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Quarterly Progress Report:
High Temperature Membranes for
H₂S and SO₂ Separations
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by

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Purpose and Goals of Research

High temperature membrane separation techniques have been applied to gas mixtures involved in coal utilization. For coal gasification, H_2S has been removed from the syn-gas stream, split into hydrogen which enriches the syn-gas, and sulfur which can be condensed from an inert gas sweep stream. For coal combustion, SO_2 has been separated from the flue gas, with concentrated SO_3 produced as a by-product.

Both processes appear economically viable but each requires fundamental improvements: both the H_2S and SO_2 cells require more efficient membranes and the H_2S cell needs a more efficient anode. Membranes will be fabricated by either hot-pressing, impregnation of sintered bodies, or tape casting. Research conducted during the present quarter is highlighted, with an emphasis on progress toward these goals.

I. H₂S Removal Cell

Introduction

This electrochemical cell purges a fuel gas contaminated with H₂S. This is done by reducing the best Lewis acid in the gas stream. In this case, H₂S is reduced by the following:

A membrane which contains sulfide ions in a molten salt electrolyte will act to transport the ions across to the anode. If the membrane is impermeable to H₂ diffusion from the cathode side, an inert sweep gas can be used to carry the vaporous oxidized sulfur downstream to be condensed.

Research Summary

Membrane testing in the full-cell environment has been successful in H₂S removal applications, but largely ineffective for obtaining high current efficiencies due to hydrogen leakage through the membrane. A preprocessed zirconia membrane successful in past experiments was implemented as a *bubble pressure barrier* along with a fabricated zirconia membrane to truncate hydrogen cross-over from the process gas.

An alternative material forming a stabilized conductive cathode under 100 ppmv H₂S conditions is possible with Co. Development of a Co cathode identical in porosity and pore size to aforementioned nickel cathodes was successfully fabricated and utilized experimentally this quarter.

Test involving electrolyte evaporation as a mode of system failure were performed with electrolyte filled crucibles. Evidence suggested significant electrolyte loss prompting in-situ cell correction to reduce such losses.

Experiments

Run #17

A full cell experiment conducted this quarter incorporated a fabricated Co cathode (80% porous), housings of MACOR (machineable ceramic), a fabricated zirconia membrane (69% porous), and an anode material of Ni (85% porous). Aluminum foil gaskets served as the radial process gas sealant.

Stoichiometric removal of CO₂ at the cathode, addition at the anode were observed before applying H₂S to the cell; however, severe material problems prompted shut down after 24 hours of operation.

Run #18

Another full cell experiment conducted this quarter incorporated a fabricated Co cathode (80% porous), housings of MACOR (machineable ceramic), a fabricated zirconia membrane (69% porous) coupled with a purchased zirconia membrane (66% porous) to control process gas cross-over, and an anode material of Ni (95% porous). Aluminum foil gaskets served as the process gas sealant.

When the Electrochemical Membrane Separator (EMS) system reached the melting temperature of the eutectic electrolyte (~550°C), consistent loss of electrolyte created a high resistance across the cell membrane; a sustained ionic pathway between electrodes was never established although addition of electrolyte continued. Shut-down of the cell occurred after 168 hours.

Reactions/losses involving electrolytic species (e.g. Li₂CO₃) have been suggested to occur by three separate mechanisms: 1) reaction with Al gaskets to form process-gas seals, 2) evaporation at the anode where a deficiency of CO₂

exist, 3) atmospheric evaporation in the presence of oxygen. Reactions proceed by:

and

reactions of K_2CO_3 are assumed negligible due to the minute equilibrium constant compared to those with Li_2CO_3 .

Evaporation studies simulating full-cell conditions utilized electrolyte filled crucibles; losses involving CO_2 evolution (**mechanism 2**) accounted for 5% of the total electrolyte lost with **mechanism 3** emitting CO_2 for the other 95%.

Reaction 1 is not considered a factor upon conversion to the desired species.

Bubble pressure barrier

A fabricated membrane, containing zirconia fibers served as the encasement for the electrolyte, the amount corresponding to membrane porosity. The membrane creates a barrier to bulk-process-gas cross-over from cathode to anode, however diffusion of hydrogen continues. Utilization of a bubble pressure barrier similar to Molten Carbonate Fuel Cell (MCFC) technology should alleviate superfluous diffusion of hydrogen. The bpb can be implemented between either electrode (cathode/anode) and must contain adequate pore size and pore distribution relative to the membrane and electrode; the membrane and bpb must be totally quenched with electrolyte to prevent

hydrogen diffusion along with providing a pathway to transport ions between electrodes. Materials can be similar to electrode materials (e.g. Ni or Co) or metal oxides (zirconia).

Summary

Co electrodes, similar in morphology to previous nickel electrodes, were successfully utilized in Run #17 & #18, evidenced by stoichiometric transport of CO₂ applied current. Quantitative electrolyte studies proved evaporation of the electrolyte accounts for the majority of electrolyte loss; when using a bpb such losses are magnified due to the increased pore area requiring electrolyte for ionic mobility. Application of CO₂ to the sweep gas in an amount corresponding to process gases should alleviate a portion of carbonate loss.

Planned Work for Next Quarter

Work will continue with the cobalt cathodes, purchased zirconia membranes as a bubble barrier, and aluminum foil gaskets. Also a method of controlling atmospheric evaporation of carbonate will be investigated. The main focus will be on hydrogen permeability of the membrane with a bpb.

II. SO_x Removal Cell

INTRODUCTION

Successful removal of SO_x from flue gas depends on the development of a membrane able to achieve a current density of 50 mA/cm² at a total voltage of approximately 1V. Flooding of electrodes and the formation of sulfate at the electrode/electrolyte/gas interface have been identified as a problem, leading to increasing polarization over time. The resulting reduction of surface area also tends to limit the mass transfer flux, reducing the efficiency of the cell. To reduce flooding, new materials and techniques of manufacture will be investigated, in the attempt to produce a ceramic membrane of approximately 50% theoretical density. This membrane must have proper pore size distribution to ensure sufficient capillary force to prevent impregnated electrolyte from flooding electrodes, and subsequently drying the ceramic membrane. Various methods of matrix production were studied this quarter: tape casting, pressing and sintering, and slip casting. Each will be discussed in turn.

Electrolyte introduction to the cell is a continuing problem. The development of an efficient method is continuing. Ideally, the electrolyte would be introduced as powder with binder in a green body. This binder would burn away at temperatures of approximately 300° C, leaving pure electrolyte to melt and complete the ionic path necessary for the electrochemical cell. However, the ideal binder material has yet to be identified. The current binder system burns out at temperatures above the melting point

of the electrolyte. The electrolyte used this quarter was, exclusively, a 90wt%K₂S₂O₇/10wt%V₂O₅ mixture.

Electrodes used this quarter were lithiated nickel oxide. These were obtained from National Standard (Fibrex) and the Energy Research Corporation (ERC) as Ni sheets. These sheets were cut, with a resulting superficial area of approximately 20.0cm². The cut Ni was placed in a 1-2M solution of LiOH, dried, and oxidized at 600° C for 12-24 hours prior to placement in the cell. Past researchers have stated that this electrode exhibits a p-type conductance, with room resistivities on the order of 1.0-0.2Ω at room temperatures. Pore size of the National Standard Fibrex electrodes is approximately 1.0 μm. The pore size of the ERC electrode is proprietary. Other methods of manufacture of the electrodes were studied this quarter, and will be detailed as such.

Current is conducted through the cell from stainless steel 316L housings, to the electrolyte-wetted electrode, where the removal takes place. The current is then carried through the cell by the transporting species in the electrolyte. Oxidation of the transporting species occurs at the anode, and the current passes through the anode electrode to the anodic SS316L housing, and out of the cell.

Experiments this quarter have focused on the ability of the lithiated NiO electrodes to maintain high current densities in the potassium pyrosulfate/vanadium pentoxide electrolyte. Electrode response has been examined through the use of the common electrochemical techniques of cyclic voltammetry and potential step chronoamperometry.

ELECTRODES

Cyclic Voltammetry

Cyclic voltammetry was performed with the same physical set-up as previously described¹. Two references were used: a thermodynamic Ag/Ag⁺ reference electrode and a gold flag. The silver reference is a thin-walled bulb, filled with AgNO₃/KNO₃ mixture in a 62/38 mol% mixture, a low melting-point eutectic, with a silver wire. The tube is of Pyrex glass, diameter 1/4" with the bulb diameter 1/2" (see Figure 1). The thickness of the bulb walls is approximately 0.3-0.4mm.

Figure 1: Ag/Ag⁺ reference electrode.

Such references are known to pass cations²; in this case, K⁺ ions will be the migratory species. The overall reaction is thought to be:

with the two half-cell reactions thought to be:

This thermodynamic reference was used to verify the potential of the working reference electrode: the gold flag.

The system used contained a large excess of electrolyte: a total of 106.3g of potassium pyrosulfate was added. In addition, a total of 11.8g V_2O_5 was added later in the experimentation. The gold reference was 0.678 V positive of the Ag/Ag^+ reference prior to the addition of the V_2O_5 . After addition, the gold reference was 0.764 V positive of the Ag/Ag^+ reference.

The LiNiO electrodes were prepared in two ways. Both involved first flattening 99.8% pure Ni wire to form a planar electrode. This method insured conduction from the electrode to the leads, without any possible interference from solution. Electrodes were then bathed in $\geq 1\text{M}$ LiOH for a minimum of 10 minutes. The electrodes were then baked in air at 600°C for 24 hours to complete oxidation and lithiation. Resistance of the electrodes was $0.1\text{--}0.5\Omega$. A first variation on the process involved the sheathing of the electrode in a pyrex tube, which was subsequently crimped at the end to insure a tight fit, inhibiting gas evolution from the electrolyte to the sheath to the atmosphere.

The second electrode geometry involved simply placing the electrode into an uncrimped sheath, and into the melt. This second method was used to determine if there were any effects due to the heating of the sheath in a bunsen burner flame for crimping. When a flame was used, a red glow was noticed, indicating the presence of the lithium ion. No difference was seen. Electrode area was measured to $\pm 1\text{ mm}^2$.

Two scanning potentiostat/galvanostats were used. The first was a Princeton Applied Research (PAR) Scanning 362 Potentiostat. This was equipped with manual iR compensation, which entails dialing in the compensation for the system to the point of instability, and backing off for a stable scan. This scope was limited to set scanning rates of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, and 500mV/sec scanning rates. Two standard female ports were provided for monitoring the actual potential, applied potential, and current.

The second was a PAR 273 Potentiostat/Galvanostat. This machine was equipped with both current interrupt and continuous feedback iR compensation. In addition, digital input allowed any scan rate up to 10 V/sec. The machine was limited to a full-scale scan of 4.000 V, between the potentials of -10.000 to +10.000 V. Two BNC-type connectors allowed the monitoring of the current and potential. There was no difference between machines as verified by uncompensated scans on both in the same conditions.

The output from both machines was sent to either an oscilloscope or X-Y recorder. The X-Y recorder is a HewlettPackard 7015B X-Y Recorder. This recorder is equipped with a floating input with a maximum input of 40VDC, a slewing speed of 50 cm/sec minimum. The recorder was desirable for the very low signal to noise ratio, but required manual manipulation of the data for analysis.

The oscilloscope is a Nicolet 370 Digital Storage Oscilloscope. This scope allowed the recording of signals in a digital format for data processing and manipulation. However, the introduction of the scope entailed a large signal to noise ratio in some

cases which covered low-voltage responses. Potential step data was largely recorded in this machine.

Franke³ had determined that there exists in the electrolyte an electroactive vanadia complex which would have a reversible reaction (see Equation (3)) which was consistent with the species found in x-ray diffraction studies on the melt. Franke also varied the atmospheric partial pressure from pure N₂ to contain 1%SO₂ and/or 10% O₂. He saw little change in the couple with respect to the gas environment. The experimental equilibrium potential of the electrolyte was seen to vary with gas environment and concentration of vanadium pentoxide added.

The vanadia couple can also be involved in a chemical reaction with available oxygen in the melt which can be written as a two step reaction:

Franke noted that the presence of SO₂ or O₂ shifted the equilibrium of the melt in favor of the vanadia complex in the V⁺⁴ or V⁺⁵ state respectively. Again, both of these complexes were confirmed by x-ray analysis. Free SO₃ in the melt or atmosphere may also induce a change in the complex involving only vanadia in the V⁺⁵ state. In this way, SO₃ may be stored in the melt.

Figure 2: Cyclic voltammtery using a gold working electrode. $v=500\text{mV/sec}$

Cyclic voltammetry was first performed using a gold working electrode with a gold counter electrode, with respect to the gold reference. The oxygen partial pressure was changed from 0.30 atm O₂, 3000ppm SO₃, N₂, to 51% O₂, 1500ppm SO₃, N₂, and scan rates from 500 mV/sec to 10 mV/sec (see example in Figure 2). The peaks currents were measured. The peak of interest in this particular test is the vanadia peaks.

Using the same iR compensation, peak currents for the vanadia couple were analyzed for the reduction peak of stabilized scans of the differing O₂ partial pressures previously mentioned (see Figure 3). A decrease was noted in the peak current density with increase in the O₂ partial pressure with respect to the square root of the scan rate. In addition, the peak potential was found to be approximately 70 mV more positive for the larger O₂ partial pressure for each scan rate. On gold electrodes, therefore, the reaction of the vanadia complex tends to occur at a slower rate. This confirms the result of previous experiments that found a lower exchange current density for increasing O₂ partial pressure.⁴

The other peaks have also been identified by Franke on gold electrodes. Peak I is the reduction of the pyrosulfate ion in the reaction:

Peaks II and III are a chemical/electrochemical reaction involving the oxidation and reduction, respectively, of the sulfate species according to:

Cathodic Peaks Only

Figure 3: Peak currents for vanadia couple on Au electrodes with varying O₂ partial pressure.

This reaction is reversible, and at higher sulfate concentrations, the reduction of any sulfate present at the electrodes will be seen. However, an additional equilibria must be considered:

This equilibrium equation will reduce the amount of sulfate available for electrochemical reduction and oxidation if SO_3 is present in the melt, due to the fast nature of the reaction at 400° C. Peak IV and V are the reversible vanadia complex couple discussed above.

The above results generated current densities in agreement with the results of both Franke and Scott⁵. The objective was then to perform the identical experiments using a lithiated NiO electrode to verify the reactions occurring at the electrode, as well as the electrode kinetics. Electrodes were prepared as previously discussed, and introduced to the same melt as the gold electrodes.

McHenry⁶ had performed cyclic voltammetry on a lithiated NiO flag in the melt. He attached gold wire to a Ni wire, through a pyrex sheath, to the flag. A bubbler containing Pt catalyst for the complete oxidation of SO_2 in the gas stream to SO_3 prior to bubbling through the melt. The area of his electrode was 3.1 cm², and his reference was a gold wire in the melt.

His scan (see Figure 4) at 500 mV/sec with no iR compensation showed the presence of the same peaks as previously seen by Franke. The large pyrosulfate

Figure 4: McHenry cyclic voltammetry. $v = 500 \text{ mV/sec}$

reduction peak (Peak I) shows a diffusion-limited peak current of approximately 12.5mA; a current density of -4.03 mA/cm^2 .

Bubbling was not initially used in this research. A scan utilizing a lithiated NiO flag with iR compensation was made in an identical manner to McHenry (see Figure 5). The end-to-end resistance of the electrode use (30 cm length) was about 0.8Ω . iR drop was found to be 5Ω working to reference and 6Ω working to counter when measured by the current interrupt method prior to scanning. The initial scan showed all the expected reactions. Subsequent scanning, however, showed that the scan was not stable. The pen was lifted from the recorder but the scanning was not interrupted. There is a flattening of the oxidation peak, presumably the oxidation of sulfate. The vanadia couple, present in the initial scan, flattens also, indicating the depletion of the electroactive species from the electrode. The pyrosulfate reduction peak current decreased from -53.75 mA (off the chart) to -24.375 mA with the last scan.

Two peaks also appear as scanning continues: an oxidation peak (Peak VI) at -0.610V and an oxidation peak (Peak VII) at 1.287V. The peak current of Peak VII was actually seen to grow more positive with number of scans, then become more negative.

Bubbling was then used, and an initial scan taken (see Figure 6). The scan was first made more negative with respect to the rest potential. There appears a large reduction peak which is not consistent with the large reduction peak in the previous diagram, a shift of -0.504 V. After scanning, the system was noted to have a large concentration overpotential. Upon application of a constant current to the lithiated NiO electrode, the concentration overpotential was first seen to increase steadily, then

Figure 5: Lithiated NiO cyclic voltammetry. $v=500$ mV/sec.

Figure 6: Cyclic voltammetry with lithiated NiO. $v=500\text{mV/sec}$. Single scan.

decrease. This cycle was seen to continue irregularly if a constant current was maintained. In addition, the iR drop was measured to be about 60 Ω after the scan.

Additional scans were run on the system. Scanning was continuous, and the pen was set on the paper at different times (see Figure 7). Bubbling of SO_3 was present. As the times reached 20 minutes, there is a significant increase in the oxidation current in Peak VII and the disappearance of Peak I with the introduction of some other reduction reaction.

The emergence of large oxidation peaks has been seen with lithiated NiO electrodes by other researchers in other systems. Decker *et.al.*^{7,8} observed the lithiation of NiO for its chromic properties. They suggested a two-step electrochemical scheme for the incorporation of the Li into the non-stoichiometric NiO lattice. The first step was the non-reversible electrochemical introduction of the Li to the lattice:

The second is the actual coloring and bleaching of the electrode through oxidation and reduction respectively:

They also performed cyclic voltammetry on the electrodes in a lithium perchlorate/propylene carbonate solution using a lithium foil as a counter electrode. Their experiments showed the development of a large new oxidation peak as the system was cycled (see Figure 8). They claimed this peak was the product of, first an initiation step, followed by a reversible step after all initiation had been completed. They did

Figure 7: Continuous cyclic voltammetry. $v=500\text{mV/sec}$. Pen placed down at different times.

achieve a stabilized scan after a great number of cycles at 10 mV/sec. AC impedance measurements were also performed to confirm the presence of an initiation step followed by a stable reversible step.

Passerini *et. al.*⁹ further studied the system and proposed that poor lithiation would impart different properties to the electrode, which he showed as the emergence of a small peak for

heavily lithiated samples, as well as changes in the photocurrent and modulus responses of the heavily and poorly lithated electrodes.

The presence of electroactive species described by Franke was confirmed by the use of gold electrodes. The lithiated NiO electrode, however, saw the disappearance of electroactive species, and the emergence of other unknown species. In addition, over the course of 30 minutes of continual scanning, no stabilized voltammograms were obtained.

Figure 8: Cyclic voltammetry of Decker *et.al.* of Li solution with NiO electrode. $v=10\text{mV/sec}$.

Potential Step

The potential step technique was used by Scott with gold electrodes to help determine the electroactive species from a possible list, through the evaluation of the diffusion constant for the various reactions that might occur. He found that the only species which gave a reasonable diffusion constant was the pyrosulfate species, and that the potential steps indicated that sulfate might be the possible reduction product. He found modeling the steps to be rather difficult for potential steps over 300mV due to the non-linear interaction between faradaic current and overpotential.

Potential step experiments were performed with the lithiated NiO electrode. The potential was stepped negative from equilibrium to the potential of Peak I, the pyrosulfate reduction reaction, about -2.000 V. Bubbling was continued. One would expect a large current jump followed by a leveling of the current due to a mass transfer limitation.

The potential was stepped, resulting in a peak current density of about 217mA/cm². The current then leveled at about 10 mA/cm² after 38 seconds (see Figure 9). Any offset is due to physical error in zeroing the oscilloscope. The results of other runs are contained in Table I.

MEMBRANE WORK

X-ray analysis was performed on an amorphous SiO₂ formed by a sol-gel process, courtesy R.A. Gerhardt, School of Materials, Georgia Institute of Technology. A pure sample was first x-rayed. Sample materials were then exposed to 90wt% K₂S₂O₇/ 10wt%

Table I: Potential step results using a lithiated NiO working electrode in a 90wt% $K_2S_2O_7$ / 10wt% V_2O_5 melt at 400° C.

#	atmosphere	i_{max} , mA/cm ²	i_{level} , mA/cm ²	step, V	iR comp	bub- bling
1	0.003 SO ₃ , 0.03 O ₂ , N ₂	-217.4	-	-2.000	y	n
2		-86.46	-	-2.062	n	n
4		-21.7	-	-2.062	n	n
6		-23	-	-0.100	n	y
8		-23	unmeasur able	-0.200	n	y
10		-45		-0.500	n	y
12		-170	-11	-1.000	n	y
16	N ₂	-0.9	unmeasur able	-0.100	y	y
18		-1.4		-0.200	y	y
20		-6.1	-1.0	-0.500	y	y
22		-22.0	-4.0	-1.000	y	y
24		-85.0	-20	-2.000	y	y
26		-0.08	-	-0.025	n	n
28		-0.14	-	-0.100	n	n
30		-.053	-	-0.100	n	n
32		-0.92	-	-0.200	n	n
34		-0.92	-	-0.500	n	n
36	0.5 O ₂ 0.5 N ₂	-0.17	-0.02	-0.100	n	y
38		-.38	-0.03	-0.200	n	y
40		-1.22	-0.08	-0.500	n	y
42		-7.7	-0.07	-1.000	n	y

V_2O_5 at 400° C in Pyrex petri dishes for 48 hours.

Figure 9: Current monitored with -2.00V potential step.

Figure 10: X-ray result of SiO_2 sol gel membrane after chemical testing.

The molten salt was seen to wet the electrolyte completely and uniformly. Excess electrolyte was present through the duration of the experiment. The samples were then cooled, and x-rayed without washing (see Figure 10). Potassium pyrosulfate/vanadium pentoxide peaks were seen. The amorphous peak seen in the pure sample was also present. An extensive analysis of the possible sulfur and vanadia species failed to show any new phases due to reaction. This result indicates a chemical inertness of this proposed matrix material, but does not verify any electrochemical stability.

Past use of ZrO membranes showed similar results initially. Amorphous ZrO was used to create a membrane and chemical testing showed the material to be stable. However, when used in the electrochemical cell, the membrane and electrolyte vanished, probably due to some electrochemical or electrochemical-chemical reaction (s). Full cell testing is needed to determine the feasibility of SiO₂ usage in this form.

Currently, the membrane is being constructed to form a 3" diameter disk. A disk of this size has never before been constructed. If feasible, the disk will allow the pre-introduction of the electrolyte, as there are no components to burn out as in the tape casting method. This may allow for stronger gas seals, and less cross-cell gas leakage due to cracks forming in the ceramic matrix with electrolyte introduction.

FUTURE WORK

Work next quarter will focus on the full cell application of the ZrO membrane, verifying its stability. In addition, new electrode material has been obtained from S.S.C., Inc. This perovskite material will need to be chemically tested prior to use in the cell.

Past research has shown the formation of sulfates of the species in perovskite compounds utilizing some of the same elements.

Analysis of the results of the electrochemical testing will conclude to determine if the lithiated NiO electrode is a feasible electrode for use in a full cell, or it would represent a limiting step. A thin-film experiment will be set up to this end. Thin films may allow greater interaction of the electrode, electrolyte, and gas, reducing the diffusion distance.

ENDNOTES

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