Electrochemical and spectroscopic investigations of the K2SO4-V2O5 molten electrolyte

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The molten \( \text{K}_2\text{SO}_4/\text{V}_2\text{O}_5 \) system has recently attracted interest due to its possible use as an electrolyte in an electrolytic \( \text{SO}_2 \) flue gas desulfurization process.\(^{1,13}\) For this process to work, a low-melting point electrolyte is required. The eutectic composition 60 mol \% \( \text{K}_2\text{SO}_4/40 \) mol \% \( \text{V}_2\text{O}_5 \) has been reported to melt at 463°C \(^{1,1450}\) or 430°C \(^{8,3}\); it is preferable to the ternary \( (\text{Li}_0.78\text{Na}_{0.085}\text{K}_{0.138})\text{SO}_4 \) eutectic which melts at 512°C.\(^{8}\)

The main discrepancy between the two phase diagrams of the \( \text{K}_2\text{SO}_4-\text{V}_2\text{O}_5 \) system published so far\(^{4,5}\) is the claimed existence of two different compounds, i.e., with the compositions \( \text{V}_2\text{O}_5\text{K}_2\text{SO}_4 \) and \( 5\text{V}_2\text{O}_3\text{K}_3\text{SO}_4 \), respectively, based on powder X-ray data. No reports on the possible vanadium oxide or sulfate complexes formed in the melt are available. Nor has the redox chemistry or compound formation in this system during interaction with flue gas, or any gas, been reported. On the other hand, the \( \text{K}_2\text{SO}_4-\text{V}_2\text{O}_5 \) molten system has been explored extensively (Ref. 7 and references therein) because it is considered to be a realistic model melt of the industrial vanadium oxide-based \( \text{SO}_2 \) oxidation catalyst used for sulfuric acid production.\(^{3,5}\) Here, vanadium (V) oxo sulfate complexes such as \( \text{VO}_2\text{SO}_4 \), \( \text{VO}^2\text{SO}_4 \), \( \text{VO}^3\text{SO}_4 \), and their oligomers appear to be dominant among the melt species present.\(^{7}\)

Recently\(^{10}\) the X-ray structure of the compound \( \text{Cs}_4(\text{VO})_2\text{O}((\text{SO}_4))_4 \) has been clarified, showing dimeric \( \text{VO}_4^{2-} \) units joined by an oxide bridge and achieving hexacoordination by the additional ligands of bidentate-coordinated sulfate groups. A similar structure was found\(^{11}\) for the analogous K and Rb compounds. In melts in contact with \( \text{SO}_2 \)-containing gases, V(V) is partly reduced to V(IV) (Ref. 12 and references therein). Further, VO\(_2\text{SO}_4\) \(_{2}\) units were isolated, as evidenced from infrared and electron spin resonance spectroscopy. These compounds might be involved in the electrochemically observed plating and stripping reactions.

Experimental

We analyzed this complex molten salt eutectic with two basic techniques: cyclic voltammetry was used first to determine the electrochemical activity due likely to the reduction and oxidation of bulk, as opposed to minor, species. Most reductions and oxidations did not conform to diffusion-limited theory, and indicated the presence of stripping reactions. By Raman spectroscopy V(V) polymers were identified in the melt consisting predominantly of \( \text{VO}_2\text{SO}_4\) \(_2\) and \( \text{VO}_2\text{SO}_4\) \(_3\) units, while \( \text{VO}_3\text{SO}_4\) \(_2\) units were also detected. By reduction of the eutectic mixture with \( \text{SO}_2 \), a V(IV) and a V(III) compound, most probably \( \text{K}_2(\text{VO})_2\text{SO}_4\) \(_3\) and \( \text{K}_2\text{V}((\text{SO}_4))_3\), were isolated, as evidenced from infrared and electron spin resonance spectroscopy. These compounds might be involved in the electrochemically observed plating and stripping reactions.

The electrodes and melt were encased in a glass container that protruded from a high-temperature furnace (in-house manufacture) which was maintained at 480°C. This allowed positive atmospheric control as seals could be made at lower temperature.

The potential was controlled by an EG&G PAR model 273 scanning potentiostat/galvanostat with digital IR compensation and a 4 V scanning range. Output was monitored by a Hewlett Packard 7015B X-Y recorder with 200 V maximum floating peak input, optional time and voltage scales, a 50 cm/s slew speed with an overshoot of ≤2% of full scale, and a very low signal/noise ratio. Scans began at the rest potential with respect to the pseudo-reference, and the potential was allowed to return to that rest potential between scans.

The 60 mol \%/40 mol \% \( \text{K}_2\text{SO}_4/\text{V}_2\text{O}_5 \) mixture (450 g total) was prepared by mixing \( \text{K}_2\text{SO}_4 \) (Fisher, dried for 24 h at 250°C in air and kept in a dessicator until used) with \( \text{V}_2\text{O}_5 \) (Sigma, used as received) in the proper weight percentages. This mixture was milled with alumina media for 24 h prior to use.

Gas compositions were controlled by using premixed \( \text{SO}_2/\text{O}_2/\text{N}_2 \) (Matheson) or by mixing 99.99% \( \text{O}_2 \) (Air Products) as needed with Matheson flowmeters. Three gas compositions were used: 100% \( \text{N}_2 \), 50% \( \text{O}_2/50\% \text{~N}_2 \), and 300 ppm \( \text{SO}_2/3\% \text{~O}_2/\text{N}_2 \). Scans were performed with gas flowing over the surface of the melt. Upon changes of atmosphere, gas was allowed to bubble through the melt overnight.

High-temperature Raman spectroscopy.—Sample preparation.—The samples were prepared by mixing \( \text{V}_2\text{O}_5 \) (Cerac, Pure 99.9%) and \( \text{K}_2\text{SO}_4 \) (Fluka) which was dried by heating in vacuo at 300°C for 4 h. All handling of chemicals and filling of the Raman optical cells (made of cylindrical fused silica tubing (6 ± 0.1 mm o.d., 2 ± 0.1 mm i.d., and ~4 cm long for the part containing the molten salts)) took place in a nitrogen-filled glove box. The samples were sealed under a low pressure (ca. 0.2 atm) of \( \text{O}_2 \) (L’Air Liquide, 99.99%) in order to stabilize vanadium in the pentavalent state and were equilibrated at 540°C for up to 7 days before recording the
Raman spectra. Dark red-brown melts were obtained in this way. Sealing the samples under oxygen proved to be critically important for avoiding partial self-reduction of V(V) to V(IV) whereby a gradual color change to dark green and precipitation of crystalline solids would take place.

Raman spectra.—Raman spectra were obtained by exciting with the 647.1 nm line of a Spectra Physics Stabilite model 2017 krypton-ion laser and the 488.0 nm line of a Spectra Physics model 164 argon-ion laser. The scattered light was collected at an angle of 90° (horizontal scattering plane), rotated with a Spex 1403 0.85 m double monochromator possessing a vertical entrance slit and equipped with a −20°C cooled RCA photomultiplier and EG&G/ORTEC rate meter and photon-counting electronics. The optical furnace (suited for recording Raman spectra at temperatures up to 950°C) used and the procedures followed for obtaining Raman spectra at high temperatures have been described in detail elsewhere.14 It should be pointed out here that recording of the Raman spectra at elevated temperatures from these very dark-colored, viscous, and hygroscopic melts was very difficult due to strong absorption of the incident exciting laser light. In certain cases, in order to enable the successful recording of Raman spectra, light reflected and/or dispersed from the walls of the quartz sample containers had to be masked by proper adjustment of the monochromator entrance slit height.

IR and ESR spectroscopy.—The infrared spectra were recorded for samples in KBr on a Perkin Elmer 1710 Fourier transform infrared (FTIR) spectrometer. Electron spin resonance (ESR) spectra were recorded on grounded samples at room temperature in the X-band on a Bruker EMX EPR spectrometer.

Results

Cyclic voltammetry.—A typical stabilized scan in the SO2/O2/N2 environment can be seen in Fig. 1. The first positive scan from rest resulted in peaks I1 and II1. Peak Ic was observed during the next negative scan. After reversing at the negative switching potential, two additional peaks, IIc and IIIc, were observed, followed by a large oxidation peak Ia and smaller oxidation peak IIa. Peaks Ic and IIc were not observed when the first scan was negative from the rest potential, although all other peaks were observed. Scans were generally found to be stable after the first positive scan when initially scanning positive; or, when initially scanning negative, with the first scan.

An unusual reduction is indicated by the presence of peaks IIc and IIIc only on the return scan. Peak Ia appears to be a stripping peak due to its characteristic shape and size. Peak currents (ip) are substantial, exceeding 1 A/cm² in many cases, indicative of reduction and oxidation of readily available species at high concentration.

The dependence of these peaks on one another became apparent when the negative switching potential was allowed to increase while holding the positive switching potential at +2.000 V (vs. pseudo-reference; chosen as a switching potential well positive of observed peaks) and scanning at 500 mV/s. Figure 2 shows stabilized scans for the process, in which the first scan is positive and shows peaks Ia and IIa, and subsequent stable scans. A substantial effect of switching potential and peak dependence can be observed visually with these new scans. This dependence was seen for all atmospheres and is shown here for the SO2/O2/N2 environment. Figure 3 shows the peak potentials (Ep) and current densities with changes in negative switching potential; Fig. 4 shows peak potentials and peak current densities vs. the square root of the scan rate. Peak potentials for I1 and II1 did not vary with the square root of the scan rate. These results are again for the SO2/O2/N2 environment.

Most of the peak currents do not conform to theoretical diffusive limitations (absolute peak current density varying linearly with the square root of scan rate and a positive slope). Incomplete \( iR \) compensation likely contributed to the observed effect, and slow kinetics may also be possible. Finally, the negative switching potential had a strong effect on the peak current density and potential, with \( i_p \) and \( E_p \) increasing with decreases in the negative switching potential for most peaks.

Three peaks did approach diffusion-limited theory: I1, II1, and Ia. The dependence of \( i_p \) on the square root of the scan rate in different atmospheres is shown in Fig. 5, 6, and 7. Of these, the constant

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Figure 1. Typical cyclic voltammogram of a 500 mV/s scan of \( \text{K}_2\text{SO}_4/\text{V}_2\text{O}_5 \) melt at 480°C under 3000 ppm SO2/3% O2/N2 atmosphere on gold electrodes. Reduction current is positive and negative potential is to the right.
potentials of peaks II_1 and I_c with scan rate suggested a reversible mechanism, whereas the variance of I_1 potentials with scan rate suggested an irreversible mechanism. The $E_{p/2}$ values of peak I_c were used to determine approximate values of $n$ using

$$n = \frac{2.2RT}{(E_p - E_{p/2})F} \quad [1]$$

To evaluate $\alpha n$ for peak I_1

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

was used. Peak II_1 could not be satisfactorily evaluated due to the error associated with $E_{p/2}$ measurement of the recorded voltammograms. The results are shown in Table I. Uncompensated IR may introduce a positive error in $n$ of about 3 to 4 mV. Uncompensated impedance arising from thin films at the electrode surface, however, could lower the apparent value of $n$. For these reasons, the actual number for $n$ was deduced to be 1 equiv/mol, and $n_a$ 2 equiv/mol with an $\alpha$ of 0.5.

For peaks II_1 and I_c it is possible to infer the term $C_iD_i^{1/2}$ for each curve using the $n = 1$ equiv/mol determined for peak I_c and assuming a value of $n = 1$ equiv/mol for peak II_1 applying

![Figure 2. Effect of changes of negative switching potential on cyclic voltammograms at 500 mV/s.](image1)

![Figure 3. Peak currents and potentials at varying negative switching potential. Lines denote best linear fit.](image2)
For peak I₁, the $n$ and $a_n$ derived earlier were used with
\[ i_p = 0.4463nFC_i \left( \frac{nF}{RT} \right)^{1/2} v^{1/2} D_i^{1/2} \]  
[3]

to determine $C_i D_i^{1/2}$. These values are listed in Table II.

The small effect of the O₂/N₂ and the larger effect of SO₂/O₂/N₂ in comparison to the N₂ environment was expected. Boreskov\(^\text{15}\) showed that O₂ has a penetration depth of 100-200 Å in sulfate-vanadia melts, whereas SO₂ has a very high apparent solubility, due to possible reactions with the melt. With the electrodes immersed 3 cm, these melt properties became apparent. This also indicates a stronger mechanism dependence on SO₂ than O₂, i.e., an indirect chemical oxidation by oxygen.

To provide further insight into the initial conditions of the melt, the $C_i D_i^{1/2}$ ratios were calculated for peaks I₁ and II₁ in comparison to peak I₂ (see Table III). Assuming peak I₁ represents V(IV) in chemical equilibrium in the melt, it is possible to compare observed concentration ratios with theoretical values. Based on the equation

\[ \Delta G_f^o (750 \text{ K}) = 96.45 \text{ kJ/mol} \]  
[5]

at 477°C and $P_{O_2} = 0.03$ atm, data for $\Delta G_f^o$ from the thermochemical tables of JANAF\(^\text{16}\) predict a ratio of $C_{V_{5+}}/C_{V_{4+}}$ of $9.0 \times 10^3$. While far different from any ratio determined, both show V(V) to be very much the dominant vanadia oxidation state. The difference suggests that composition and interactions in the melt are not ideal.
Because a reversible peak was observed immediately upon moving negative from the rest potential with respect to our pseudo-reference, and a smaller diffusion-limited peak was observed immediately when the potential became positive of the rest potential, it was assumed that the pseudo-reference was resting at the V(V)/V(IV) couple. The additional observations discussed below lend evidence to this assumption.

Raman spectroscopy.—Several binary K$_2$SO$_4$-V$_2$O$_5$ mixtures were placed in cells sealed under 0.2 atm of oxygen and Raman spectra of the melts obtained after equilibration were recorded in the temperature range 450-570$^\circ$C. The data obtained did not indicate any temperature dependence for the relative Raman intensities. The only temperature-dependent feature appears to be the increase of the signal-to-noise ratio in the lower-temperature region. Therefore, data are presented for representative samples at 490$^\circ$C which was the lowest temperature at which all samples studied were in the liquid state. Finally, it should be pointed out that the 647.1 nm excitation used overlaps with the tail of the electronic charge-transfer transition of V(V) and therefore the spectra obtained are very likely to be of preresonance character leading to enhancement of the band intensities due to the V(V) species present.

Figure 8 shows Raman spectra obtained for the molten K$_2$SO$_4$-V$_2$O$_5$ mixtures with compositions X(V$_2$O$_5$)$_x$ = 0.33, 0.40, 0.45, and 0.50 (spectra b-e). Spectra obtained for the molten reference systems V$_2$O$_5$:K$_2$S$_2$O$_7$:2K$_2$SO$_4$ (a) and NaVO$_3$ (f) are also included in Fig. 8 for comparison. The Raman spectrum of the V$_2$O$_5$:K$_2$S$_2$O$_7$:2K$_2$SO$_4$ mixture has previously been assigned$^{17,18}$ to the molten complex species VO$_2$(SO$_4$)$_2$ (presumably occurring as an oligomer of polymer) formed by the reaction

$$V_2O_5 + S_2O_7^{2-} + 2SO_4^{2-} \rightarrow 2VO_2(SO_4)_2^{2-}$$

[6]

The Raman spectra of fused alkali metavanadates have not been published before. The spectra obtained for molten NaVO$_3$ are in fair

<table>
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<tr>
<th>Atmosphere</th>
<th>Peak I$_c$, n, equiv/mol</th>
<th>Peak I$_1$, n, equiv/mol</th>
<th>Peak I$_c$, n, equiv/mol</th>
<th>Peak I$_1$, n, equiv/mol</th>
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<tbody>
<tr>
<td>SO$_2$/O$_2$/N$_2$</td>
<td>0.46 $\pm$ 0.05</td>
<td>0.87 $\pm$ 0.28</td>
<td>0.62 $\pm$ 0.03</td>
<td>0.78 $\pm$ 0.19</td>
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<td>O$_2$/N$_2$</td>
<td>0.38 $\pm$ 0.11</td>
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<td>0.90 $\pm$ 0.02</td>
<td>0.95 $\pm$ 0.14</td>
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<tr>
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<td>0.62 $\pm$ 0.33</td>
<td>0.78 $\pm$ 0.19</td>
<td>0.81 $\pm$ 0.10</td>
<td>0.91 $\pm$ 0.20</td>
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</table>

Table II. Values of $C_iD_i^{1/2}$ for peaks I$_c$, I$_1$, and II$_1$, under different atmospheres.

<table>
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<tr>
<th>Atmosphere</th>
<th>$C_iD_i^{1/2}$ $\times 10^7$, mol/cm$^3$ (cm$^2$/s)$^{1/2}$</th>
<th>$C_iD_i^{1/2}$ $\times 10^7$, mol/cm$^3$ (cm$^2$/s)$^{1/2}$</th>
<th>$C_iD_i^{1/2}$ $\times 10^7$, mol/cm$^3$ (cm$^2$/s)$^{1/2}$</th>
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<tr>
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<td>O$_2$/N$_2$</td>
<td>3.68</td>
<td>O$_2$/N$_2$</td>
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<tr>
<td></td>
<td>N$_2$</td>
<td>3.57</td>
<td>N$_2$</td>
</tr>
<tr>
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<tr>
<td></td>
<td>N$_2$</td>
<td>2.95</td>
<td>N$_2$</td>
</tr>
<tr>
<td>Peak II$_1$</td>
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<td></td>
<td>O$_2$/N$_2$</td>
<td>0.11</td>
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</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>0.18</td>
<td>N$_2$</td>
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agreement with previously reported spectra of “quenched” NaVO₃ melts. The NaVO₃ crystal structure reveals that the compound consists of infinite chains of tetrahedral VO₄ units sharing corners and the same structural model can be adopted for molten NaVO₃. Attempts to obtain Raman spectra for molten KVO₃ failed due to complete absorption of the laser line by the very dark melt. The spectra obtained for molten NaVO₃-Na₂SO₄ mixtures showed no bands due to sulfate groups, indicating that no complex formation occurs between VO₃⁻ and SO₄²⁻. The bands due to free uncoordinated SO₄²⁻ are probably obscured by the VO₃⁻ bands of which the intensities might in turn have been strongly enhanced due to the resonance conditions described above. Excitation of the K₂SO₄-V₂O₅ melts with compositions X(V₂O₅) = 0.33 and 0.40 (spectra b and c) gives rise to characteristic bands at 1043, 982, 875, 670, 605, 489, 450, 362, and 220 cm⁻¹, which are all polarized except for the 220 cm⁻¹ band which is depolarized. This can be interpreted as indicating a low symmetry for the complex(es) formed, but it could also be a result of the preresonance character of the spectra. The spectra appear to consist mainly of superposition of bands due to VO₃⁻(SO₄)²⁻ and VO₃⁻ [spectra (a) and (f), respectively] plus the 982 cm⁻¹ shoulder band and the strong broad band at 875 cm⁻¹, which however is present but much weaker in spectrum (a) of VO₂(SO₄)²⁻. Formation of the VO₂(SO₄)²⁻ and VO₃⁻ units can be accounted for by the reaction

\[ V_2O_5 + 2SO_4^{2-} \rightarrow VO_3(SO_4)_2^{2-} + VO_3^- \]  

An increase in the V₂O₅ mole fraction results in (i) enhancement of the 982 cm⁻¹ shoulder band intensity which is resolved in spectrum (e) of the 1:1 K₂SO₄-V₂O₅ molten mixture and (ii) extreme lowering of the signal-to-noise ratio due to very strong absorption of the excitation line from the dark melt which made the recording of the Raman spectra very difficult. The 1043 cm⁻¹ band is assigned to the terminal stretching of the short V=O involving hexacoordinated vanadium of the VO₂(SO₄)₂⁻ complex unit. The 982 cm⁻¹ band is assigned to terminal V=O stretching involving tetra- or pentacoordinated vanadium of the VO₃⁻ unit which appears to be formed in significant amounts in samples with increasing V₂O₅ contents, where it is stoichiometrically favored over the VO₂(SO₄)²⁻ and formed according to the scheme

\[ V_2O_5 + SO_4^{2-} \rightarrow VO_2SO_4^{2-} + VO_3^- \]  

The 950 cm⁻¹ band contains contributions from terminal S-O stretchings of SO₄²⁻ groups and terminal V-O stretchings of the VO₃⁻ groups where vanadium is also tetracoordinated. The 875 cm⁻¹ band is assigned to bridging S-O stretchings involving oxygen coordinated to vanadium. Detailed assignment of the remaining bands is beyond the scope of the present article.

IR and ESR spectroscopy.—Compounds formed by reduction of the eutectic melt in SO₂ atmosphere have been isolated and characterized. The chemicals of the mol % K₂SO₄/V₂O₅ eutectic mixture were weighed in a glass ampule and sealed under 0.9 atm SO₂. The molar ratio of SO₂ to V₂O₅ was four, making a complete reduction to V(III) possible. The ampule was heated to 600°C in a ceramic tubular furnace for 1 h and then slowly cooled to 100°C during 50 h by a linear temperature program before it was removed from the furnace. The ampule was inspected in a microscope, and small, light-green, bluish green, and black crystals were observed. The light-green crystals could be isolated after opening the ampule whereas the bluish green crystals could not be separated from the black matrix of the solidified eutectic melt. The light-green crystals were too small for single-crystal X-ray investigations, but chemical analysis and IR spectroscopy could be carried out.

The IR spectrum of the compound is displayed in Fig. 9. The spectrum exhibits typical features of coordinated sulfate groups with ν₁ at 980 cm⁻¹ and ν₃ split into three components at 1010, 1140, and 1225 cm⁻¹. The ν₂ and ν₃ bending modes are found below 700 cm⁻¹ as expected. The spectrum is very similar to what has earlier been recorded for the V(III) compound Na₃V(SO₄)₃. Furthermore chemical analysis [atomic absorption spectroscopy (AAS)] of the green crystal showed a molar ratio K/V = 2.92 in close agreement with the expected formula K₃V(SO₄)₃, for the potassium analogue of Na₃V(SO₄)₃.

The ESR spectrum of the bluish green-black matrix mixture is shown in Fig. 10. The spectrum is almost isotropic with g⊥ = 1.968(1) and ΔH∥ = 99(2) G. Because V(V) of the matrix and V(III) of the green compound are ESR silent, these possible contaminants will not interfere with the spectrum of a V(IV) compound. Indeed, the observed spectrum is identical with the spectrum of the V(IV) compound, K₃(VO)₃(SO₄)₃ isolated earlier from K₂S₂O₇-V₂O₅ melts reduced by SO₂.

Discussion

Consider the initial constituents, V₂O₅ and K₂SO₄, and the original molar ratio V/K of charging: 0.80/0.60 or 1.33 (two vanadium ions per 1 mole V₂O₅). The ratio of peak I₁ to that of I₃ averages 1.22. In the SO₂/O₂/N₂ atmosphere, this ratio differed by only 8.3%. If the major component of change is the oxidation state and availability of V(V), and this was the ratio of initially available vanadium to sulfate, this trend would be expected, modified by complex-melt interaction.

The ratio of peak I₁ to II₁ decreased significantly as the atmosphere became more reducing. Peak I₁ relative to that of peak II₁ also

Figure 9. Infrared spectrum of the isolated V(III) compound in KBr.

Figure 10. ESR spectrum of the isolated V(IV) compound. The isotropic g value and the linewidth (ΔH∥) are as indicated.
decreased, but at what was apparently a much faster rate. If it is assumed, as before, that $I_1$ represented initially available V(V), it would be expected that the more reducing the atmosphere, the less V(V) would be available due to greater reduction to lower vanadium oxidation states. An increase in peak $I_1$ combined with a decrease in peak $I_2$ would best explain this significant change in ratios. If peak $I_2$ represented initially available V(IV), the observed trend would comply with expectations.

Equilibrium of vanadium according to

$$V(V) + SO_3^{\text{aq}} \rightleftharpoons V(IV) + SO_4^{\text{aq}} \rightleftharpoons V(III) + SO_3^{\text{aq}} \quad [9]$$

is important using vanadium-based systems. It is generally accepted that vanadium cannot be reduced to V(II) or the metal vanadium in melts containing chlorides, metaphosphates, or sulfates.

The results of the Raman spectroscopic study show that at least three different V(V) species coexist in the 60/40 mol % K$_2$SO$_4$-V$_2$O$_5$ melt. It appears that the predominant complex units formed are the VO$_4^{3-}$ and VO$_2$(SO$_4$)$_2^{3-}$ and that the VO$_2$SO$_4$ unit is also formed to a lesser extent. Increasing amounts of VO$_2$SO$_4$ are found for X(V$_2$O$_5$) > 0.40. Reactions 7 and 8 account for the formation of the above complex units. The VO$_2$SO$_4$ species is most probably polymeric in the molten state as in the crystalline state forming infinite chains of tetrahedral VO$_4$ units sharing corners, Eq. 10.

$$\text{(VO}_2\text{SO}_4)_n^{3n^-} \quad [10]$$

Adding sulfate to the vanadate melt does not appear to affect the VO$_2^-$ chains but dissolves as uncoordinated SO$_3^{2-}$. This is supported by phase studies of the binary KVO$_3$-K$_2$SO$_4$ system which show that no compound is formed. The VO$_2$(SO$_4$)$_2^{3-}$ complex occurs most probably also in the form of polymeric chains and VO$_2$SO$_4$ units in the usual distorted octahedral environment illustrated by

$$\text{(VO}_2\text{O})_n^{2n-} \quad [11]$$

Finally, the VO$_2$SO$_4$ species may similarly form polymeric chains in which the VO$_2$SO$_4$ units are linked by bidentate bridging sulfate groups and possess four-coordinated V(V) in a distorted tetrahedral environment as indicated by recent nuclear magnetic resonance (NMR) studies on molten CsVO$_2$SO$_4$. A simple structural model describing this configuration is depicted by

$$\text{(VO}_2\text{SO}_4)_n^{2n-} \quad [12]$$

It is evident that mixed copolymeric chains may be also formed consisting of the three complex units. It should be pointed out that the relative positions of the V=O stretching modes for the three complex units VO$_2$(SO$_4$)$_2^{3-}$, VO$_2$SO$_4^-$, and VO$_2$ at 1043, 982, and 950 cm$^{-1}$ is in conformity with the respective coordination numbers for the vanadium atom 6, 4, and 4 discussed above. It is known as a general hard-and-fast rule that the V=O bond length is significantly shorter in VO$_2$ rather than in VO$_4$ environments whereby a higher V=O stretching frequency is expected for the former in the Raman spectrum. Furthermore the values of 982 and 950 cm$^{-1}$ for the tetracoordinated V(V) species indicate a shorter V=O bond for VO$_2$(SO$_4$)$_2^{3-}$ and a more uniform environment around vanadium in VO$_2$(SO$_4$)$_2^{3-}$.

Reduction of the possible V(V) entities to V(IV) may take place by the following electrode processes

$$\text{VO}_2^- + \text{SO}_3^{2-} + e^- \rightleftharpoons \text{VOSO}_4 + 2 \text{O}^{2-} \quad [13]$$

$$\text{VO}_2\text{SO}_4^- + e^- \rightleftharpoons \text{VOSO}_4 + \text{O}^{2-} \quad [14]$$

$$\text{VO}_2\text{(SO}_4)_2^{3-} + e^- \rightleftharpoons \text{VO}(\text{SO}_4)_2^{2-} + \text{O}^{2-} \quad [15]$$

These three reductions of V(V) may all occur at nearly the same potential, i.e., corresponding to peak $I_1$ at ~0.7 V, overlapping each other on the scan; or alternatively, one of the reactions, probably Eq. 13, may be so dominant that the others are hidden.

Work by Franke and Winnick, and Bazavara et al. proposed the following reduction of vanadium

$$[\text{K}_2\text{O-V}_2\text{O}_5\cdot4\text{SO}_3] + 2\text{e}^- \rightleftharpoons [\text{K}_2\text{O-V}_2\text{O}_4\cdot3\text{SO}_3] + \text{SO}_4^{2-} \quad [16]$$

occurring at approximately $E_p = +0.7$ V vs. Ag/Ag$^+$ in pyrosulfate melts. The number of electrons involved in the V(V) reduction varied from one to two depending on the gas composition. Other electrochemical studies of Durand and Bjerrum in pyrosulfate melts showed the reduction to be a one-electron reaction as in the present study in sulfates. However, the polymeric vanadium (V) complexes present in the 60% K$_2$SO$_4$-40% V$_2$O$_5$ melt investigated here differ from the predominantly dimeric V(V) species found in pyrosulfate melts up to 33% V$_2$O$_5$. Therefore, the redox processes taking place in the different media may be fundamentally different. Voltammetric investigations of Dojcimovic and others showed vanadium reduction to a mixed state in a LiCl/KCl melt as 6V$_2$O$_5$ + 2Li$^+$ + 4e$^- \rightleftharpoons Li_2O + 2V_2O_4 + 4V_2O_3 + O^{2-} \quad [17]$

with the reduction of V(V) to V(IV) at ~0.6 V vs. Ptv/Pvt$^+$ reference. With the one-electron process, peak $I_1$ is very likely the reduction of vanadium.

Peak $I_2$ represents additional reduction of V(V). As scanning slowed, peak $I_2$ and III, current increased, while peak $I_c$ showed a relatively linear fit with $1/n$. Peaks $I_2$ and III, were not dependent on diffusion; they were effectively nonexistent initially. They did depend on the fact that V(V) was first reduced at peak $I_c$. As the switching potential neared the peak potential for peak $I_c$, peaks lc and II, overlapped, suggesting that they are identical reactions.

Because the VOSO$_3$ formed initially, by reduction on the cathode (Eq. 13 and 14), is able to react with SO$_4^{2-}$ of the solvent, the actual compound precipitating might be K$_2$(VO$_2$SO$_4$)$_3$ that was formed by reduction of the eutectic with SO$_2$ (see previous section). Formation of the V(III) salt K$_2$V(SO$_3$)$_3$ could take place through the following reactions

$$\text{VOSO}_4 + \text{SO}_4^{2-} \rightleftharpoons \text{VO}(\text{SO}_4)_2^{3-} \quad [18]$$

$$\text{VO}(\text{SO}_4)_2^{3-} + 2\text{e}^- \rightleftharpoons \text{V}(\text{SO}_4)_2^{2-} + \text{O}^{2-} \quad [19]$$

$$3\text{K}^+ + \text{V}(\text{SO}_4)_2^{2-} + 2\text{SO}_4^{2-} \rightleftharpoons \text{K}_2\text{V}(\text{SO}_3)_3 \quad [20]$$

As V(IV), e.g., as K$_2$(VO$_2$SO$_4$)$_3$, or VOSO$_3$ is only partially soluble, and V(III), e.g., as K$_2$V(SO$_3$)$_3$ has a very low solubility, peak potential shifts were due to uncompensated plating on the electrode surface. Peak heights would be expected to increase if this solidification occurred. Previously presented melting curves showed a relatively conductive solid. If a conductive solid deposited on the electrode, the effective electrode area would increase, resulting in an apparent current increase. Theoretically the current density would be identical while the apparent current density increases.

Consideration of the large stripping peak $I_1$ supports these analogies. The height and size of this oxidation peak were directly dependent on reduction levels. As more coulombs were passed at potentials greater than $E_p(I_1)$, currents were observed to rise. If species were being reduced as proposed and plating on the electrode, a stripping peak would be expected. In addition, the peak $I_2$ potential was near the peak $I_c$ potential, supporting the argument that both repre-
sent oxidation of vanadia; peak II of V(IV) and peak I of V(IV) and V(III) formed at peaks I, II, and III.

Peak II is presumed to be the oxidation of available sulfate according to

\[
SO_4^{2-} + 2e^- + \frac{1}{2} O_2 \rightarrow SO_3 + \text{O}_2
\]

which has been proposed by Franke and Winnick, and found to exist 0.5 V from the vanadium redox couple they explored. In addition, E° between this sulfate oxidation and the V(V) reduction was estimated using JANAF thermochemical ΔG° data to be −2.344 at 700 K for a sulfate melts without compensation for Nernstian effects. Further, as the negative shifting potential was increased, peak II became peak I, suggesting it was an identical reaction. This proof in combination with I analysis and the n = 2 equiv/mol determined earlier left little doubt that peak II represented sulfate oxidation.

The change in height of peak II after reduction occurs is explained by the coordination ability of vanadium. As vanadium is reduced, less sulfate (or oxide) can complex per single vanadium, evidenced by the reactions presented above. This would free sulfate (or oxide) for oxidation, thereby increasing peak II currents, as well as shift peak potential due to concentration changes, both of which were observed. Bubbling was not readily observable due to the opaque melt and apparent viscosity. Any SO₃ produced would be effectively adsorbed by the melt.

Knowledge of the pseudo-reference was also gained through these experiments. Based on arguments presented above and potential analysis, the pseudo-reference is probably schematically represented by the reaction V(V) + e⁻ → V(V) in the SO₂/O₂/N₂ atmosphere used at the reference electrode, due to the relative proximity of vanadia couples and sulfate oxidation peaks. Further, its potential is defined by the (reference) gas composition, which will set the V(V) of V(V) equilibrium. Even large changes in the bulk electrolyte, from which the reference electrode is isolated, will have little to no effect on the reference. The proposed reactions for the observed peaks are shown in Table IV.

It is important to note every reduction of vanadium shown results in the formation of an oxide ion, enhancing SO₃ removal. It can be concluded on the whole that the extremely large peak currents indicate high electrochemical activity of the melt, probably due to electrochemical utilization of V(V) and SO₄²⁻. Any limit in this melt must therefore be due to mass transfer of these bulk species.

It is not possible to determine directly the concentration of the active species from estimates of diffusivities which vary widely, if the active species had been studied. In an aluminate melt, V(V) was reported to have diffusivities of 3.7 × 10⁻⁷ cm²/s at 1370°C and 2.1 × 10⁻⁸ cm²/s at 1460°C. V(V) was also reported to have a diffusivity of 5.9 × 10⁻⁸ cm²/s in phosphoric acid. In a LiCl/KCl melt at 450°C Scrosati and Laithin reported the diffusivity of V(V) as 2.68 × 10⁻⁵ cm²/s. In a K₂SO₄/V₂O₅ melt, V(V) was reported to have a diffusivity of 2 × 10⁻⁶ cm²/s at 400°C. However, the concentration of K₂SO₄ and V₂O₅ can be estimated in the melt if ideal mixing and similarity between liquid and solid densities are assumed. Total density was evaluated using

\[
\frac{1}{\rho} = \frac{1}{\rho_i} \sum (\text{wt} \%)_i
\]

as suggested by Reid et al.

An effective concentration of sulfate (as K₂SO₄) was calculated as C_{K₂SO₄} = 9.85 × 10⁻³ mol/cm³ and an effective concentration of V(V) (as V₂O₅) was calculated as C_{V₂O₅} = 6.56 × 10⁻³ mol/cm³. Using these values of concentration, the previously obtained values of CD₂/³ shown in Table II could be used to determine diffusivity, listed in Table V. The very low diffusivities emphasize the nonidealties in the melt, suggesting strong species interaction.

### Conclusions

The low-melting mixtures of V₂O₅ with K₂SO₄ allow facile reduction of the V(V) to V(IV) in oligomeric form with the concurrent release of oxide ions (O²⁻). Further reduction to V(III) is possible, with further oxide production. The V(III) compounds are highly insoluble in the melt, however. The oxide ions are readily neutralized by available dissolved SO₃, forming sulfate ions. Vanadium ions in the oxidation states III or IV are reoxidized to V(V) electrochemically, well positive of the potential necessary for sulfate oxidation. These results indicate that this melt will indeed be a good choice for the electrochemical membrane electrolyte: the SO₃ present in the flue gas will be readily neutralized at the cathode by oxide ions in the membrane. The V(V) and V(III) is chemically oxidized back to V(V), and so is available again for electrochemical reduction.

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