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Dennis McHenry^a; Jack Winnick^a

^a Georgia Institute of Technology School of Chemical Engineering, Atlanta, GA

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NEW MATRIX MATERIALS FOR MOLTEN ELECTROLYTE MEMBRANES

Dennis McHenry

Jack Winnick

Georgia Institute of Technology
School of Chemical Engineering
Atlanta, GA 30332-0100

ABSTRACT

An electrochemical flue gas desulfurization process has been developed and shown to remove 98+% of SO_2 from simulated flue gas (0.3% SO_2) by flow past an electrolyte-filled membrane. An applied electric field preferentially removes SO_2 and produces a concentrated by-product stream of SO_3 . The only reagent required for the process is electricity; this permits the process to have favorable economics.

The electrolyte is retained by a matrix of inert powder which forms a membrane. The matrix is designed to retain the molten electrolyte and prevent electrode pore flooding; flooding reduces interfacial area and increases the electrical requirements. New membrane formulations have been tested for increased electrolyte retention; the preparation of membranes with borosilicate glass or zeolites as the matrix is presented. The capillary action of the zeolite is higher than that of the porous electrodes. This enables the process to operate with a higher mass transfer area, allowing higher current densities. Polarization is compared with that of a MgO -based membrane.

BACKGROUND

While most membrane gas purification processes utilize a pressure gradient to drive the separation, it is possible, in some situations, to use an electrical field instead. If the species to be removed from the mixture is ionizable, or convertible to ionized species, the separation can be done with high selectivity at low cost^{1, 2, 3}.

These membrane systems selectively remove one chemical species from a mixture, ionically transport it across a membrane via a potential gradient, and then regenerate the chemical on the other side of the membrane. Using this principle, a process has been developed which electrochemically removes sulfur oxides from flue gas (0.3% SO_2). The membrane serves the dual purpose of providing a path for ionic migration of sulfur oxyanions and separating the flue gas from the enriched sulfur oxide by-product gas. This membrane consists of molten electrolyte retained in the interstices of an inert matrix by capillary action.

In order to carry current to the reaction zone, electrodes, electronic conductors, are required at both faces of the membrane. The present configuration of the SO_x removal system is shown in Figure 1. Sulfur oxides in the flue gas diffuse into the porous perovskite cathode and react with the electrolyte; the porous

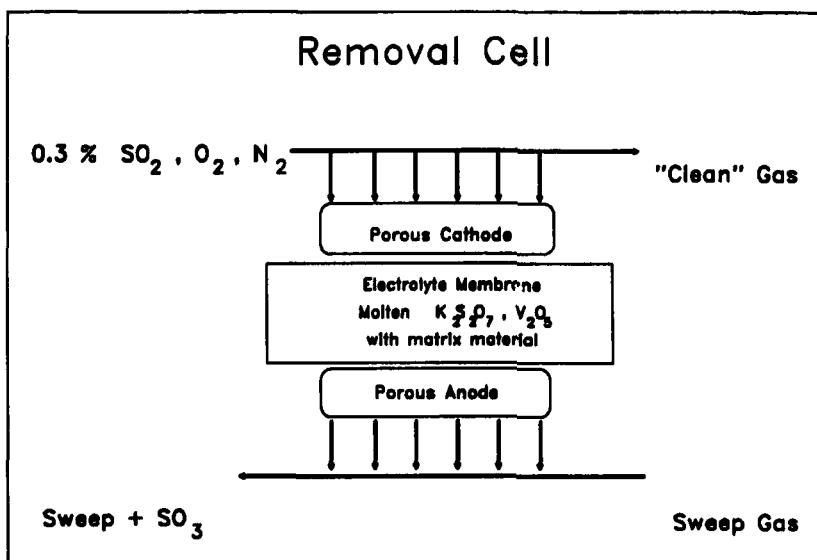


Figure 1. Removal Cell

perovskite electrodes have been shown to be ideally suited to this system. (Details on perovskite electrode fabrication and properties can be found elsewhere^{4, 5}). The electrolyte is a mixture of potassium pyrosulfate ($\text{K}_2\text{S}_2\text{O}_7$) and 5 wt.% vanadium pentoxide (V_2O_5), which melts near 300° C, allowing the system to be retrofitted to coal-fired utility boilers.

Previous researchers^{6, 7} have deciphered the electrochemistry as the following steps. At the cathode, pyrosulfate is reduced.



The sulfur dioxide is oxidized to trioxide



to facilitate removal from the gas phase to the electrolyte.



These reactions yield a net cathodic reaction of



The sulfate ion migrates under the influence of the electrical field to the anode, where it is oxidized to sulfur trioxide, which desorbs and can be further processed to sulfuric acid or oleum ($\text{H}_2\text{S}_2\text{O}_7$).



The overall reaction chemistry,



shows that the electrolyte acts only as a transport medium, in that there is neither a net consumption or generation of $\text{K}_2\text{S}_2\text{O}_7$.

When this SO_x removal process is compared to a conventional limestone scrubber, several advantages are noted, namely:

- i. the reagent is electricity, not limestone
- ii. a saleable by-product, instead of sludge
- iii. no need to reheat the flue gas before discharge
- iv. attractive economics.

To date, the process has been developed to the point where it will stoichiometrically remove up to 98% of influent sulfur oxides (0.3% SO_2), when a pre-oxidation catalyst is used to enhance reaction (2). However, the polarization performance of the membrane is lower than expected, due to electrolyte leakage from the membrane. It is thus necessary to find alternate membrane matrix materials to reduce this leakage.

MEMBRANE THEORY

In the electrolyte membrane, a matrix of particles is used to immobilize the molten electrolyte with matrix interstitial spaces retaining the electrolyte through capillarity. Since a porous electrode is on each side of the membrane and exerts its own capillarity, membrane capillarity must exceed that of the electrode pores in order to prevent electrolyte from leaking out of the membrane and into the electrodes. However, there should be a thin film of electrolyte on the electrode pore walls to maximize the gas/electrolyte interfacial area.

Arendt and Curran⁸ found that poor polarization performance in the molten carbonate fuel cell was due in large measure to flooding of the electrodes with molten electrolyte resulting from excessive overlap of the matrix and electrode

pore distributions. To prevent this occurrence, the matrix interstice size distribution should be one order of magnitude smaller than the electrode pores.

Arendt later states⁹ "that the matrix material and resulting membrane must

- (i) be chemically and physically stable for extended periods
- (ii) provide an appropriate interstice size distribution, stable in time, to complement the electrode structures, thereby providing optimum electrochemical performance
- (iii) be of minimum crystallite size, consistent with the stability and interstice distribution criteria to maximize the liquid electrolyte volume fraction and ionic conductivity of the membrane."

These criteria are required in the SO_x electrochemical removal system as well for optimum performance.

In the initial configuration of the SO_x removal process, the matrix material of choice was MgO , which formed a membrane of insufficient capillarity, allowing the electrodes to flood with electrolyte. This caused an immediate reduction in the available interfacial area available for gas/electrolyte interaction, reducing system performance. In addition, the electrochemical step, reaction (1), occurs where there is electrode/electrolyte contact. The reduced interfacial area impedes reaction (3), causing an accumulation of sulfate ions with several resultant problems. A concentration overpotential increases with sulfate accumulation. The sulfate ions are more basic than pyrosulfate, pushing the cathodic potential more negative. Sulfate ions also raise the melting point of the mixture, freezing the electrolyte in the electrode pores after sufficient time. In light of these problems, several new materials were investigated to decrease the interstice size, increase the membrane capillarity and increase the available gas/electrolyte interfacial area.

EXPERIMENTAL

A. Materials.

The initial matrix material tested was a finely divided (1.5 μm) MgO powder. The second material was a borosilicate glass (Corning 7740), available from Corning at less than 37 μm (< 400 mesh). This material could be further processed in an attritor mill or ball mill for size reduction. Several zeolites (Silicalite, 13x, 4A and 5A) were tested; only Silicalite was feasible as a matrix material. Several samples of silicon carbide and silicon nitride produced by a proprietary process developed by Phillips Petroleum Company (materials A, B, and C herein) were tested as alternate matrix materials.

B. Membrane Fabrication.

Several steps are needed to make an homogeneous membrane. The electrolyte is prepared by mixing 5 wt. % V_2O_5 in $\text{K}_2\text{S}_2\text{O}_7$ (J.T. Baker), melting to decompose any bisulfates (from pyrosulfate manufacture) and form an homogeneous electrolyte. The mix is cooled and milled to a powder, which can be added to the matrix material in the next step.

Selected weight fractions of matrix material and pre-mixed electrolyte were milled for 24 hrs. The mill was scraped and the fine powder placed in a three-inch diameter stainless steel piston and cylinder between layers of aluminum foil. The above procedures were carried out in a dry box whenever possible, since the electrolyte is hygroscopic and decomposes to bisulfates upon exposure to water. The die was then loaded into an oven, at 150° C for three hours. At this time, the top piston was fitted and the powder pressed under 1500 psi. The die was returned to the oven for heating to the hot press temperature, given in Table I. After three hours at this temperature, the die was removed and pressed again at 1500 psi. The outer cylinder was stripped and the pistons and membrane were returned to the oven to slowly cool (~ 100° C/hr).

Studies showed that the MgO matrix reacted with the electrolyte to form a new matrix material, $K_2Mg_2(SO_4)_3$, as discussed in Results and Discussion, below. To permit this reaction to go to completion, the MgO-based membranes had a processing step added, in which the MgO and electrolyte were allowed to react at 400° C for three hours. The resultant mass was cooled and reground before the milling and pressing steps.

Alternate membrane formulations were partially optimized to give a membrane with the best retention and polarization for the material. Certain materials were unable to perform better than the MgO-based matrix and were discarded without further optimization.

C. Full Cell Testing.

The housings (Figure 2) and full cell arrangement (Figure 3) were used to test the performance of the membranes. The electrodes fit into machined recesses, which are gold plated to provide for good electrical contact. Gas enters the inlet tube and flows over the electrode in channels machined in the housings, Figure 2, which form a sandwich on the membrane. The assembly is placed in a custom furnace and held together by an air-driven piston, which provides for a good seal around the housing periphery. The gas exits through the outlet tube, which is used to route gold wire to the electrode. Although a commercial SO_2 oxidation catalyst is available to enhance the SO_2 oxidation reaction, a plug of platinized silica gel was added to the inlet tubes in the bench scale apparatus for this purpose, as depicted in Figure 3. At 400° C, complete conversion of SO_2 to SO_3 is achieved over this catalyst¹⁰. The V_2O_5 in the electrolyte acts to oxidize the electrochemically generated SO_2 from reaction (1).

Full cell test conditions are given in Table II. Constant current was applied across the cell and potentials were monitored over time. The reference electrode was a platinum wire bathed in the same gas as that supplied to the cathode (0.3% SO_2 , 3.0% O_2 in N_2). Cathodic overpotential was determined by subtracting the rest potential from the actual potential, if the rest potential had been stable for more than one-half hour.

Post-mortem analysis focused on determining the level of pore flooding. Electrodes were weighed before and after the full cell tests and then washed and reweighed to check the amount of electrode weight gain. From the weight change, the volume of electrolyte in the electrode and the percent flooding were calculated.

Table I. Membrane Parameters

<u>Matrix</u>	<u>Weight %</u>	<u>Particle Size, μm</u>	<u>Hot-Press Temp., $^{\circ}\text{C}$</u>	<u>percent of theo. density</u>
MgO-based	3.	1.0 - 5.	275.	95.
Glass, 24 hr.	50.	0.5 - 10.	207.	94.
Glass, 140 hr.	40.	0.1 - 4.	210.	84.
Silicalite	26.	5.	208.	83.
Phillips A	40.	proprietary	210.	74.
Phillips B	35.	"	270.	89.
Phillips C	33.	"	272.	80.

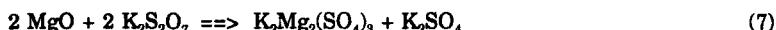
Table II. Operating Conditions

<u>Matrix Material</u>	<u>Figure</u>	<u>Gas, cc/min</u>	<u>Pre-Ox Catalyst?</u>	<u>i_{lim}, mA</u>	<u>$^{\circ}\text{C}$</u>
MgO	5, 8.	36.5	Yes	14.4	400.
MgO	6.	88.	No	34.6	425.
24 hr Glass	5, 8.	46.4	No	18.1	400.
140 hr Glass	6.	47.3	No	18.4	425.
Silicalite	5, 8.	57.	No	22.1	400.

RESULTS AND DISCUSSION

A. MgO.

Early membrane development work used MgO as the matrix material. Franke¹⁰ found the optimized membrane composition to be 13 wt.% MgO, 86 wt.% K₂S₂O₇, and 1 wt.% V₂O₅. He also found that the MgO reacted with the pyrosulfate to form a new matrix material, K₂Mg₂(SO₄)₃.



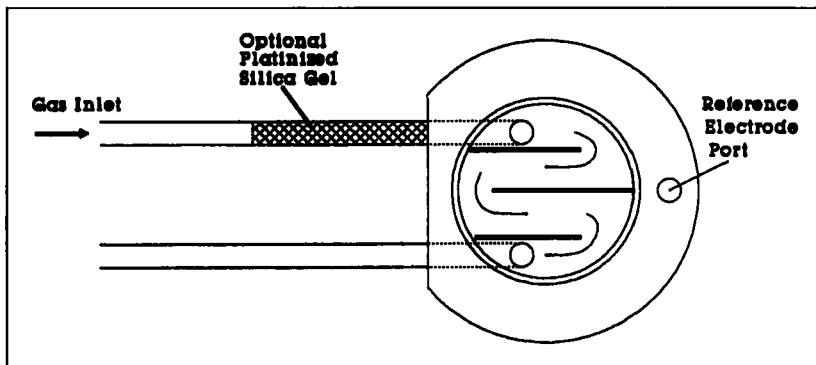


Figure 2. Cell Housing

According to the equilibrium of this reaction, the resultant membrane had 34 wt.% electrolyte; the remainder was the new matrix material. Scanning electron microscope analysis showed the new material to have a particle size of $\sim 10 \mu\text{m}$, as compared to 1 - 5 μm for the MgO precursor. This growth in particle size forces a commensurate growth in the size of the interstices and a reduction in the capillarity of the membrane.

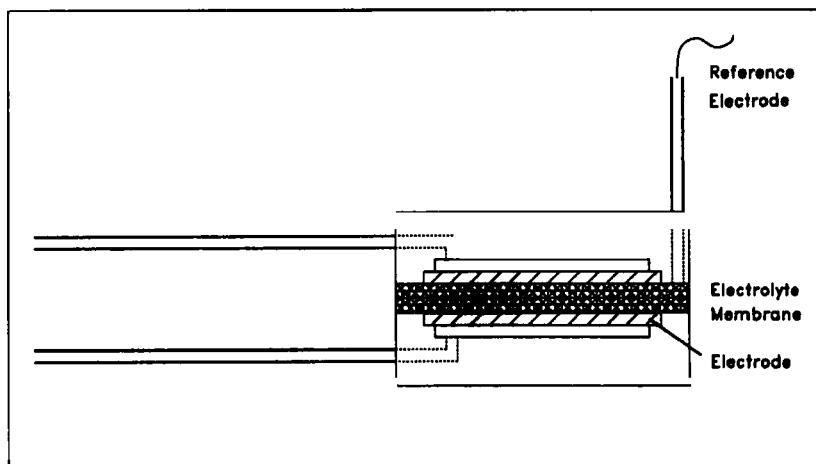


Figure 3. Assembled Removal Cell

When these membranes were tested in the full cell, the electrode pores rapidly flooded with electrolyte, causing the associated problems mentioned above. Therefore, this matrix was used as a basis for comparison with other membrane formulations. The polarization behavior of a MgO-based membrane is documented in Figure 4¹⁰. Data from another run is used as a base case in the other figures. These runs used the platinized silica gel catalyst to oxidize all SO_2 to SO_3 (see Table II).

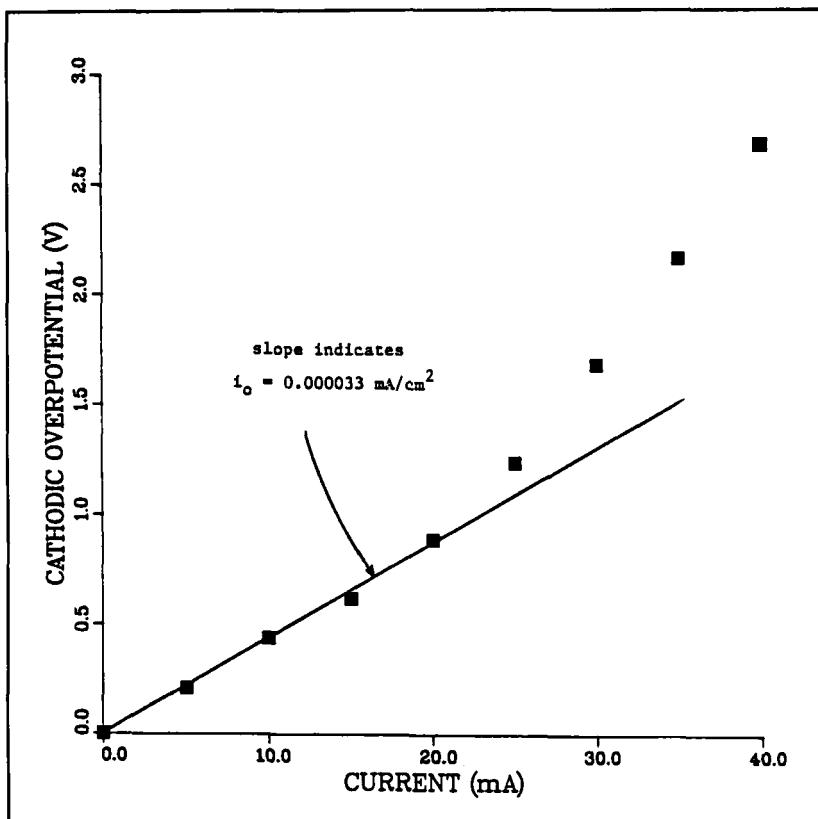


Figure 4. 400° C; 100 cc/min SO₂ mix. Ref. 10.

Post-mortem analysis of electrode weights could not be completed with these membranes because the extent of flooding prevented removing the electrodes from the surface of the membrane.

B. Borosilicate Glass.

The first attempts to optimize a membrane with this matrix material proved the particle size distribution was too wide to retain the electrolyte. To reduce the particles, the glass was ball milled for 24 or 140 hours. Milling for 24 hours gave a maximum particle size of 10 μm .

Figure 5 shows that 24 hour milled glass behaves like the MgO-based membrane. This is expected because of the similar particle size distributions of both materials. Although no platinized silica gel pre-oxidation catalyst was used, gas analysis showed 60% conversion of SO₂ to SO₃ at 400°C, due to the presence of V₂O₅ in the electrolyte. Post-mortem analysis of the electrodes showed the pores to be 80 volume % full of electrolyte. Visual and optical microscope observations showed the

electrode pores to be loaded with glass particles, carried along in the electrolyte.

After 140 hours of milling, the average particle was 1 μm , with a maximum of 4 μm . Significant improvement is seen when this material is used as the matrix. The data in Figure 6 were collected at 425° C after the current had been applied for 40 - 45 minutes. Without a pre-oxidation catalyst, the conversion of SO_2 by V_2O_5 was 75% at this temperature. The electrode used in this run had larger pores, as shown in Figure 7, decreasing its capillarity.

The membrane with the 140 hr. milled glass is capable of supporting four times the current of the base case MgO . The formulation of this membrane has not been optimized, so some further improvement may be possible. Post-mortem analysis showed a moderate level of flooding, with few glass particles carried along in the electrolyte.

C. Silicalite.

Silicalite particles have been formulated into a membrane which has shown significant improvement over the MgO base case. In Figure 5, the Silicalite handles three times the current with an equal polarization. This improved performance continues when the current is left on for an hour, Figure 8. Note that the Silicalite and the 140 hr. milled glass have equal performance in Figure 8, although the operating conditions differ. In the present run, a normal electrode was used, giving it a higher capillarity compared to that used with the 140 hr. glass matrix. While the particles of glass are smaller, the Silicalite would appear to present the same capillarity because of its porous nature.

Post-mortem analysis revealed that greater than 100% of the pore volume was filled with electrolyte. This anomaly is due to deposits of electrolyte on the surface of the electrode.

D. Phillips Materials.

No polarization data is available for membranes made from any of the Phillips matrix materials, as the formulations have not been optimized to date. The present formulations have shown the materials to provide excellent electrolyte retention, to the point of preventing the electrode pores from establishing a thin film of electrolyte. This lack of wetting has caused a limited gas/electrolyte interface, a high ionic resistance between the electrodes and high current densities at the limited contact areas. High current densities cause high local sulfate concentrations, which freeze, rapidly degrading the performance. All post-mortem analyses with these membranes have shown the electrodes to have a small weight gain. Data from several runs show that less than 5% of the pore volume contains electrolyte. The matrices have greater retention than desired, but this difficulty should be solved with further optimization of the membrane formulations.

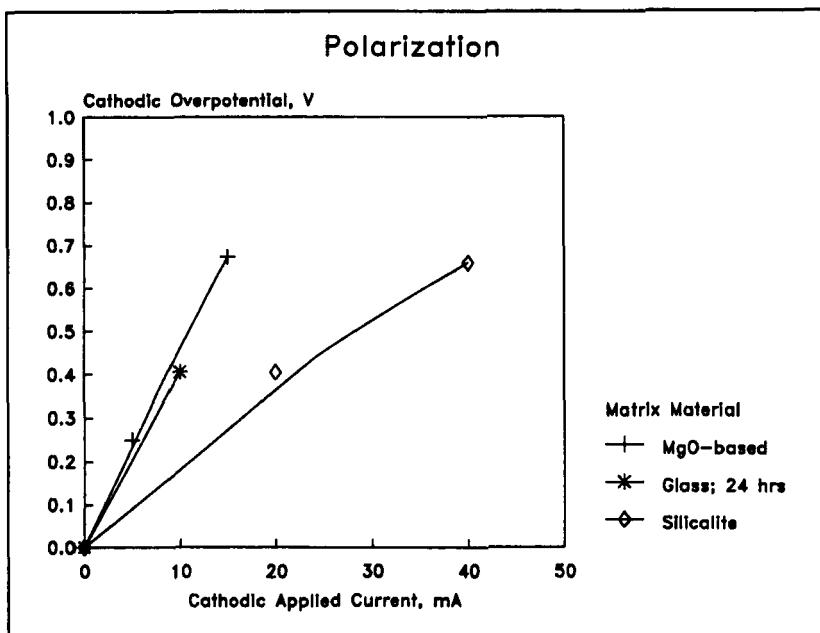


Figure 5. 400°C; Current on 15 mins.

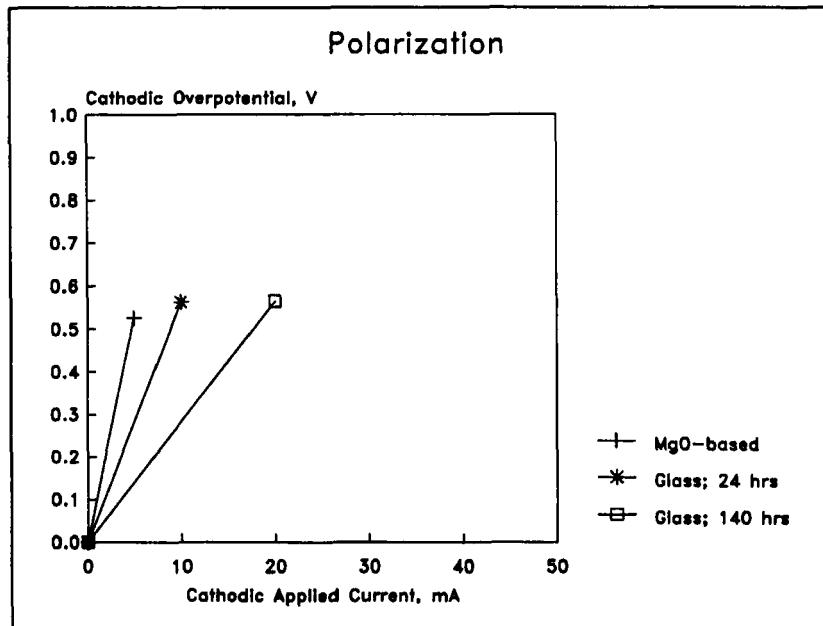


Figure 6. 425°C; Current on 40-45 mins.

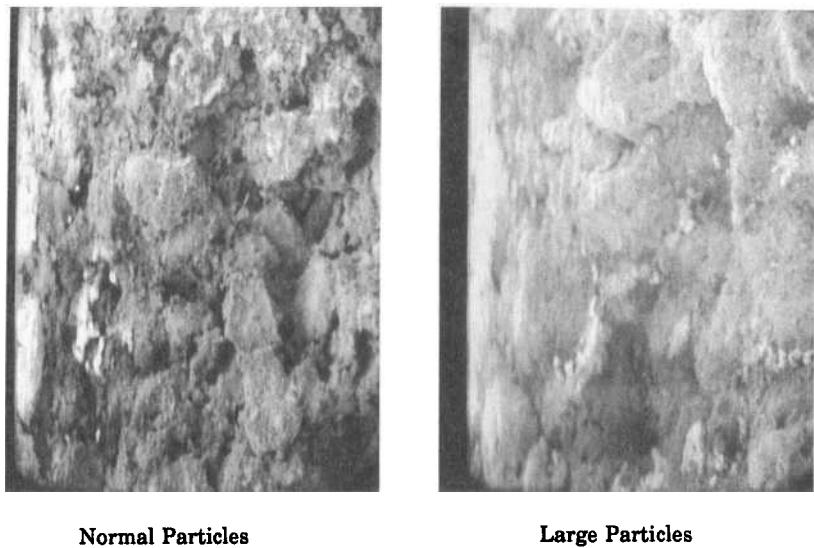


Figure 7. SEM of Electrodes Made from Different Sized Precursors

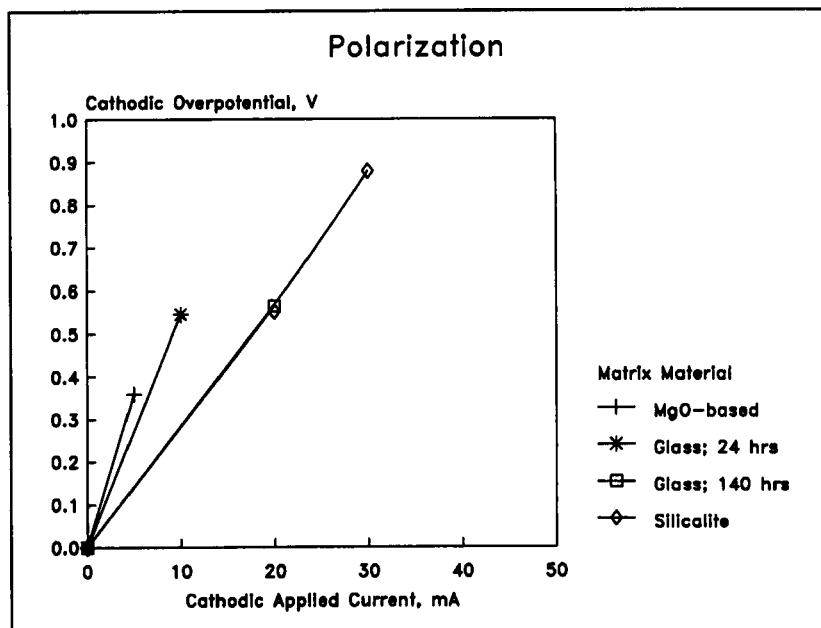


Figure 8. 400° C; Current on 60 mins.

CONCLUSIONS

A variety of matrix materials is available for use in formulating a molten salt electrochemical membrane.

The capillarity of the membrane matrix must prevent the porous electrodes from withdrawing excessive electrolyte and flooding. Several matrix materials have been tested, with mixed results. Borosilicate glass, milled for 140 hours, and Silicalite have improved the electrolyte retention and polarization, relative to the MgO-based matrix membranes. This reduction in flooding allows the electrochemical cell to handle three times the current for the same overpotential.

Membranes made with the proprietary materials from Phillips have not been optimized. The present formulations contain excess particles and voids, reducing the electrode/electrolyte contact area. This causes a high cell resistance and low current throughput. These formulations do have the benefit of extreme retention of the molten electrolyte in the fabricated membranes. Optimizing the fraction of matrix in the membrane should improve the performance of the membrane. Additionally, changing the electrode pore distribution will help correct this problem.

Acknowledgements

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