New molten salt electrolytes have been designed and tested for their application as electrolytes in an electrochemical membrane used for removal of SO₂ from power plant off-gases. The melts exhibit good thermodynamic stabilities in the electrochemical environment. Polarizations during full cell tests are quite low compared to previous investigations. However, gas analysis tests performed during measurements of removal performance combined with electroanalytical investigations of the polarization behavior during galvanostatic tests show that these types of removal devices need improvement of cathodic interface area, since current efficiency decreases when the supply of reactants is limited. These observations suggest that a new optimized cathode pore structure for optimal cathodic interfacial area must be developed.

INTRODUCTION

The conventional process for removal of SO₂ from flue gas from fossil based power plants, the limestone process, is a cost heavy installation, which produces large amounts of gypsum. This either has to be deposited or further processed into a mediocre quality gypsum. Compared to this, the estimated operation costs of an electrochemical membrane process running at 250 A/m² with a full cell polarization of 0.5-1.0 Volt will only require 10-30% of the running costs of the limestone process.¹ Installation investments for the two processes are comparable. Furthermore, the membrane process produces oleum or sulfuric acid in high purity, which can be sold directly or if preferred, reacted with the lime or limestone to produce high quality gypsum.

The membrane process is designed like the molten carbonate fuel cell (MCFC) but is using a SO₄²⁻/S₂O₇²⁻ based molten salt electrolyte instead of CO₃²⁻. This gives the obvious advantage that the scale-up technology from the MCFC development experiences can be reused for the flue gas cleaning membrane process. Compared to an MCFC fuel cell, which easily runs with > 5000 A/m², the technical goal of reaching the 250 A/m² milestone for the sulfate membrane process might seem easy to overcome.
Figure 1: Principal schemes of the MCFC and SO2 removal cell. Note that the main difference is the fact that the MCFC unit produces electricity, while the SO2 process requires an applied electric field in order to work.

Figure 1 illustrates the similarities and differences between the two mentioned processes. The change in electrolyte, combined with the decrease in operating temperature (the SO2 removal process is aimed at working at 380-450°C) introduces several difficulties with respect to mass transfer and possible electrochemical side reactions.2

For a sulfate based electrolyte, Schmidt and Winnick have proposed the following overall electrochemical pathway for SO3 removal:3

\[
\text{Cathode: } \frac{1}{2}O_2 + 2e^- \rightarrow O_2^-
\]

\[
\text{Electrolyte/cathode interface: } SO_3 + O_2^2- \rightarrow SO_4^{2-}
\]

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

A set of reaction schemes which were supported by early fundamental research on the Li2SO4-Na2SO4-K2SO4-system,4 indeed seems to fit well to general electrolytic chemistry of oxo-anion melts. Franke and Winnick1,5 used mixtures of V2O5 and K2S2O7 as electrolytic media, and they found that the change in chemical environment combined with the lower temperature of operation, changed the removal pathway into:

\[
\text{Cathode: } 2S_2O_7^{2-} + 2e^- \rightarrow 3SO_4^{2-} + SO_2
\]

\[
\text{Electrolyte: } SO_4^{2-} + SO_2 + \frac{1}{2}O_2 \rightarrow S_2O_7^{2-}
\]

\[
\text{Electrolyte/cathode interface: } SO_3 + SO_4^{2-} \rightarrow S_2O_7^{2-}
\]
Anode: \[ \text{SO}_4^{2-} + \text{V}_2\text{O}_2^{+} + 2e^- \rightarrow \text{SO}_3 + \frac{1}{2}\text{O}_2 \]  

This agrees well with results obtained by Durand et al.\textsuperscript{6} and Bjerrum et al.\textsuperscript{7} Since \( \text{SO}_2 \) was generated inside the membrane, in the electrolyte, an addition of 1 wt \% \( \text{V}_2\text{O}_5 \) to the \( \text{K}_2\text{S}_2\text{O}_7 \)-based melt was done in order to supply the electrolyte with catalytic activity for in-situ re-oxidation of formed \( \text{SO}_2 \). This process ran successfully at temperatures lower than 400\textdegree C, as long as \( \text{SO}_3 \) was fed to the cathode compartment instead of as supplied from the power plant off-gas - \( \text{SO}_2 \) and \( \text{O}_2 \). Thus, in both cases, a pre-oxidation step, with a catalytic reactor transforming

\[ \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3 \]  

was necessary. This step introduces some extra technical and economical difficulties, since this is another chemical engineering unit, with extra economic costs and potential economic hazard. Therefore, this step is going to be integrated in the state of the art electrochemical removal device, to make it a viable alternative to the current removal processes. The electrolyte system to be used in this cell, is quite similar to the relatively well known industrial supported-liquid-phase catalyst for \( \text{SO}_2 \) oxidation. This system is known to have a complex chemistry\textsuperscript{8,9}, further complicated by adding electrochemical steps. When \( \text{V}_2\text{O}_3 \) is added to a \( \text{M}_2\text{S}_2\text{O}_7/\text{M}_2\text{SO}_4 \) (\( \text{M} = \text{Li, Na, K, Rb, Cs} \)) melt it dissolves through the reaction:

\[ \text{V}_2\text{O}_3 + 2\text{S}_2\text{O}_7^{2-} \rightarrow (\text{VO})_2\text{O}(\text{SO}_4)_4^{4+} \]  

followed by sulphate coordination, depending on the vanadium and sulphate activity:

\[ (\text{VO})_2\text{O}(\text{SO}_4)_4^{4+} + 2\text{SO}_4^{2-} \rightarrow 2\text{VO}_3(\text{SO}_4)_2^{3+} + \text{S}_2\text{O}_7^{2-} \]  

while \( \text{SO}_2 \) will reduce the \( \text{V}(\text{V}) \) species in equations 9 and 10, e.g.:

\[ (\text{VO})_2\text{O}(\text{SO}_4)_4^{4+} + \text{SO}_2 \rightarrow 2\text{VO}_3(\text{SO}_4)_2^{2+} + \text{SO}_3 \]  

in a \( p(\text{SO}_2)/p(\text{SO}_3) \) dependent equilibrium. Schmidt et al.\textsuperscript{10} investigated the electrolysis and the complex chemistry of the \( \text{K}_2\text{SO}_4-\text{V}_2\text{O}_5 \) system at 480\textdegree C, and found the formation of different chemical species compared to the pyrosulfate based system. \( \text{V}_2\text{O}_3 \) dissolves in molten potassium sulfate according to:

\[ n\text{V}_2\text{O}_3 + 2n\text{K}_2\text{SO}_4 \rightarrow (\text{VO}_3)_n + (\text{VO}_2(\text{SO}_4)_2^{3+})_n + 4n\text{K}^+ \]  

where \( n \) is an integer, and here denotes the extent of polymeric oxo vanadium species formed.

**EXPERIMENTAL**

**Materials**

Preparation of the molten salt: The electrolyte was mixed from pure, dry potassium pyrosulfate, synthesized in laboratory as previously described\textsuperscript{11} from \( \text{K}_2\text{S}_2\text{O}_8 \).
K₂S₂O₈ and V₂O₅. Cs₂SO₄, K₂SO₄, Li₂SO₄ and Na₂SO₄ were analytical grade from Merck. The electrolyte composition was found by a decanting procedure, which was chosen in order to obtain a mixture with high solubility of sulfate, vanadium while still maintaining a reasonable good SO₂ oxidation catalyst. First the eutectic mixture of K₂SO₄ and V₂O₅ (40%:60%) was mixed in the ratio 1:1 with the ternary sulfate (Li, Na, K)₂SO₄ eutectic and fused at 700°C. Hereafter, the melt was cooled to 510°C within 8 hours. Large parts of the salt had now solidified, but some remaining drops of liquid were decanted and analyzed. The resulting low melting sulfate-vanadia mixture was then mixed further with a (K₂S₂O₇)₅V₂O₅ salt, in order to obtain even lower temperature of fusion of the melt, and hereby at the same time ensuring a proper alkali metal composition with respect to catalytic capabilities.

Performance testing. Housings for bench scale testing of removal performance were made from machined 316 stainless steel. The two identical housings had 8 or 20 cm² circular wells for electrodes and gas channels to provide baffled gas flow to the electrode. The electronically-conductive housings also served as current collectors.

The pieces were assembled with electrodes in the wells and the ceramic matrix sandwiched between the two housings. The top housing has a hole drilled in it for possible use of a reference electrode and could also be used if electrolyte addition was necessary. The assembled cell was placed in a brick furnace, and the temperature was controlled with a Barber-Coleman Model 122B controller connected to a double-pole solenoid which controlled the temperature within ±2°C. A PAR 173 potentiostat/galvanostat was used to control current applied to the cell. Cell potentials were monitored both on the LCD display on the potentiostat/galvanostat and by Simpson 460 multimeters. Simulated flue gas with the composition 0.3% SO₂, 5% O₂, ~ N₂ provided by Air-Gas was fed to the compartment containing the cathode, while N₂ from Air Products was fed to the anode side as purge gas. Analysis of SO₂ content was performed with a Perkin Elmer AutoSystem XL gas chromatograph, equipped with a Supelco 60/80 Chromosorb 102 2×1/8" column and a Flame Photometric Detector (FPD) which conveniently only monitored sulfur species, thus eliminating possible separation problems of effluents. SO₃ concentrations were determined by absorbing the effluent in de-ionized water followed by pH measurements, following a procedure developed by Franke. Any positive error in reading due to partial absorption of SO₂ in the sample was regarded as insignificant.

RESULTS AND DISCUSSION

The purpose of this work is to test the removal performance for this new molten salt electrolyte mixture. This is done by measuring the SO₂ and SOₓ (SO₂ + SO₃) concentrations of the outlet from the cathode chamber (flue gas side of the membrane) at steady state at different current densities. This can then be calculated as moles SO₂ removed as a function of Faradays of electrons supplied according to the equation:

$$N(SO_x) = \frac{i}{2F}$$  \[13\]

Where N(SOₓ) is the flux of sulfur oxides originating from SO₂ in the flue gas through the membrane. The removal performances at various temperatures is observed in Figure...
where it is seen that at low current densities the outlet \( SO_X \) levels as a function of current density corresponds quite well to a 2 electron process with 100% current efficiency. In fact, formally the current efficiencies exceed 100% compared to the inlet \( SO_2 \) content of 2800 ppm. This effect is increasing with temperature and is ascribed to a chemical zero current removal mechanism. This mechanism can be explained by a number of chemical reactions, given here with the cathodic reaction going from the left to the right:

\[
2SO_2 + O_2 \leftrightarrow 2SO_3 \quad [14] \\
SO_3 + 2V^{IV}_2O(SO_4)_3^{4-} \leftrightarrow SO_2 + 2V^{V}_2O_2(SO_4)_2^{3-} + S_2O_7^{2-} \quad [15] \\
SO_3 + 2V^{V}_2O_2(SO_4)_2^{3-} \leftrightarrow (V^{V}_2O_2O(SO_4)_4^{4-} + SO_4^{2-} \quad [16] \\
SO_3 + SO_4^{2-} \leftrightarrow S_2O_7^{2-} \quad [17]
\]

Equations 15-17 will occur spontaneously in the reverse direction at the anode, when a sweep gas going through the chamber continuously carries away gaseous \( SO_3 \). The last point of each data series in Figure 2 corresponds to the highest point where 100% current efficiency was observed. At higher current densities datapoints deviated from this removal mechanism, in such a way that higher \( SO_X \) levels than expected were observed. These datapoints are not shown here for clarity reasons. This effect seems to be a change in the electrochemical reaction mechanism, where the new mechanism doesn’t involve or precede the uptake, or release, of gaseous \( SO_X \) components – at least not at any significant level. This hypothesis was supported by observing that a further increase in applied current density up to 250 A/m\(^2\) at 470°C had no effect on the output level of \( SO_X \), which would stay at a constant level of around 30% removal. Increasing temperatures, as seen in Figure 1a and 1b, didn’t have significant effect on the first \( SO_2 \) oxidation step (1a), but the apparent zero current removal mechanism benefited significant from this. Furthermore, the threshold value of the current density where the unwanted change in cathodic electrochemical mechanism decreases with increases temperature. This leads to the observation that the side-reaction, which will be further discussed below, apparently, becomes more dominant at elevated temperatures. Therefore, a lower temperature of operation, which is also better from an economical and practical point of view, would be preferable from a selectivity point of view. This will of course be at the expense of “free” zero current removal, and will therefore indeed require 2 electrons for each \( SO_2 \) molecule removed.

Figure 3 shows polarizations required for for running the electrochemical cell galvanostatically. Figure 1a shows anodic and cathodic polarizations at 470°C. The polarization behaviour can be modelled by the solid lines in Figure 1b, using the Butler-Volmer equations. For the cathodic reaction parameters of \( \eta_{n} = 37.8 \text{ A/m}^2 \) with \( \alpha_{c,\text{cathodic chamber}} = 0.74 \) describes the behaviour and for the anodic reaction the parameters are of \( \eta_{n} = 16.7 \text{ A/m}^2 \) with \( \alpha_{c,\text{cathodic chamber}} = 0.32 \). In this work, these parameters should be considered merely a guidance for the electrochemistry discussed here. A paper with more thorough treatment of this type of data for this system is in progress. Compared to earlier studies with other electrolytes\(^{13,15}\) the polarizations observed here are quite low. We believe that this is because this electrolyte molten salt mixture is designed in such a way that the minor changes in the chemical environment due to the applied electric field doesn’t have any severe influence in solubilities of any sulfate or vanadia species. In earlier work, solid depositions in the cathode of sulfate and/or vanadia species have been observed. Polarizations in the present range does in fact present a viable economic
outlook with this membrane process, given of course, that the selectivity issues mentioned above are solved.

Figure 2: a) SO$_2$ emission levels as a function of galvanostatically applied current in a 20 cm$^2$ full cell arrangement at steady state conditions at various temperatures. b) SO$_X$ emission levels at same conditions as a. The linear fits correspond to a line calculated from zero current outlet level of SO$_X$ and assuming a 2 electron removal mechanism for the removal cell. The flow rate to the cathodic chamber is 310 ml/min, and a N$_2$ sweep gas at a flow rate of 60 ml/min was led through the anodic reaction chamber.

The chemistry of the 2 electron removal pathway in this electrolyte melt and the competitive side reactions is best explained by the following overall cathodic reaction:

Electrochemical reduction of vanadia species:

$$2V^V (SO_4)_{2-}^{3-} + 2e^- + 2S_2O_7^{2-} \leftrightarrow 2V^{IV}(SO_4)^{4+} + 2SO_4^{2-}$$  \[18\]

This is likely to be the key cathodic reaction and the chemical environment near the cathode electrolyte interface will then decide if the removal mechanism will work as expected or undergo side reactions which will alter the chemical nature of the electrolyte.
If the cell is working well, $\text{SO}_3$ will be readily available from Equation 14, which will combine with the product of the cathodic reaction:

$$\text{SO}_3 + 2\text{V}^{IV}(\text{SO}_4)_3^{4-} \Leftrightarrow \text{SO}_2 + 2\text{V}^{V}(\text{SO}_4)_2^{3-} + \text{S}_2\text{O}_7^{2-}$$ \[19\]

Where the produced $\text{SO}_2$ is formally cancelled out with the second oxidation in Equation 14. In this case the anodic reaction will probably proceed via one or several of the following reactions:

$$2\text{SO}_2^{2-} \Leftrightarrow 2\text{SO}_3 + \text{O}_2 + 4\text{e}^-$$ \[20\]

$$2\text{S}_2\text{O}_7^{2-} \Leftrightarrow 4\text{SO}_3 + \text{O}_2 + 4\text{e}^-$$ \[21\]

$$2(\text{VO})_2\text{O}(\text{SO}_4)_4^{4-} + 4\text{SO}_4^{2-} \Leftrightarrow 4\text{VO}_2(\text{SO}_4)_2^{3-} + \text{O}_2 + 2\text{SO}_3 + 4\text{e}^-$$ \[22\]

$$2\text{VO}_2(\text{SO}_4)_2^{3-} \Leftrightarrow 2\text{VO}_3^- + \text{O}_2 + 4\text{SO}_3 + 4\text{e}^-$$ \[23\]

It is observed that all reactions follow the rule that 2 electrons need to take part in order to release one molecule of $\text{SO}_3$. When using this reaction scheme, possible side reactions would most likely occur because of insufficient mass transfer of $\text{SO}_3$ into the melt. At higher current densities, this would mean that the cathodic reaction product from Equation 18 wouldn’t react with $\text{SO}_3$, but instead be allowed to migrate to the anode and react as:

$$2\text{SO}_4^{2-} + 2\text{V}^{IV}(\text{SO}_4)_3^{4-} \Leftrightarrow 2\text{V}^{V}(\text{SO}_4)_2^{3-} + 2\text{e}^- + 2\text{S}_2\text{O}_7^{2-}$$ \[24\]

Which is the reverse reaction of Equation 18. The result will then be that the electric field only is used for removing $\text{V}(IV)$ and $\text{V}(V)$ species back and forth in the membrane with no net result. Figure 4, showing polarization behavior with time backs this explanation well. After the electric field is introduced the anodic polarization is significantly higher.
than the cathodic. This is because of the rather high overpotential required\textsuperscript{5,6,7} to oxidize $\text{S}_2\text{O}_7^{2-}$ as part of the chemical reactions suggested in Equations 20 - 23.

![Figure 4: Polarization data at 90 A/m\textsuperscript{2}, corresponding to 90% of current needed stoichometrically to remove 2700 ppm SO\textsubscript{2} entirely from the flue gas side. Left) Long term behaviour. Right) Detailed short term behavior.](image)

However, since the V(IV) species formed in Equation 24 is continuously produced at the cathode, and migrates towards the anode, the concentration of the electroactive V(IV) is increasing at the anode. Since the $E^0$ of the V(V)-V(IV) redox equilibrium is expected to be around 0 Volt\textsuperscript{5,6}, the decrease of anodic polarization over time in Figure 4 is a result in a Nernstian influence due to the change in the composition of the electrolyte.

**CONCLUSIONS**

A new electrolyte candidate for use in the electrochemical cell for sulfur oxide removal from flue gas has been developed. The thermodynamic properties of the molten salt makes it a well suited salt mixture for this process with respect to expected polarization behaviour of the cell, and thus the general economic perspective. Gas removal analysis combined with observations of polarization behaviour has been used to deduce the mechanistic steps in the electrochemical pathway of this electrolyte. Furthermore, the most likely explanation of the loss of current efficiency has been given. The results suggest that the electrolyte itself, seems to be a suitable candidate, with proper catalytic capacity, and with an unknown chemical robustness towards possible side reactions in the melt. However, since a significant deviation from 100% current efficiency is observed around above 20 A/m\textsuperscript{2}, the conclusion must be that the electrochemical system is unable to carry SO\textsubscript{3} across the gas liquid interface at a significant rate. Therefore, future work will have to focus on a critical matching of the pore structures of the ceramic components - with special attention to the wetting capabilities and surface area of the cathode.
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