

Oil & Natural Gas Technology

DOE Award No.: DE-FE0000408

Quarterly Report
July 2010 – September 2010

Post Retort, Pre Hydro-treat Upgrading of Shale Oil



Submitted by:
Ceramatec Inc
2425 S. 900 W.
Salt Lake City, UT 84119

Prepared by: John H. Gordon, PI

Prepared for:
United States Department of Energy
National Energy Technology Laboratory

October 22, 2010



Office of Fossil Energy

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EXECUTIVE SUMMARY

In the 4th quarter both upgrading reactor and electrolysis endeavors switched to lithium as the alkali metal reactant with good success; however, sodium results to-date have been better.

Also in the 4th quarter a reactor run was made where methane was the hydrogen supplying gas rather than hydrogen. The initial result was very encouraging. Methane rather than hydrogen as the source would improve the process economics.

Our issues with our Perkin Elmer CHNS analyzer are not resolved. We have ordered an analyzer from LECO and have requested Perkin Elmer to take back their equipment. They still want to try to resolve the technical issues.

Expenditures to date are close to budget.

PROGRESS, RESULTS, DISCUSSION

Task 1.0: Project Management Plan

The PMP was updated within 30 days and submitted to the Project Manager (Quarter 1).

Task 2.0: Upgrading Development

This task is related to developing the process of treating shale oil, or heavy oil at elevated temperature and pressure in the presence of an alkali metal, either sodium or lithium and also a hydrogen source, either hydrogen gas or methane (natural gas) to form an oil stream with reduced levels of sulfur, nitrogen and heavy metals and also in the process reducing the viscosity and increasing the API gravity. The object here is to determine the impact of various reaction parameters on product quality.

Sub task 2.1: Analytical Capability

Analytical Laboratory Set up

The Perkin-Elmer 2400 CHNS analyzer, due to several disadvantages that the manufacturer was not aware of, will be returned. Order for new CHNS has been placed with LECO, another vendor. Meanwhile we continue to send the samples for analysis to Huffman Laboratories. The swap of instruments has not affected the progress of the project.

Sub-task 2.2: Upgrading Reactor and Separation Setup

Experimental

Several additional experiments were performed on upgrading of Red Leaf shale oil (RL), (oil shale Exploration Company shale oil (OSEC) and San Joaquin heavy crude oil (SJ) aimed towards parametric optimization. All the experiments were performed with using Sodium or Lithium as the alkali metal, 200 gm of oil as raw material, 1000 psig pressure and reaction time of 60 minutes. Upon reaction, the product was subjected to centrifuging to separate the solid fraction (sulfides and possibly heavy metals) from liquid. Table 1 below shows the list of different experiments.

Table 1: List of experiments Performed

Expt #	Feedstock	Alkali Metal	Details	
			Temperature (°C)	Quantity of lithium (g)
1	RL	Li	375	1.8
2	RL	Li	275	1.8
3	RL	Li	375	0.9
4	RL	None	375	None
5	OSEC	Li	375	1.8
6	OSEC	Li	275	1.8
7	OSEC	None	375	None
8	SJ	Li	375	1.8
9	SJ	Li	275	1.8
10	SJ	None	375	None

Key experiments from previous set of runs were repeated. These experiments included upgrading of all three raw materials at 375 C in presence of 6 g of sodium metal. Table 2 below lists the details of these experiments.

Table 2: List of repeat experiments Performed

Expt #	Feedstock	Alkali Metal	Details	
			Temperature (°C)	Quantity of sodium (g)
1	RL	Na	375	6.0
2	OSEC	Na	375	6.0
3	SJ	Na	375	6.0

Results and Discussions

CHNS measurements were performed on raw material samples and product samples. Compositional analysis for all the three raw material samples is shown in Table 3 below and Table 3 lists analysis results for products.

Table 3: C, H, N and S Composition of Raw Materials

Raw material	C (%)	H (%)	N (%)	S (%)
RL	85.48	12.33	1.48	0.25
OSEC	84.83	12.74	0.47	0.84
SJ	85.70	11.27	0.76	1.54

Table 4: C, H, N and S Composition of Products (Upgrading using Li metal)

Experiment number	C (%)	H (%)	N (%)	S (%)
1 (RL)	85.15	12.49	1.23	0.10
2 (RL)	84.88	12.33	1.35	0.18
3 (RL)	85.71	12.28	1.35	0.22
4 (RL)	85.69	12.29	1.33	0.25
5 (OSEC)	85.36	12.69	0.38	0.40
6 (OSEC)	84.59	12.62	0.40	0.66
7 (OSEC)	85.38	12.77	0.39	0.77
8 (SJ)	85.38	11.32	0.72	1.30
9 (SJ)	85.33	11.60	0.70	1.50
10 (SJ)	85.70	11.46	0.71	1.46

Table 5: C, H, N and S Composition of Products (Upgrading using Na metal)

Experiment number	C (%)	H (%)	N (%)	S (%)
1 (RL)	85.86	13.05	0.64	0.03
2 (OSEC)	86.41	13.36	0.16	0.02
3 (SJ)	85.56	11.72	0.68	0.27

SimDist

All the samples obtained from experiments 1 through 10 (Table 1) and 1 through 3 (Table 2) were subjected to SimDist analysis using HP 6890 GC. Both the shale oil samples being very light, more than 95% of material boiled in the 9 through 13 carbon range. Hence the impact of upgrading process could not be quantified towards heavy to light hydrocarbon conversion. For San Joaquin heavy crude (Expt #3, Table 2), it was observed that after the upgrading process, boiling point was reduced by 26 °C at 60% mass boil -off indicating improvement in oil quality.

Conclusion

As observed from Table 4, Lithium metal based upgrading did not show substantial removal of nitrogen and sulfur. Table 5 shows the results from Na based upgrading process. Sulfur reduction

of 88%, 97.6% and 82.4% was measured for RL, OSEC and SJ feedstocks respectively. Nitrogen reduction of 56.7%, 65.9% and 10.5% was measured for RL, OSEC and SJ feedstocks respectively. Na based upgrading has shown more promising results compared to Li based upgrading in case of RL and OSEC feedstocks for removal of both nitrogen and sulfur where as sulfur removal has been We continue to investigate effect of other conditions such as temperature and metal loading for Lithium based processes.

Schedule

The progress of Task 2 is as per schedule.

Subtask 3.1 – Membrane fabrication

The Recipient shall fabricate and characterize sodium conductive and lithium conductive membranes.

Characterization of the Membranes Shear Strength by the Ring-on-Ring Test

Experimental Setup

The following is the procedure for a Ring-on-Ring Test using the ASTM Standard C1499-04 performed to obtain strength and Weibull data. An Instron 5566 with a load cell of 1 kN was used. The support structure had a radius on the compressive side, b, of 6.5mm and a radius on the tension side, a, of 9.5mm. A thin piece of tape was placed on the compressive side to keep the broken disc pieces together. The bottom ring of the test fixture was taped onto the bottom platform of the testing instrument. A ball was held with the top ring fixture through lowering until it contact was made with the ceramic. The rate for the applied load was 0.5mm/min. Data was collected every 50ms. Figure 1, below, is a schematic and picture of the test fixture and the instrument used. Multiple tests, including Nasicon and Lisicon, were performed with this method.

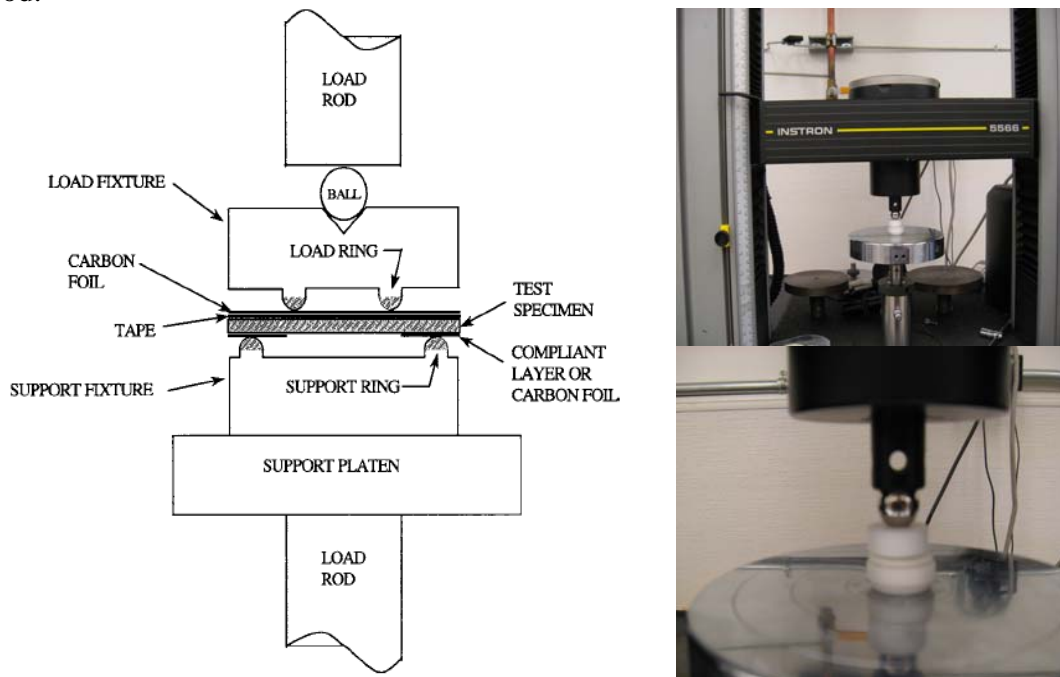


Figure 5. Left Diagram of experimental setup. Right picture of test fixture used for the experiment

Test Results for First Set of NaSICON Samples

The first test included 29 Nasicon ceramic membranes fabricated with the dimensions of 24mm in diameter and 500µm thick. From the data obtained a Weibull Plot was formed to determine the weibull modulus, Figure 2. The characteristic strength, the point at which 63.2% of the parts will fail, was estimated from the plot to be equal to 90 MPa, whereas the weibull modulus is 4.

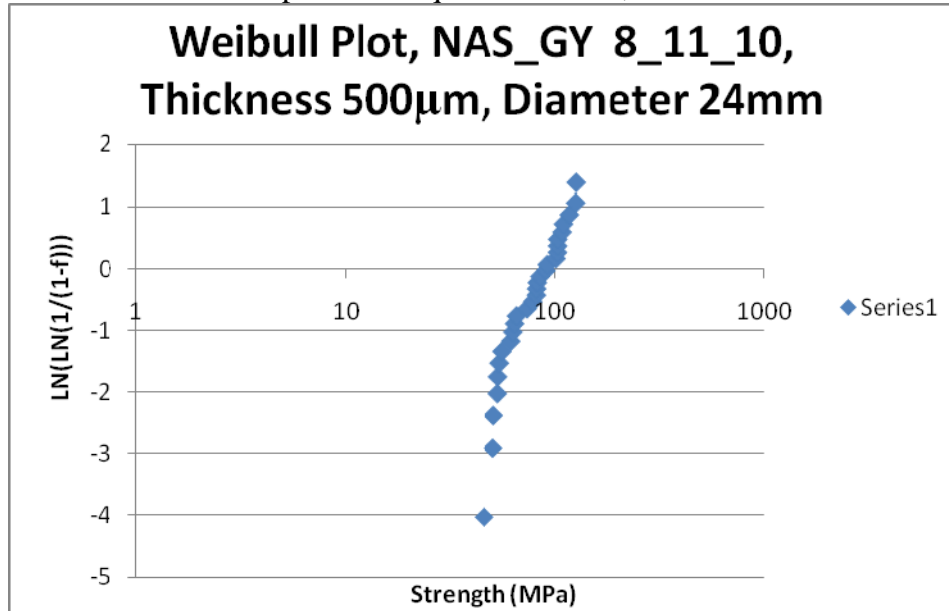


Figure 6. Weibull Plot from the results of the Ring on Ring test using Nasicon samples

The modulus of 4 is very low. This means there is a large variation in strength for the lot of ceramics. Two possible reasons for this are some samples were not completely flat and the deflection required to break the ceramic was too high. The sample size needs to be modified to thicker samples so the deflection will be less. This test will be performed again using the same 24mm diameter and 1mm thick parts.

Test Results for the Second Set of NaSICON Samples

The second set consisted of 10 samples with a thickness of 1mm. The thicker samples showed a tighter distribution of shear strength as shown in Figure 3. The weibull modulus was 8.2 and the calculated characteristic strength based on the data was 92.73 MPa.

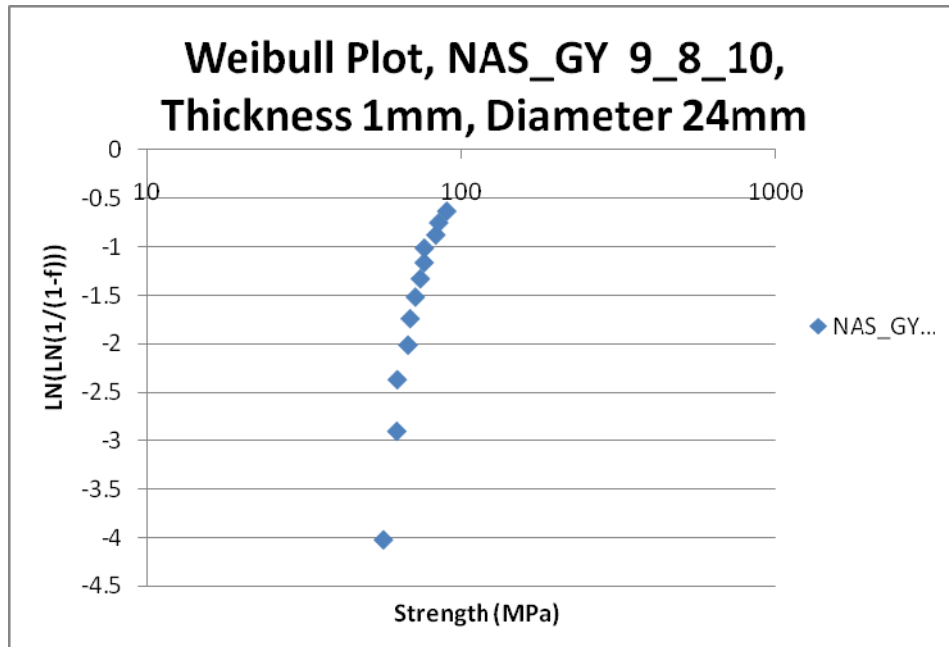


Figure 7. Strength distribution of 1mm thick Nasicon samples

The characteristic stresses from the two tests are very similar. However, a higher modulus was obtained through higher selection standards. Excessively warped ceramics were not used in the test and the ceramics were properly examined sorting out samples where the crack originated from the edge causing them to be invalid according to the ASTM standards.

Test Results for Lisicon 45B Samples

The test consisted of 26 samples of Lisicon 45B with the dimensions of 500µm thickness and 24mm in diameter. The set of samples showed a large distribution of strength. The weakest sample was 60 MPa and the strongest was 126 MPa. The characteristic strength was 108 MPa and the weibull modulus was 5.2.

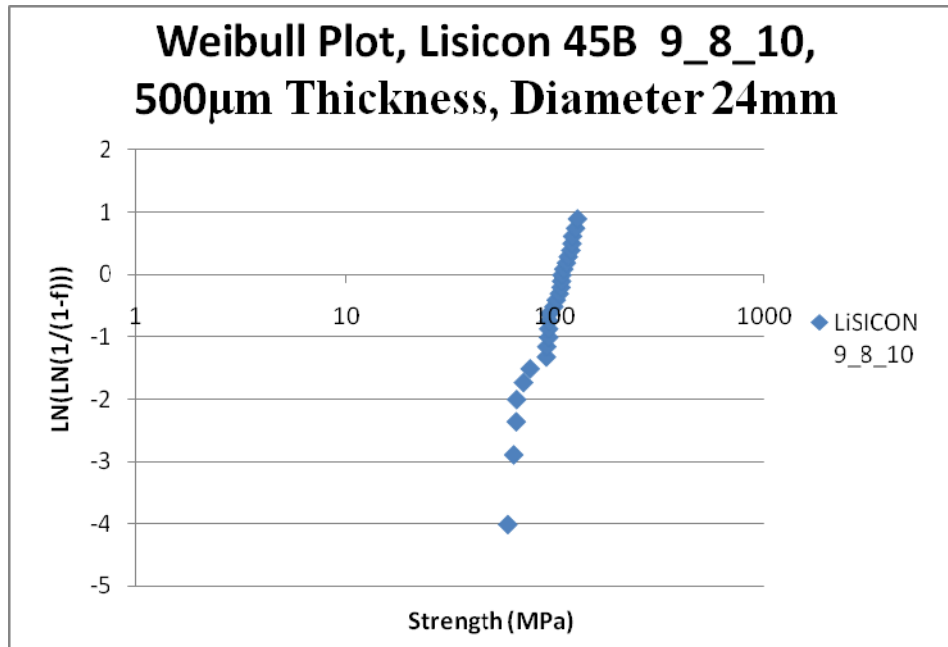


Figure 8. Lisicon 45B strength data distribution for 500µm samples.

The testing results of all sets of samples shows that both Nasicon and Lisicon have a large variability in strength resulting in a low weibull modulus. They both have very similar elastic modulus of 92 MPa and 108 MPa for Nasicon and Lisicon, respectively.

What are the implications of these results? There have been many successfully designed flow cells constructed and are on-line using Nasicon Membranes; however, the membranes are relatively thick, about 1.2mm. The 1mm thick parts had the best Weibull modulus. We should continue this testing and see if there are ways through processing to improve the Weibull modulus in 500 micron membranes.

Subtask 3.2 – Seal testing

Ceramatec shall evaluate various seal approaches for compatibility with the alkali metal and the metal polysulfide at various temperatures.

No activity during this period.

Subtask 3.3 – Cell design and set up

Ceramatec shall design benchtop cells for two types of operation, one where the alkali metal is molten and one where it plates onto a current collector. Reactors and catholyte transfer means will be provided to prepare alkali metal sulfide of differing composition and transfer to the cell. The cells will be designed to accommodate multiple reference electrodes, operate at various elevated temperatures. The cells will have features designed to facilitate sulfur removal and be designed to operate within a dry enclosure.

Electrolysis Test Cell Design

The existing alkali metal recovery test cell has been redesigned during this reporting period. Figure 5 shows a 3-D rendition of the new cell with its most important components. One of the main features of the cell is that the anolyte and catholyte compartments are symmetric and fully interchangeable. In addition, the cell can be run in a continuous dual flow arrangement with respect to the catholyte and anolyte solutions; and it can be oriented either horizontally or vertically. In Figure 5, the electrolyte solutions would flow from left to right. A flow distributor piece, with perforated plates, is located upstream of both anode and cathode compartments. The external dimensions of the cell are approximately 3"x3"x1", while the catholyte and anolyte compartments are approximately 2"x2"x0.5". The body of the cell is made out of chemical resistant Acetal Copolymer. The distance from the cathode and anode electrodes to the ceramic membrane can be each independently adjusted by a set of four springs that are compressed by four screws during the assembly process. Similarly to the previous Test Cell design, the 1.5" in diameter ceramic membrane is epoxied to a PTFE coated Stainless Steel plate that is positioned between the catholyte and anolyte compartments. The two halves of the cell are sealed against the membrane assembly plate by two O-rings, which are compressed by four screws on each side. The electrical connection between the external power supply and the electrodes is achieved by a current collector plate that distributes the current from a wire to the four screws that are in contact with the four corners of the electrode surface. The rectangular electrodes have dimensions (1.65"x1.75") and can be easily machined in different materials such as graphite, glassy carbon, titanium, tungsten, stainless steel and others. The cell can be assembled "dry", outside the glove box, and then the electrolytes can be loaded into the catholyte and anolyte compartments through inlet and outlet ports.

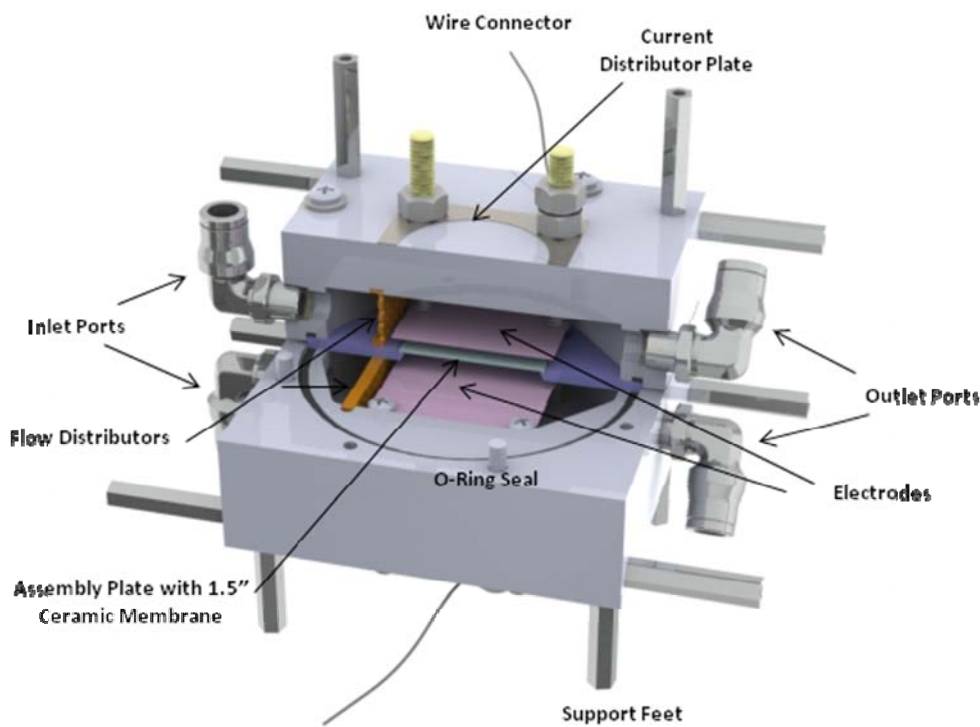


Figure 5. 3-D Rendition of the new Test Cell design

Installation of a New Dry Glove Box in the Electrolysis Lab

A new glove box has been added to the Electrolysis Lab during this quarter to handle moisture sensitive materials. The glove box (Plas Lab Model 818-ABD) is made of Plexiglas of dimensions 48”W x 29”D x 32”H and with an internal volume of 25.8 ft³. The box has been plumbed to the existing dry air supply system and a new moisture sensor has been installed in the exhaust line to monitor the moisture level of the atmosphere inside the chamber. This new asset will be mostly used to assemble/disassemble electrolytic test cells, to prepare and characterize electrolyte solutions and to store moisture sensitive chemicals. On the other hand, the first glove box will be dedicated to run test cells. This separation of tasks between the two boxes will help to make the lab work more efficient and to improve the safety of all lab operations. Figure 6 shows a photograph of the new box alongside the old one.



Figure 6. [A] Dry glove boxes in the Electrolysis Lab [B] New moisture sensor installed on the exhaust pipe of the new glove box

Procurement of a 16-channel Galvanostat/Potentiostat Instrument and a Lab Oven

Ordered and installed a 16-channel potentiostat/galvanostat testing instrument from Arbin Instruments (model BT2000). This device will allow us to conduct advanced electrochemical measurements of up to 16 test cells simultaneously.

In addition, a forced convection oven (Despatch model LBB1-23-1), with a temperature range of 35°C to 204°C, has been added to the lab. The oven will allow us to run the test cells at temperatures above lab ambient conditions. Figure 7 shows a photograph of the new equipment.



Figure 7. 16-channel Potentiostat/Galvanostat Arbin BT2000 instrument and lab oven installed in the Electrolytic Lab

Subtask 3.4 – Cell operation

The Recipient shall operate cells under various conditions including variation of the current density, electrode gap, temperature, electrolyte, polysulfide order, and alkali metal. Current will be measured as a function of applied voltage. Periodically cell operation will be interrupted and cell contents analyzed to determine current efficiency. In Phase 1 the alkali metal polysulfide will be synthesized from alkali metal and sulfur and will not contain appreciable impurities which may flow through from an actual upgrading process as will occur in Phase 2.

Study of Electrolytes for Sodium and Lithium Recovery Cells

Continue investigation to identify suitable electrolytes to be used in sodium and lithium recovery cells. During this reporting period, two new solvents EG and Gamma-BL have been added to the list. Figure 8 shows the ionic conductivity of all the solvents tested up to date. Figure 9 reports the solubility of Sodium Tetrasulfide (Na_2S_4) in most of these solvents at ambient temperature. EG has similar solubility to MF. The ionic conductivity of three different anolyte systems for sodium recovery cells is shown in Figure 10. As a general conclusion, MF is still the preferred anolyte solvent since it has the highest solubility for polysulfide and sulfide ions and the highest ionic conductivity. However, EG, which also has relatively high polysulfides solubility and ionic conductivity, has a cost advantage over MF. For the catholyte systems tested (Figure 11), the ionic conductivity of Gamma-BL+1M NaI is 8.5 times higher than TG+1M NaI. The latter has been the preferred catholyte so far. Data comparing the performance of Test Cells using these two catholytes is presented in the Test Cell Run Results section below. Similar ionic conductivity measurements for the anolyte (Figure 12) and catholyte systems (Figure 13 and 14) have been conducted for Lithium Sulfide (Li_2S).

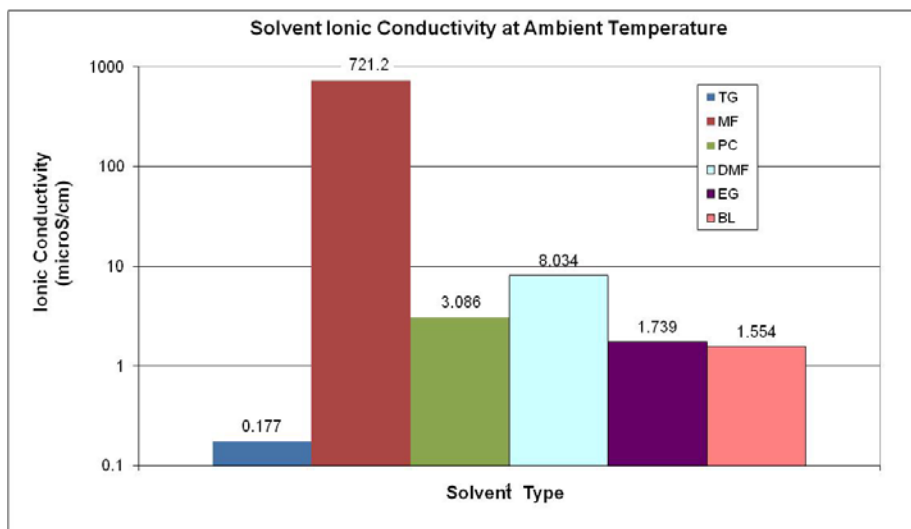


Figure 8. Ionic conductivities of all the solvents evaluated up to date

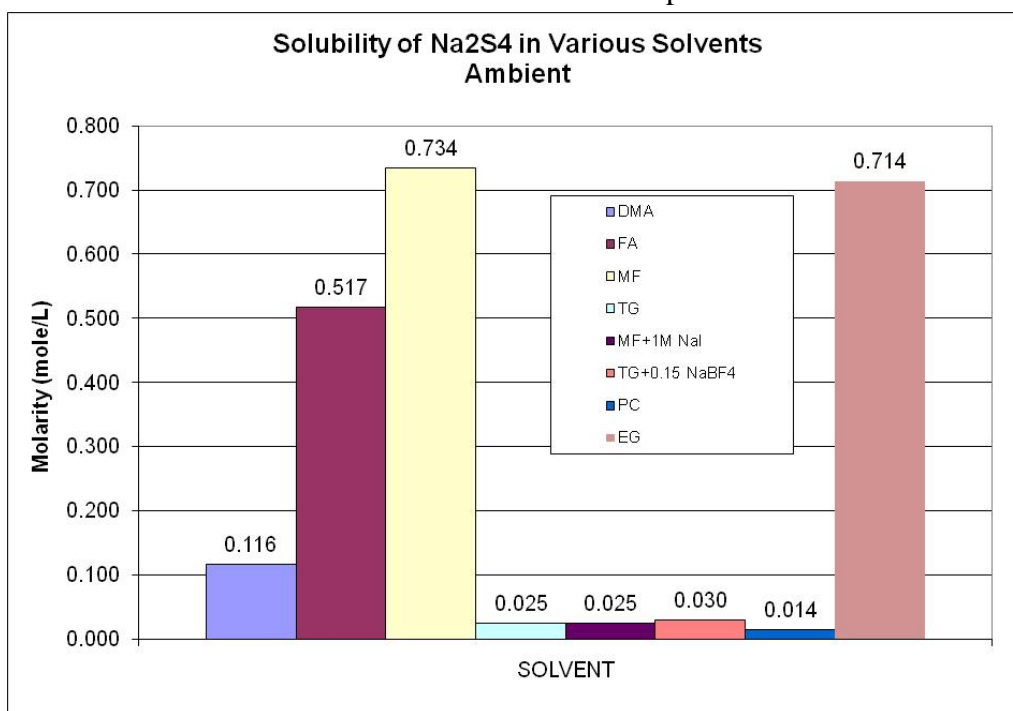


Figure 9. Solubility of Na₂S₄ in various solvents

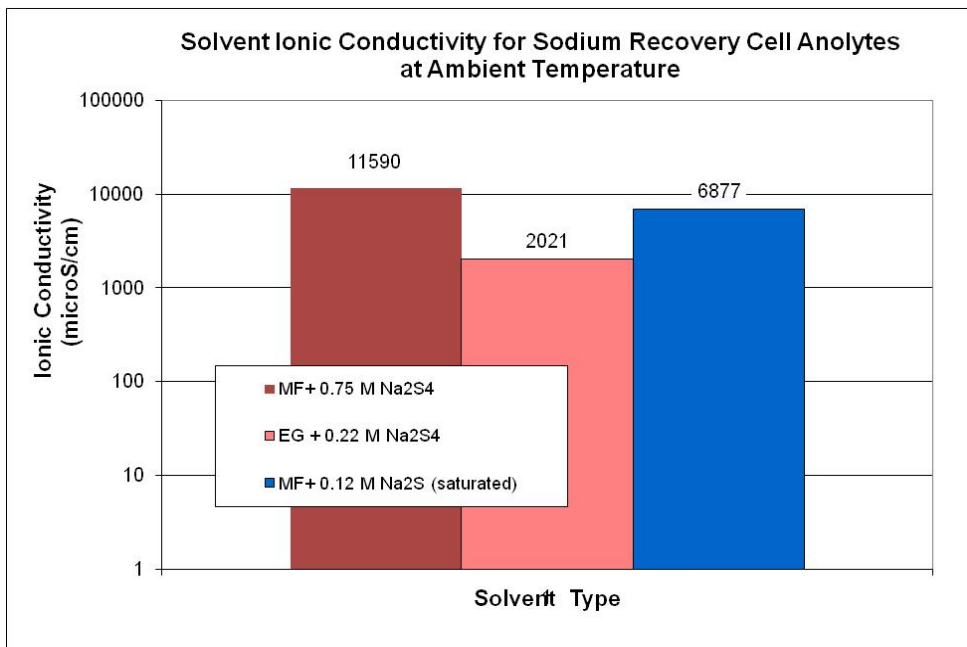


Figure 10. Ionic conductivity of anolytes for sodium recovery cells

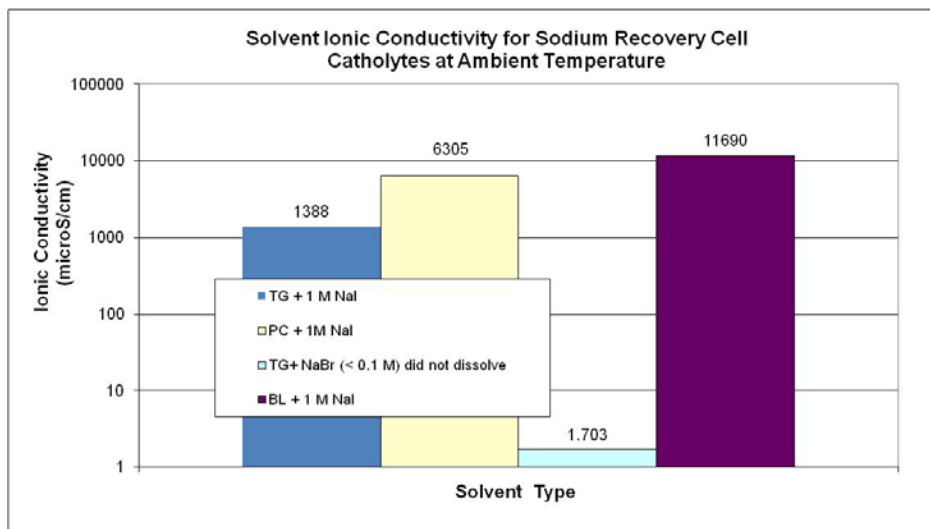


Figure 11. Ionic conductivity of catholytes for sodium recovery cells

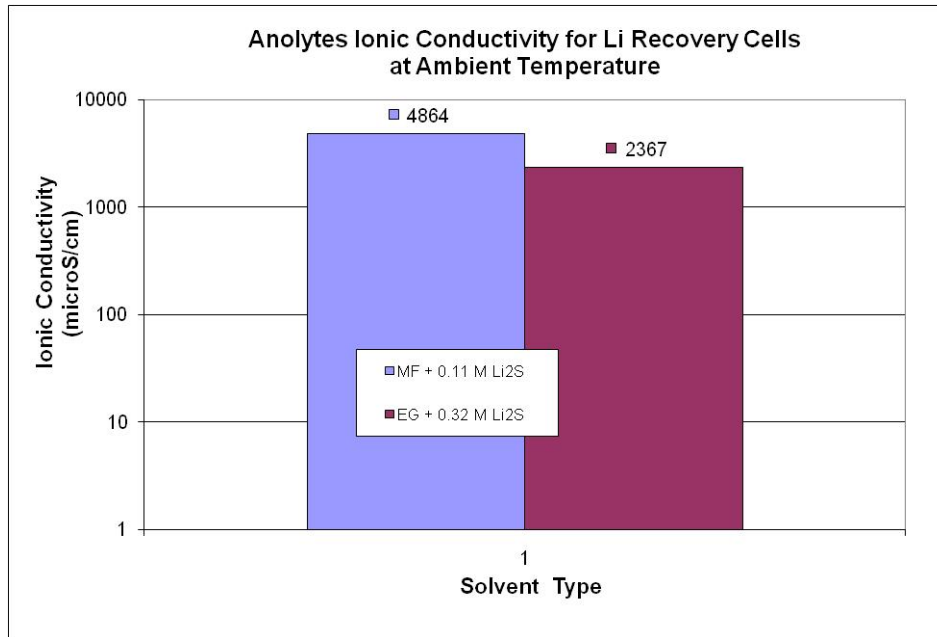


Figure 12. Ionic conductivity of analytes for lithium recovery cells

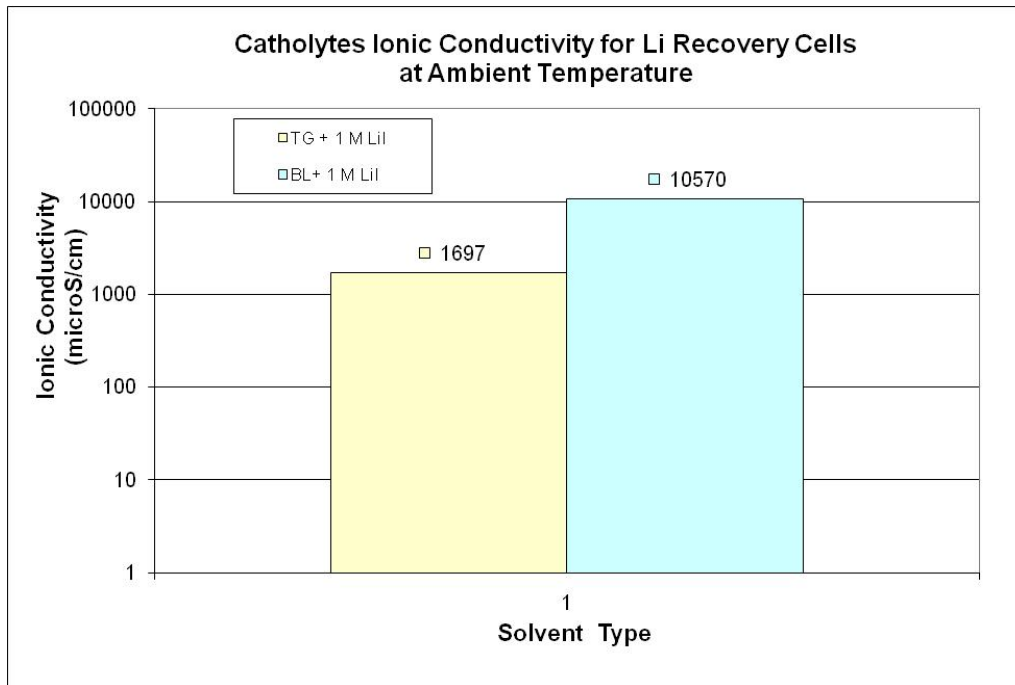


Figure 13. Ionic conductivity of catholytes for lithium recovery cells

Test Cell Runs Results

Sodium Recovery Test Cell Runs

A total of 20 Sodium recovery Test Cells have been assembled and run during this reporting period. Out of the 18 runs, 10 were conducted using the standard Test Cell design with 1.5” in di-

ameter membranes. The other 10 runs were done using the Glass Test Cell with 1" in diameter membranes. Table 1 summarizes the properties of each of the cells and the test operating conditions. The effect of different catholyte solvents (TG, Propylene Carbonate, and Gamma-BL); anolyte solvents (MF, and EG); sulfide ion type, as starting raw material in the anolyte, (S^{2-} vs. S_4^{2-}); membrane thickness (0.7-1.0 mm); and operating temperature (21°C, 50°C, 60°C, and 70°C) were studied on the cells performance.

The following are the most important findings learned from these set of tests.

- a. All the replicate data points that we have obtained with the system MF + Na_2S_4 (anolyte) and TG+NaI (catholyte) have shown that the cell quickly deactivates after successive voltage sweeps. We believe that this deactivation is caused by the formation of an insoluble deposit on the anode electrode surface and/or the anode-side of the Nasicon membrane. Operating the cells at higher temperatures (e.g. 70C vs. 50C or vs. ambient temperature) helps in delaying the onset of the deactivation process but it does not prevent it from eventually happening.
- b. EG has been successfully tested as anolyte solvent in one test cell run (Na Glass Test Cell 20100825). The solvent has similar sodium polysulfide solubility (Na_2S_4) and ionic conductivity to MF. This test cell run has also proven that the solvent has a wide electrochemical window to be effectively used in the recovery of sodium metal from sodium polysulfides. While further testing will need to be conducted to fully qualify this solvent, it seems as a good cheaper alternative to MF.
- c. Gamma-BL was used as the catholyte solvent in one test cell (Na Glass Test Cell 20100812). Unfortunately, the test showed that the selectivity of the desired sodium reduction reaction with this solvent was very low.
- d. Sodium Sulfide (Na_2S), instead of Sodium Polysulfide (Na_2S_4), was used in Glass Test Cell 20100812. The data shows that the cell operated very stable at 5mA (1 mA/cm^2) for approximately seven hours before a sudden increase in the operating voltage was observed. Post-test analysis of the cell revealed that the reason was a cracked membrane.
- e. Unfortunately, all NaSICON-GY membranes assembled and tested up-to-date in sodium recovery test cells have failed. Even though the tests covered a wide range of operating conditions, the ultimate end result of the runs was always the breakdown of the membrane. Most of the membranes show extensive cracking, staining, and pitting corrosion. The low reliability of the material in the highly corrosive sodium polysulfide environment is an area of major concern. The use of other existing NaSICON formulations is under consideration.

Table 6. Sodium Recovery Test Cells assembled and tested during the reporting period

Cell ID#	Anolyte	Anode Electrode	Membrane	Catholyte	Cathode Electrode	Operating Conditions
Na_20100709	0.75 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., 1 mm thick	1M NaI in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50C
Na_20100714	0.76 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., 0.945 mm thick	1M NaI in PC	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 21C
Na_20100722	0.74 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., t=1 mm thick	1M NaI in PC	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50 C
Na_20100728A	0.50 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., t=0.958 mm thick	1M NaI in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50 C
Na_20100728B	0.50 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., t=1 mm thick	1M NaI in TG.	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50 C
Na_20100804	0.50 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., t=0.706 mm thick	1 M NaI in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50 C
Na_20100806	0.36 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., t=0.962 mm thick	1 M NaI in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50 C
Na_20100811	0.36 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., t=0.711 mm thick	1 M NaI in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50 C
Na_20100816	0.38 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., t=0.948 mm	1 M NaI in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50 C
Na_20100819	0.42 M Na ₂ S ₄ in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	NaSICON GY 1.5" Diam., t=1 mm thick	1 M NaI in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 50 C
Na Glass Test Cell 20100716	0.8M Na ₂ S ₄ in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=1 mm thick	1M NaI in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 21 C
Na Glass Test Cell 20100719	0.75M Na ₂ S ₄ in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=1 mm thick	1M NaI in TG,	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 21 C
Na Glass Test Cell 20100720	0.75M Na ₂ S ₄ in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=1 mm thick	1M NaI in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 50 C
Na Glass Test Cell 20100721	0.77 M Na ₂ S ₄ in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=1 mm thick	1M NaI in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 60 C
Na Glass Test Cell 20100803	0.5 M Na ₂ S ₄ in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=1 mm thick	1M NaI in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C
Na Glass Test Cell 20100806	0.34 M Na ₂ S ₄ in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=0.714 mm thick	1M NaI in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C
Na Glass Test Cell 20100812	0.35 M Na ₂ S ₄ in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=0.700 mm thick	1M NaI in γ -BL	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C
Na Glass Test Cell 20100825	0.4 M Na ₂ S ₄ in EG	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=0.922 mm thick	1 M NaI in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C, Anolyte Agitation
Na Glass Test Cell 20100913	0.19 M Na ₂ S in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=0.700 mm thick	1 M NaI in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C, Anolyte Agitation
Na Glass Test Cell 20100928	0.33 M Na ₂ S ₄ in MF	Titanium foil (1" Diam.) 3 mm to membrane	NaSICON-GY 1" Diam., t=1 mm thick	1 M NaI in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C, Anolyte Agitation

Lithium Recovery Test Runs

Lithium Test Cells were assembled and tested for the first time during this reporting period. In total, 13 cells were run. Similarly to the Sodium Test Cells, the two available designs were used. Table 2 summarizes the properties of each of the cells and the test operating conditions. A number of parameters such as catholyte solvent (TG, and Gamma-BL); anolyte solvent (Ethylene

Glycol, and MF); membrane thickness (0.5 -1 mm); and anode electrode material (Titanium mesh, Titanium foil, Platinized Titanium, Vitreous Carbon, and Tungsten foil) were investigated. All the cells were run in batch mode at 70°C. The following are the most important findings learned from these set of tests.

1. Cyclic Voltammetry scans (Figure 14) revealed that, as opposed to sodium cells, lithium recovery test cells do not get deactivated (polarized) after successive voltage sweeps. Even after tens of hours of operation, the cells remain fully active with little change in the overall cell resistance. The scans also show a high degree of reversibility of the lithium metal redox reaction.
2. LiSICON 45B membranes (1" and 1.5" in diameter) demonstrated an excellent reliability in the constant current tests. In fact, none of the 13 test cells assembled and run in this reporting period resulted in the failure of the membrane. In most of the cases, the tests were ended either because of the breakdown of the epoxy seal or due to the corrosion of the Titanium anode electrode. As an example, Figure 15 shows the operating cell voltage versus total run time at 5 mA (1 mA/cm²) for Li Glass Test Cell 20100820. The longest running time, out of all the lithium cells tested so far, was logged by Li Glass Test Cell 20100921 at 130 hours.
3. EG and MF were both successfully used as the anolyte solvent in lithium recovery cells. However, the ionic conductivity of the anolyte MF+Li₂S is approximately 3-4 times higher than that of the EG+ Li₂S system. Given the low solubility of Lithium Sulfide (Li₂S) in these solvents (or in any other solvents tested so far), the anolyte solution is the dominant component of the total cell resistance. Therefore, in our tests MF is preferred over EG since higher cell current densities can be run for the same voltage drop penalty. This is illustrated in Figure 16, where the voltage sweeps of a test cell with MF [A] vs. a test cell with EG [B] are compared. However in a large scale industrial process, the lower cost of EG might offset the advantage of its lower ionic conductivity.
4. Similarly to the results found with the sodium recovery cells, Gamma-BL is not a good catholyte solvent as it significantly reduces the selectivity of the lithium reduction reaction.
5. The anode side surface of all the LiSICON 45B membranes tested in lithium recovery cells showed an intense blue coloration (Figure 17). The formation process of this thin blue layer is still unknown. SEM/EDS analysis of the membranes did not detect any structural damage. X-Ray Diffraction (XRD) analysis identified a new phase (Lithium Titanium Phosphate Oxide) in the blue region, which is different than the basic LiSICON composition (Lithium Titanium Phosphate). We do not have any indication, so far from our tests, that this new phase has any detrimental effects on the cell's performance.
6. The selection of the material of construction of the anode electrode is very important. The anode has to be chemically resistant to the anolyte solution and need not to compete with the polysulfide ion in the oxidation reaction. The first lithium recovery cells assembled had titanium anode electrodes. It was quickly learned that this material is not suitable for this appli-

cation (Figure 18 [A] and [B]). Vitreous (glassy) carbon (Figure 18 [C]), graphite, tungsten, and platinized titanium (Figure 18 [D]) were all successfully tested.

Table 7. Lithium Recovery Test Cells assembled and tested during the reporting period

Cell ID#	Anolyte	Anode Electrode	Membrane	Catholyte	Cathode Electrode	Operating Conditions
Li_20100823	0.15 M Li ₂ S in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	LiSICON 45B 1.5" Diam., 0.5 mm thick	1M Lil in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 70 C
Li_20100830	0.11 M Li ₂ S in MF	Titanium mesh (1.65"x1.75") 2 mm to membrane	LiSICON 10B (non-hermetic) 1.5" Diam., 0.5 mm thick	1M Lil in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 70 C
Li_20100901	0.28 M Li ₂ S in MF	Glassy Carbon (1.65"x1.75") 2 mm to membrane	LiSICON 45B 1.5" Diam., 0.5 mm thick	1M Lil in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 70 C
Li_20100909	0.24 M Li ₂ S in MF	Platinized Titanium (1.65"x1.75") 2 mm to membrane	LiSICON 45B 1.5" Diam., 0.5 mm thick	1M Lil in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 70 C
Li_20100920	0.21 M Li ₂ S in EG	Glassy Carbon (1.65"x1.75") 2 mm to membrane	LiSICON 45B 1.5" Diam., 1 mm thick	1M Lil in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 70 C
Li_20100923	0.15 M Li ₂ S in MF	Glassy Carbon (1.65"x1.75") 2 mm to membrane	LiSICON 45B 1.5" Diam., 1 mm thick (Reused from Li_20100920)	1M Lil in TG	303 SS disk (1.3" Diam.) 5 mm to membrane	Batch, 70 C
Li Glass Test Cell 20100813	0.1 M Li ₂ S in MF	Titanium foil (1" Diam.) 3 mm to membrane	LiSICON 45B 1" Diam., 0.5 mm thick	1M Lil in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C
Li Glass Test Cell 20100818	0.1 M Li ₂ S in MF	Titanium foil (1" Diam.) 3 mm to membrane	LiSICON 45B 1" Diam., 0.5 mm thick	1M Lil in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C
Li Glass Test Cell 20100820	0.1 M Li ₂ S in MF	Titanium foil (1" Diam.) 3 mm to membrane	LiSICON 45B 1" Diam., 0.5 mm thick	1M Lil in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C
Li Glass Test Cell 20100902	0.34 M Li ₂ S in EG	Titanium foil (1" Diam.) 3 mm to membrane	LiSICON 45B 1" Diam., 0.5 mm thick	1M Lil in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C
Li Glass Test Cell 20100914	0.32 M Li ₂ S in EG	Tungsten foil (1" Diam.) 3 mm to membrane	LiSICON 45B 1" Diam., 0.675 mm thick	1M Lil in TG	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C
Li Glass Test Cell 20100921	0.31 M Li ₂ S in EG	Tungsten foil (1" Diam.) 3 mm to membrane	LiSICON 45B 1" Diam., 1 mm thick	1M NaI in γ -BL	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C, Anolyte Agitation
Li Glass Test Cell 20100929	0.49 M Li ₂ S in MF	Tungsten foil (1" Diam.) 3 mm to membrane	LiSICON 45B 1" Diam., 1 mm thick	1M NaI in γ -BL	Titanium foil (3/4" Diam.) 3 mm to membrane	Batch, 70 C, Anolyte Agitation

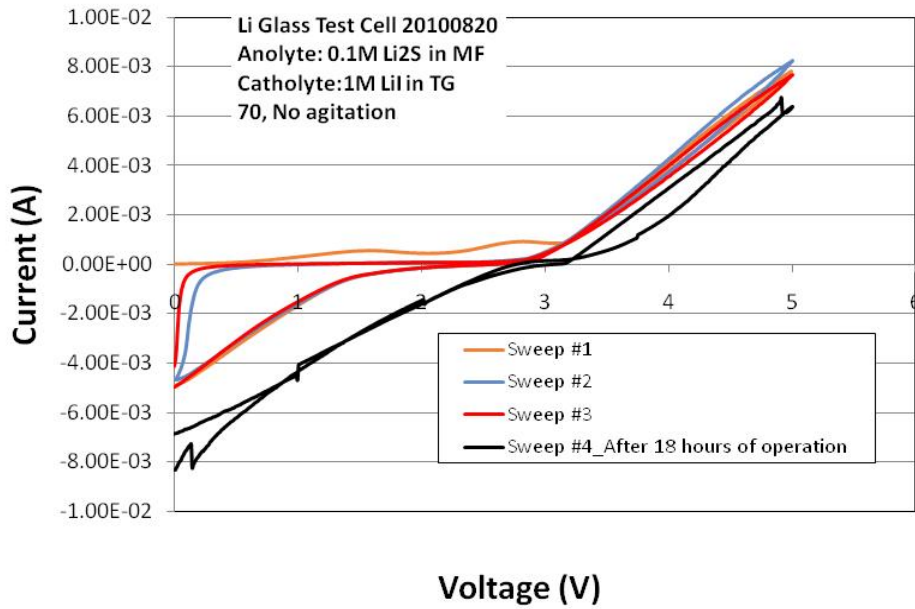


Figure 14. Cyclic voltammogram scans for Li Glass Test Cell 20100820

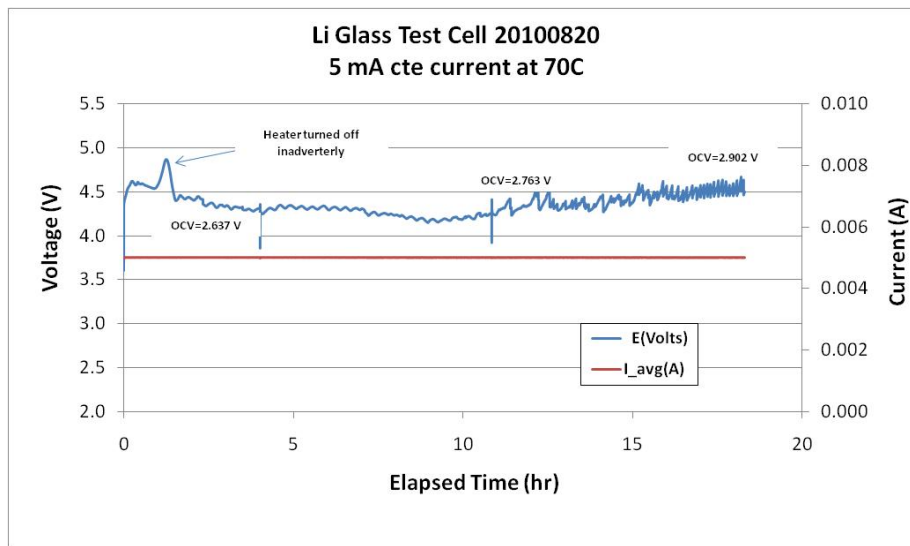


Figure 15. Operating voltage versus elapsed time at 5 mA for Li Glass Test Cell 20100820

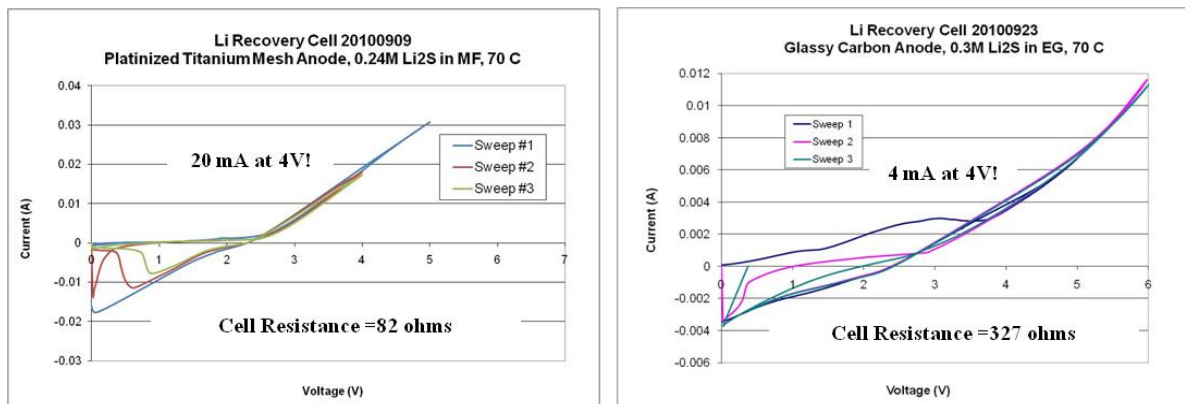


Figure 16. Cyclic voltammogram scans for Li_20100909 Test Cell with 0.24M Li_2S + MF anolyte [A] and for Li_20100923 Test Cell with 0.3M + EG anolyte [B]

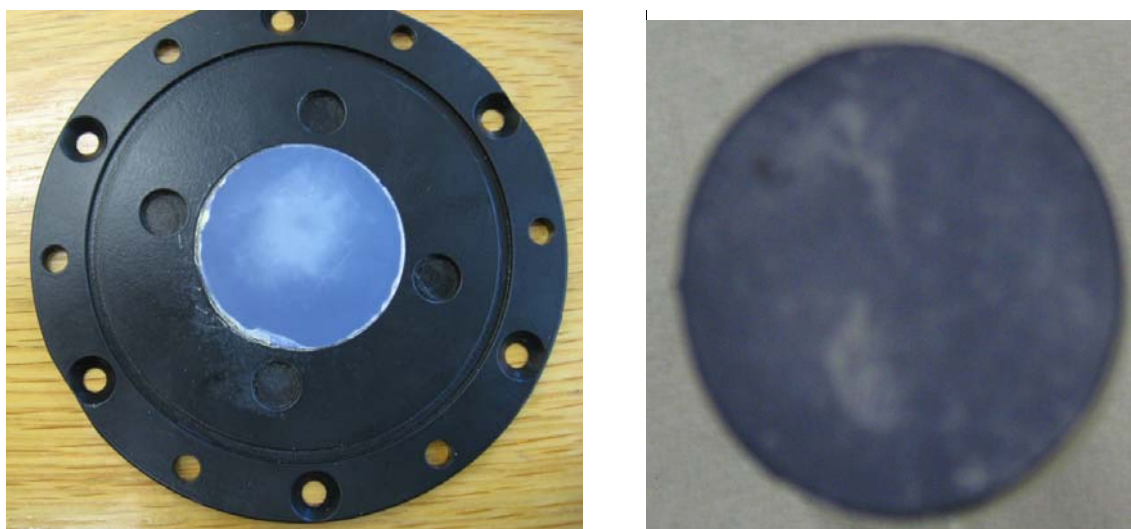


Figure 17. Anode side of LiSICON 45B membrane from Li_20100901 Test Cell [A] and from Glass Test Cell 20100929 [B]

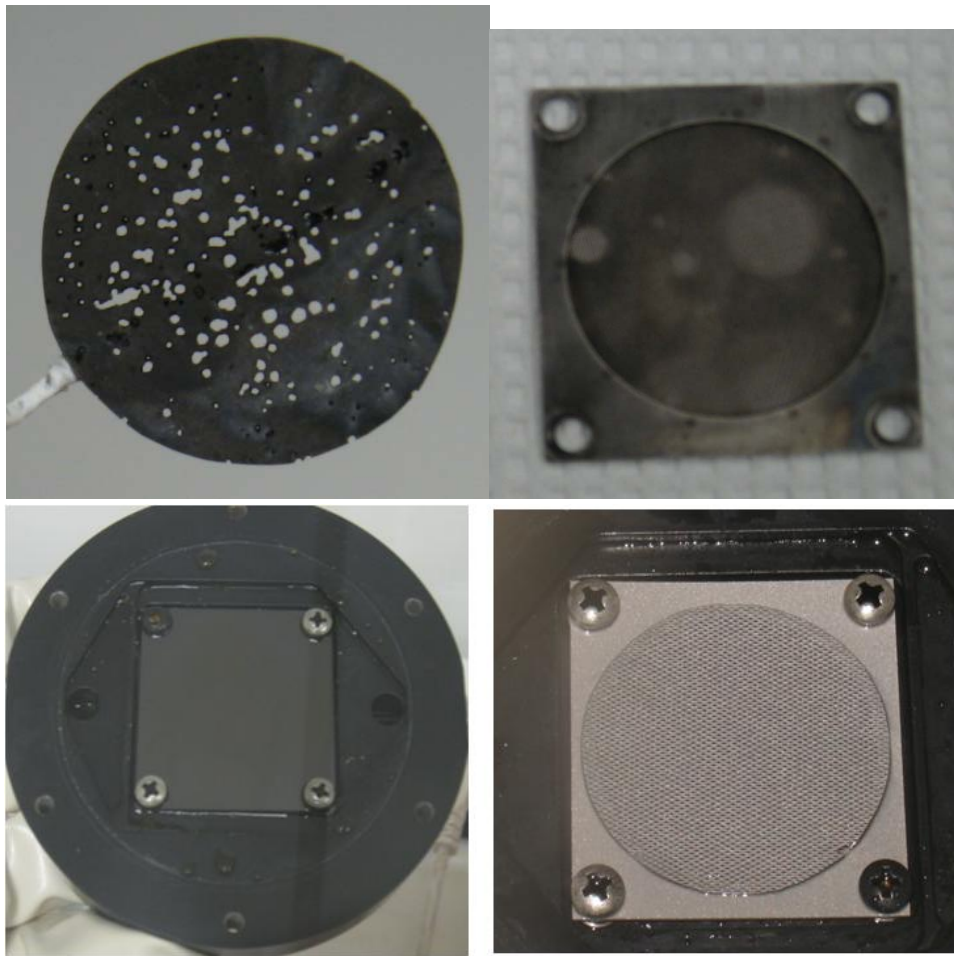


Figure 18. Corroded Titanium anode electrodes used in lithium recovery cells [A] and [B], Glassy carbon electrode [C], and Platinized Titanium mesh electrode [D]

Task 4.0 – Analysis

Subtask 4.1 – Develop upgrading process model

Ceramatec shall evaluate several process variables in Task 2 which will impact the effectiveness of impurity removal, saturation, coking, and alkali metal utilization. In addition, the shale oil source and initial composition is likely to be a factor. Extent of hydrogen donation gas added and presence of hydrotreating catalyst will affect the extent of upgrading. A preliminary model based on the data from Task 2 will be constructed.

No progress on this task to date. Plan to begin in the 5th quarter.

Subtask 4.2 – Develop electrolysis process model

Ceramatec shall analyze data from Task 3 and a performance model will be developed. Various factors such as membrane thickness, type of alkali metal, electrode configuration and cell design would be included in the model considerations.

No progress on this task to date. Plan to begin in the 5th quarter.

Subtask 4.3 – Preliminary cost analysis

The Recipient shall incorporate the models from Subtasks 4.1 and 4.2 into a preliminary cost model. Based on the preliminary cost analysis, a selection will be made between sodium and lithium as the most promising alkali metal for further pursuit in Phase 2.

No progress on this task to date.

Task 5.0 – Reporting

The 4th Quarterly Report is presently submitted.

CONCLUSION

Our conclusion at this point is that levels of both sulfur and nitrogen can be removed from shale oil with the process tested. More optimization is required. So far process has been more effective with shale oil than with Heavy Oil. Sodium results appears to be more effective than lithium in the upgrading process.

COST STATUS

The monthly costs of the 4th quarter are shown in Table 7, along with the projected costs stated in the Project Management Plan.

Table 7. Project costing profile for the 4th Quarter

	Jul-10		Aug-10		Sep-10		Q4		
	Projected	Actual	Projected	Actual	Projected	Actual	Projected	Actual	
Direct Labor		23,900.78		25,167.69		22,977.77		72,046.24	
Benefits	32%	7,648.25		8,053.66		7,352.89		23,054.80	
Overhead	41%	9,799.32		10,318.75		9,420.89		29,538.96	
Total Burdened Labor		41,348.35		43,540.10		39,751.55		124,640.00	
Direct Materials / Spec Test		31,448.57		48,587.12		30,137.80		110,173.49	
Equipment								-	
Travel		1,407.61				-		1,407.61	
Subtotal		74,204.53		92,127.22		69,889.35		236,221.10	
G&A	29%	21,519.31		26,716.89		20,267.91		68,504.12	
Total monthly		77,646.32	95,723.84	82,998.66	118,844.11	79,387.24	90,157.26	240,032.22	304,725.22

Our costs in the 4th quarter were higher than the projection because there was a lag in ordering equipment early in the project that carried through. Overall the project is behind in spending by approximately 7% over the first 12 months.

Figure 10 shows a plot of the total monthly costs and the initially projected costs versus time and figure 11 shows the cumulative monthly costs versus time. Also shown in figure 11 is the fraction of actual over planned cumulative expenses.

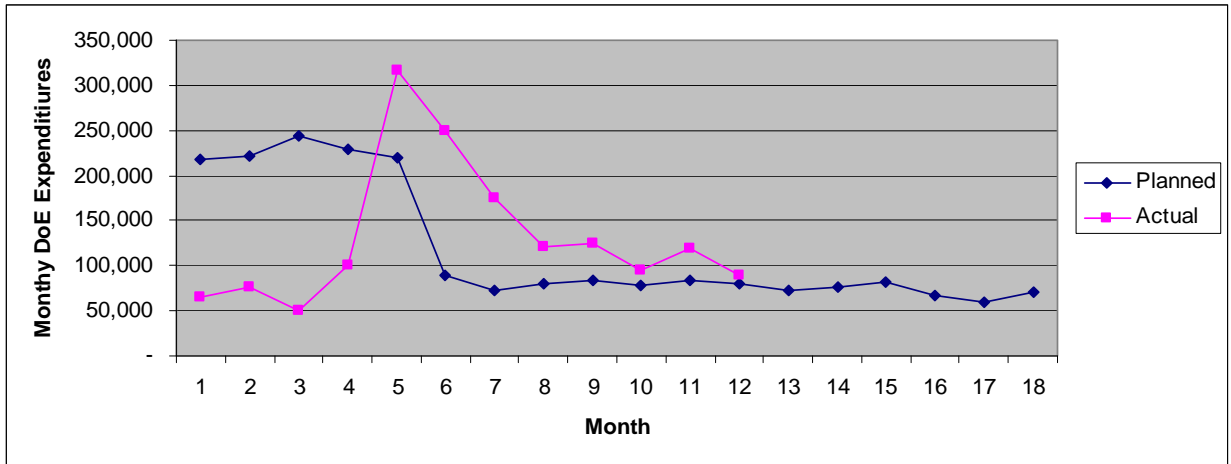


Figure 19: Projected and actual monthly costs over time

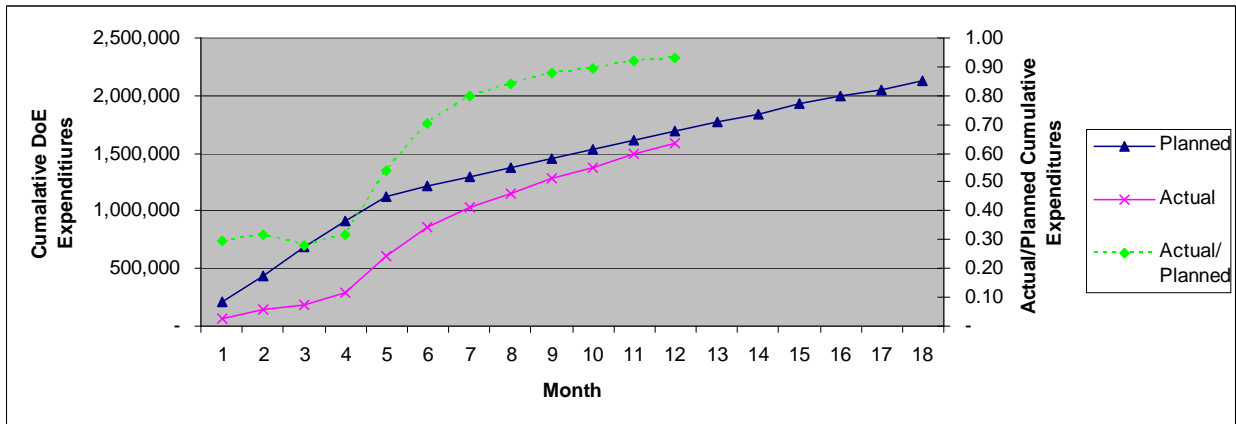


Figure 20: Projected and actual cumulative costs over time

MILESTONE STATUS

Table 8: Milestone log for 3rd Quarter

Milestone No.	Task / Sub-task	Project Milestone Description	Planned Start Date:	Planned End Date:	Actual Start Date:	Actual End Date:	Comments
1	1	Updated PMP	9/29/09	10/29/09	9/29/09	10/26/09	
2	2.1	Analytic capability established	9/29/09	3/1/10	9/29/09	3/23/10	Analytical capability has been established as stated in the PMP. Operators have been trained on GC. ICP and CHNS are operational
3	2.2	Complete upgrading exp. Setup	9/29/09	3/29/09	9/29/09	3/26/10	Upgrading set-up has been completed including HAZOP and pre-start up safety review. The reactor set up has been ready to be operational as of Friday, March 26, 2010.
4	2.3	Complete process runs	3/30/10	1/3/11	3/26/10		Process runs underway
5	3.1.1	Complete membranes for Phase 1	9/29/09	7/5/10	9/29/09	9/20/10	Membrane fabrication has exceeded demand for fabrication. Mechanical characterization was complete on September 20, 2010.
6	3.3	Cells ready for operation	4/13/10	2/28/11	4/13/10		Cells were ready for operation on time. Initial cells testing began running 4/26/10 when sufficient sodium polysulfide was synthesized.
7	4.3	Preliminary cost model complete	2/8/11	3/14/11			

Milestone 5 was scheduled for completion in the 3rd quarter but is being pushed out to the 5th quarter. The delay was necessary to bring the membranes to an improved level of leak tightness before characterizing in terms of physical properties.

ACCOMPLISHMENTS

- ✓ Reactor tests with Lithium have begun with encouraging results
- ✓ Reactor tests with methane have begun with encouraging results
- ✓ Mechanical strength tests were performed on Nasicon and Lisicon disks
- ✓ Lithium has been recovered from cells stripping metal from lithium polysulfide through a Lisicon membrane

PROBLEMS OR DELAYS

Our Perkin Elmer CHNS analyzer has been unsatisfactory. We have ordered a LECO analyzer as a replacement. In the meantime samples have been sent to an outside lab for analysis. **PROD-**

UCTS

No products to report at this time.

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

13131 Dairy Ashford, Suite 225
Sugar Land, TX 77478

1450 Queen Avenue SW
Albany, OR 97321-2198

2175 University Ave. South
Suite 201
Fairbanks, AK 99709

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