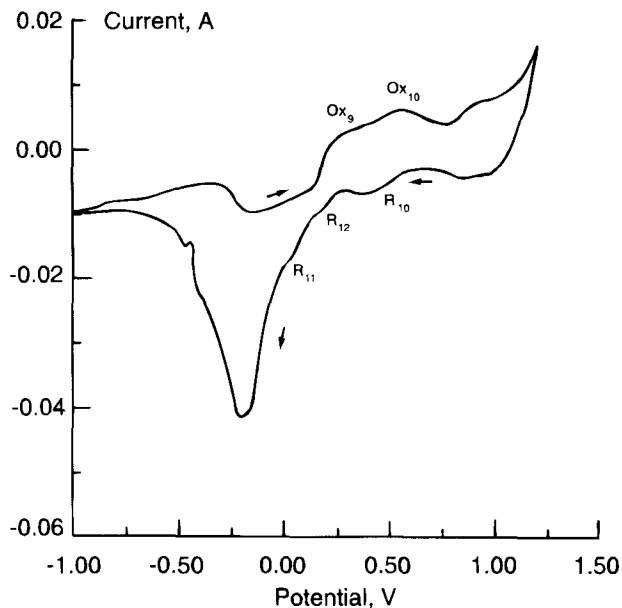


Fig. 8. Voltammetric curve obtained with a gold electrode in molten $K_2S_2O_7-KHSO_4$ (10 m/o)- V_2O_4 (sat.) at 400 mV/s and 440°C in Ar atmosphere.

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_a) participating in the rate defining stages

$$E_p - E_{p/2} = -1.857 \frac{RT}{\alpha n_a F} \quad [13]$$

where E_p and $E_{p/2}$ are peak and “half-peak” potentials (*i.e.*, the potentials at $I = I_p/2$), respectively; α is the transfer coefficient; n_a 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 α equals 0.5.²⁴ Calculated numbers of electrons are given in Table I. Similar to the “dry” $K_2S_2O_7-V_2O_5$ melt,¹ $V(V) \rightarrow V(IV)$ and $V(IV) \rightarrow V(V)$ in molten $K_2S_2O_7-KHSO_4-V_2O_5$ 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 $K_2S_2O_7-V_2O_5$.

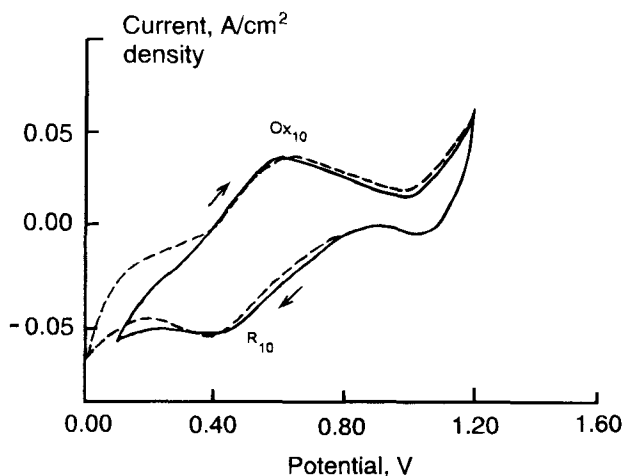


Fig. 9. Voltammetric curves obtained with a gold electrode in molten $K_2S_2O_7-10$ m/o V_2O_5 (solid line) and molten $K_2S_2O_7-10$ m/o V_2O_5-10 m/o $KHSO_4$ (dashed line) at 100 mV/s and 440°C in Ar atmosphere.

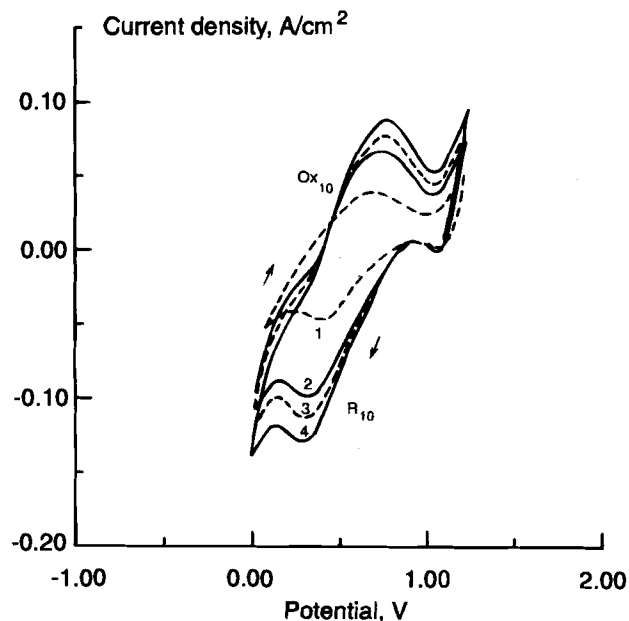


Fig. 10. Effect of the potential scan rate on the voltammetric curves obtained with a gold electrode in molten $K_2S_2O_7$ -10 m/o V_2O_5 -10 m/o $KHSO_4$: 1, 1000; 2, 700; 3, 500; and 4, 100 mV/s at 440°C in Ar atmosphere.

The more positive peak potentials of V(IV) oxidation in $K_2S_2O_7$ - $KHSO_4$ - V_2O_5 (than in $K_2S_2O_7$ - V_2O_5) is a result of a change in the kinetics of this reaction.²⁴ This change can be caused by the formation of stable $VOSO_4 \cdot 3H_2O$ complexes⁸ 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 $K_2S_2O_7$ - V_2O_5 and $K_2S_2O_7$ - $KHSO_4$ - V_2O_5 melts under SO_2 /air atmosphere.—The liquid-gas $M_2S_2O_7$ - V_2O_5 / SO_2 - O_2 - N_2 system can be considered to be closer to the catalytic conditions of the industrial sulfuric acid pro-

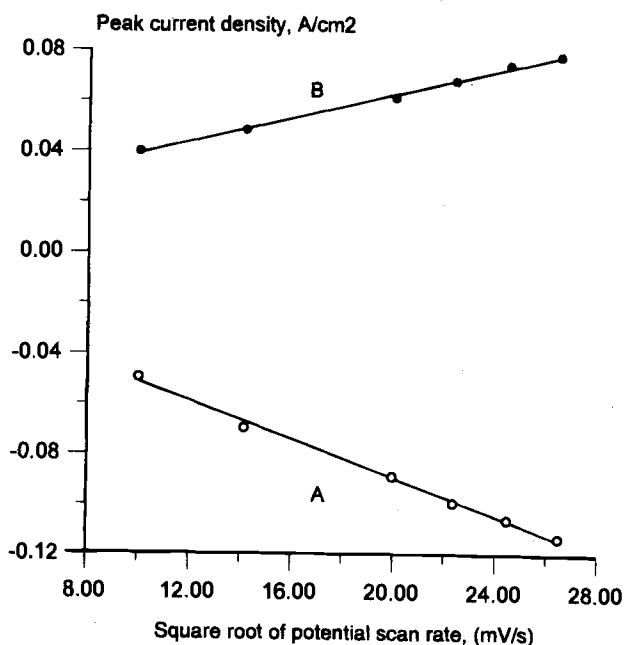


Fig. 11. Peak currents of R_{10} (A) and Ox_{10} (B) waves (Fig. 10) vs. the square root of the potential scan rate.

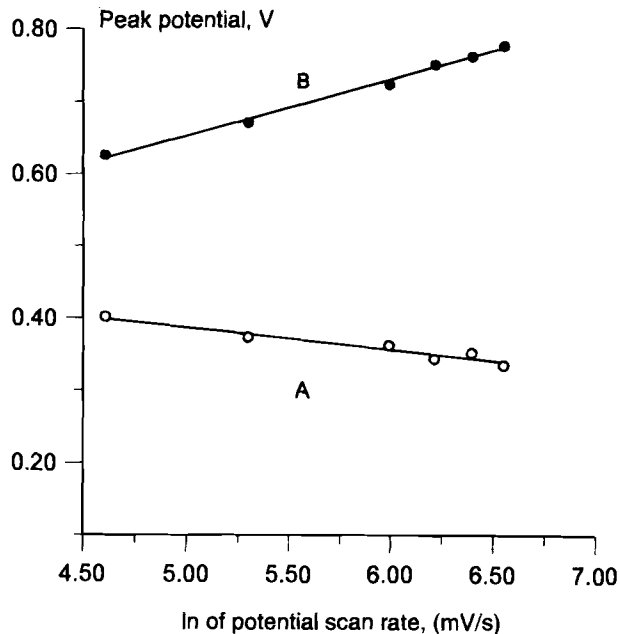


Fig. 12. Peak potentials of R_{10} (A) and Ox_{10} (B) waves (Fig. 10) vs. logarithm of the potential scan rate.

duction. Therefore additional voltammetric measurements were made in molten $K_2S_2O_7$ - V_2O_5 and $K_2S_2O_7$ - $KHSO_4$ - V_2O_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/O_2 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.

The V(IV) → V(V) oxidation kinetics in the “dry” $K_2S_2O_7$ - V_2O_5 changes from slow charge-transfer stage¹ in argon to slow preceding chemical reaction in SO_2/O_2 atmosphere (Fig. 14). Figure 14 (A) demonstrates the well-known voltammetric criterion for the slow preceding chemical reaction mechanism²⁴: oxidation peak potential moves in the negative direction with growth of the potential scan rate. After the addition of water (or $KHSO_4$) the V(IV) → V(V) oxidation kinetics, like in the argon atmosphere, becomes a slow charge-transfer kinetics²⁴ (Fig. 14B). Therefore it is easier to detect the inhibiting water effect on the V(IV) → V(V) oxidation in the SO_2/O_2 atmosphere than in argon atmosphere. Neither the SO_2/O_2 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 $KHSO_4$

Table I. Potential difference between peak and “half-peak” potentials, $E_p - E_{p/2}$, and the number of participating electrons, n_a , for the V(V) → V(IV) and V(IV) → V(V), obtained in molten $K_2S_2O_7$ containing $KHSO_4$ (10 m/o) and V_2O_5 (10 m/o) with Au electrode at 440°C.

Electrochemical wave designation	Potential scan rate (V/s)	$E_p - E_{p/2}$ (V)	n_a
Ox_{10}	0.7	0.23 ₁	0.99
R_{10}	0.7	0.20 ₀	1.14
Ox_{10}	0.5	0.19 ₂	1.19
R_{10}	0.5	0.17 ₆	1.30
Ox_{10}	0.2	0.23 ₁	0.99
R_{10}	0.2	0.16 ₆	1.28
Ox_{10}	0.1	0.22 ₄	1.02
R_{10}	0.1	0.20 ₆	1.10

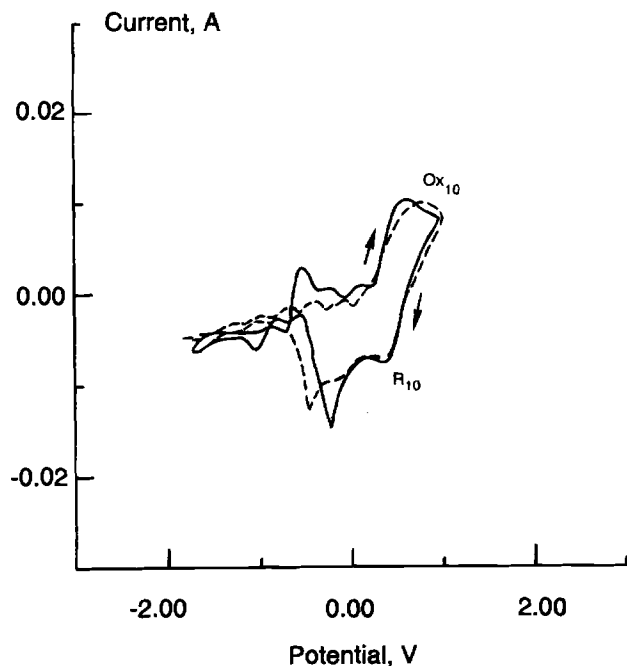


Fig. 13. Voltammetric curves obtained with a gold electrode in molten $K_2S_2O_7$ -10 m/o V_2O_5 (solid line) and molten $K_2S_2O_7$ -10 m/o V_2O_5 -10 m/o $KHSO_4$ (dashed line) at 500 mV/s and 440°C in SO_2 /air atmosphere.

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 $V(IV) \rightarrow V(V)$ oxidation and absence of the effect for the $V(V) \rightarrow V(IV)$ 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_2O_5 was studied in $K_2S_2O_7$ - $KHSO_4$ - V_2O_5 and $K_2S_2O_7$ -

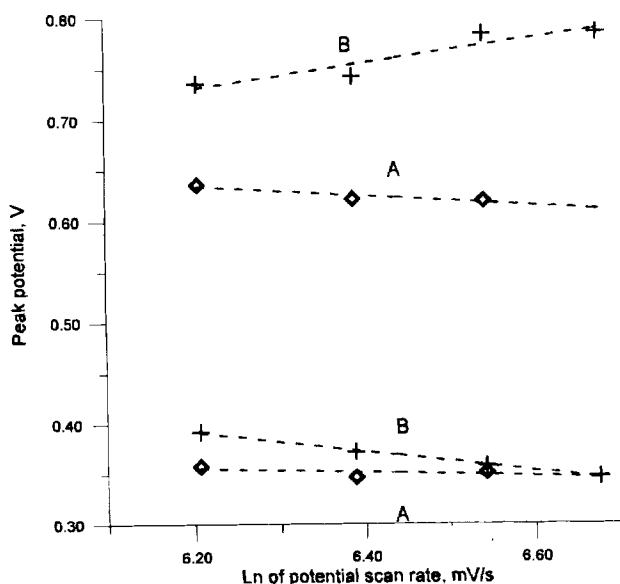


Fig. 14. Peak potentials of the $V(V) \rightarrow V(IV)$ reduction and $V(IV) \rightarrow V(V)$ oxidation voltammetric waves in dependence on the logarithm of the potential scan rate obtained in molten $K_2S_2O_7$ -10 m/o V_2O_5 (A) and molten $K_2S_2O_7$ -10 m/o V_2O_5 -10 m/o $KHSO_4$ (B) at 440°C in SO_2 /air atmosphere.

$KHSO_4$ - V_2O_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 $V(IV) \rightarrow V(III)$ reduction increasing the concentration of $V(III)$ species in the studied electrolytes.

Both reactions, the $V(V) \rightarrow V(IV)$ reduction and the $V(IV) \rightarrow V(V)$ oxidation, remain one-electron electrochemical reactions with increasing concentration of $KHSO_4$ in the molten $K_2S_2O_7$ - $KHSO_4$ - V_2O_5 system. Water has no noticeable effect on the kinetics of the $V(V) \rightarrow V(IV)$ reduction but causes higher polarizations (i.e., inhibition) of the $V(IV) \rightarrow V(V)$ oxidation both in the Ar and SO_2 /air atmospheres.

We conclude that the decreased activity of the V_2O_5 catalyst in the industrial oxidation of SO_2 to sulfuric acid, when the feed gas is moist,²⁹ is due to the increased concentration of the lower valence vanadium ions, $V(III)$ and $V(IV)$, in the $K_2S_2O_7$ melt when water is present (as $KHSO_4$). Similar conditions exist for the removal of SO_2 from industrial flue gases.

Acknowledgments

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REFERENCES

- N. J. Bjerrum, I. M. Petrushina, and R. W. Berg, *This Journal*, **142**, 1805 (1995).
- H. F. Topsøe and A. Nielsen, *Trans. Dan. Acad. Techn. Sci.*, **1**, 18 (1947).
- S. Boghosian, A. Chrissanthopoulos, D. A. Karidis, S. G. Masters, K. M. Eriksen, and R. Fehrmann, Abstract 982, p. 1497, The Electrochemical Society Meeting Abstracts, Vol. 94-1, San Francisco, CA, May 22-27, 1994.
- N. H. Hansen, R. Fehrmann, and N. J. Bjerrum, *Inorg. Chem.*, **21**, 744 (1982).
- R. Fehrmann, N. H. Hansen, and N. J. Bjerrum, *ibid.*, **22**, 4009 (1983).
- M. Frank and J. Winnick, *J. Electroanal. Chem.*, **238**, 163 (1987).
- A. Ben Hadid, G. Picard, and J. Vedel, *ibid.*, **74**, 157 (1976).
- F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., p. 668, John Wiley & Sons, Inc., New York (1988).
- M. Skyllas-Kazakos and F. Grossmith, *This Journal*, **134**, 2950 (1987).
- H. Kaneko, K. Nozaki, Y. Wada, T. Aoki, A. Negishi, and M. Kamimoto, *Electrochim. Acta*, **36**, 1191 (1991).
- R. Fehrmann, B. Krebs, G. N. Papatheodorou, R. W. Berg, and N. J. Bjerrum, *Inorg. Chem.*, **25**, 1571 (1986).
- M. P. Glazyrin, V. N. Krasil'nikov, and A. A. Ivakin, *Zurn. Neorg. Khim. (Russ. J. Inorg. Chem.)*, **27**, 3073 (1982).
- H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 4411 (1962).
- R. J. Gillespie, R. Kapoor, and E. A. Robinson, *Can. J. Chem.*, **44**, 1203 (1966).
- R. C. Paul, J. K. Puri, and K. S. Malhotra, *J. Inorg. Nucl. Chem.*, **33**, 4191 (1971).
- H. A. Videla and A. J. Arvia, *Electrochim. Acta*, **10**, 21 (1965).
- A. J. Arvia, A. J. Calandra, and H. A. Videla, *ibid.*, **10**, 33 (1965).
- D. Gilroy, *ibid.*, **17**, 1771 (1972).
- S. E. Rogers and A. R. Ubbelohde, *Trans. Faraday Soc.*, **46**, 1051 (1950).
- K. M. Eriksen, R. Fehrmann, G. Hatem, M. Gaune-Escard, O. Lapina, and V. M. Mastikhin, in *Proceedings of 9th International Symposium on Molten Salts*, C. S. Hussey, D. S. Newman, G. Mamantov, and Y. Ito, Editors, PV 94-13, p. 124, The Electrochemical Society

- Proceedings Series, Pennington, NJ (1994).
21. S. H. White and U. M. Twardoch, *ibid.*, **134**, 1080 (1987).
 22. B. J. Meehan and S. A. Tariq, *Aust. J. Chem.*, **32**, 1385 (1979).
 23. H. A. Andreasen, N. J. Bjerrum, and C. E. Foverskov, *Rev. Sci. Instrum.*, **48**, 1340 (1977).
 24. *Instrumental Methods in Electrochemistry*, Southampton Electrochemistry Group, pp. 178-227, 380, Ellis Horwood Ltd, New York (1990).
 25. N. J. Bjerrum, I. M. Petrushina, and T. Østvold, To be submitted for publication.
 26. H. Kozłowska, B. Conway, and W. Sharp, *J. Electroanal. Chem.*, **43**, 9 (1973).
 27. D. Dutta and D. Landolt, *This Journal*, **119**, 1320 (1972).
 28. A. Durand, G. Picard, and J. Vedel, *J. Electroanal. Chem.*, **127**, 169 (1981).
 29. S. Boghosian, R. Fehrmann, N. J. Bjerrum, and G. N. Papatheodorou, *J. Catal.*, **119**, 121 (1989).

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.¹⁻¹⁸ 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 atm¹⁹) 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.^{20,21} 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.²² Cook *et al.*²³ and Schwarz *et al.*²⁴ 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.^{23,24} 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 La_{1.8}Sr_{0.2}CuO₄.²⁵ 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).²⁶⁻²⁹ 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 CO₂.³⁰⁻³² 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.³⁰ 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.³³ 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 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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