New Vanadium-Sulfate-Pyrosulfate Mixed Electrolytes For Electrochemical Removal of Sulfur Oxide.

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An electrochemical cell with a catalytically active electrolyte is being developed for removal of sulfur oxides from flue gasses. Earlier measurements[1] have shown the need for a molten salt electrolyte with exceptional physiochemical stability in the temperature range 380-500°C. Demands for a working electrolyte are:

- Thermodynamically stable as liquid in the temperature range 380-600°C.
- Catalytically active for oxidation of SO_2.
- High affinity for absorption of SO_3.
- Non corrosive for stainless steel housings, ceramic electrodes and separator.

The mixture $[(Li_{0.04}Na_{0.26}K_{0.64}Cs_{0.067})_2S_{1.5}O_{5.5}]_5V_2O_5$ was found as a reasonable candidate with a melting point below 380°C and thermodynamically stable >600°C. Bench scale test of this new electrolyte candidate was performed in a stainless steel cell house with 20 cm^2 Li_XNiO electrodes and porous YSZ as separator matrix. In Figure 1 the outlet amount of SO_X from the cell is seen. At low current densities the removal rate follows the predicted Faradaic value, indicating 100% current efficiency. At approx. 2.25 mA/cm^2 (50 mA) a deviation from this is observed, and the current efficiency decreases to around 30%.

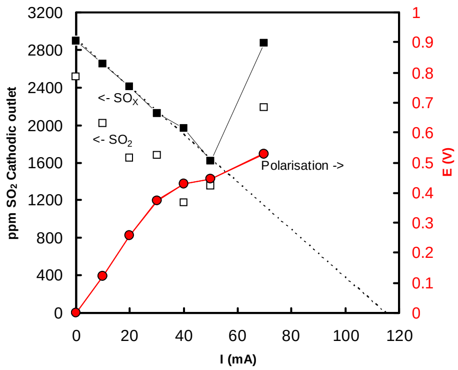

Figure 1: *Removal performance of the electrochemical cell with 310 ml/min 0.27% SO_2, 4.8% O_2, 10% H_2O, ~ N_2 going through the cathodic chamber. 80 ml/min N_2 through the anodic chamber. The dotted line indicates theoretical removal of SO_X, at 100% current efficiency.*

This behaviour is similar to earlier observed[1] for other electrolytes tested without a pre SO_2 oxidation step. One major difference was observed here compared to earlier. The polarizations of the cell during performance testing were generally much lower with this new electrolyte, providing a better economical perspective. Usually a deviation from 100% current efficiency with this type of cell is caused by a limiting current probably originating from a the lack of intermediate SO_3. The reason for this can be either poor catalytic oxidation of SO_2 or poor absorption efficiency of the electrolyte melt. However, in this case no dramatic increase in polarization was observed at the threshold point, making the chemistry more complicated. Figure 2 shows the polarization behavior over time at 100 mA (90% current compared to stoichiometric removal of SO_X at 100% efficiency).

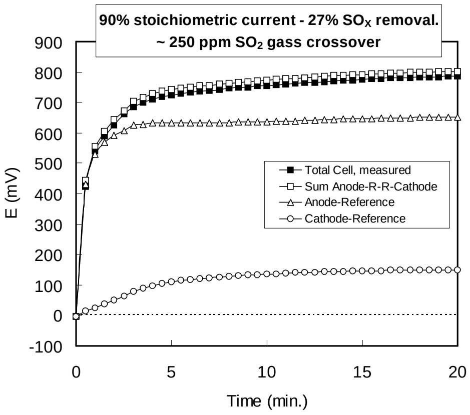

Figure 2: *Polarization over time at 20 mA (5 mA/cm^2). Cathodic polarization is plotted as positive for clarity. Same gas flows as in Figure 1.*

The most interesting observation to be made from this is the quite low cathodic polarization, approx. -140 mV even at this relatively high current. The reason for this must be due to a competing reaction present with this electrolyte. In order to explain this, a series of cyclic voltammograms was recorded with the same electrolyte placed as a bulk molten salt in a glass cell with well defined gold electrodes. From the location of the first V(V)-V(IV) redox pair it was obvious that with this electrolyte a Nernst potential of around -150 mV could be estimated, proving that in this electrolyte, indeed at redox reaction (see figure 3) capable of competing with the desired reaction is possible.

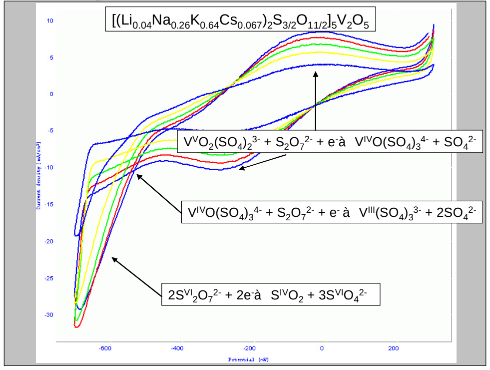

Figure 3: *Cyclic voltamograms of the electrolyte in a glass cell at 450°C after equilibration with the same flue gas Scan rates: 100, 150, 200, 250, 300 mV/s.*

References:

1. S. B. Rasmussen, K. M. Eriksen, R. Fehrmann and J. Winnick, *J. Appl. Electrochem.*, 32, 19, **2002.** (And references therein).

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