

# Oil & Natural Gas Technology

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## Quarterly Report April 2011 – June 2011

### Post Retort, Pre Hydro-treat Upgrading of Shale Oil

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## 1. EXECUTIVE SUMMARY

In the 7<sup>th</sup> quarter considerable progress was made. Liquid yields were found to rise with increasing pressure. A new impellor was changed into the reactor to improve gas/liquid interaction. On the electrolysis side, NaSICON appears to be very stable in this application. A cell has been running continuously at the target current density for over 1000 hours producing molten sodium with no change in performance. Salts from the reactor process have been dissolved in our anolyte solvent and found to yield a conductive solution from which nearly all the sodium was electrolyzed. Also, for the first time, assembled a NaSICON tube for utilization in the electrolysis process of this application. Our results to date were presented at the Gas&Oil EXPO & Conference in June 2011. The work was also presented to Dr. Ogunsola in DC. During June, twenty four liters of Cold Lake Bitumen were shipped to Ceramatec from Imperial Oil in Canada to be tested in our process. These test results will complement the results from Oil Shale and Heavy Oil.

## **2. PROGRESS, RESULTS AND DISCUSSION**

### **2.1 Task 1.0: Project Management Plan**

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

### **2.2 Task 2.0: Upgrading Development**

It is explained in detail in 6<sup>th</sup> Quarterly report.

### **2.3 Task 3.0 – Electrolysis Development**

It is explained in detail in 6<sup>th</sup> Quarterly report.

### **2.4 Task 4.0 – Analysis**

It is explained in detail in 6<sup>th</sup> Quarterly report.

## **Budget Period 2**

### **2.5 Task 5.0 – Upgrading Development**

#### **2.5.1 Subtask 5.1 - Analysis lab upgrade**

*The Recipient shall add the capability to further characterize the shale oil in terms of heavy metals, aromatics and other characteristics important to assessing the quality of the upgraded stream to the analysis laboratory. For example the following addition/capability is planned: a Fluorescence Indicator Absorption (FIA) apparatus for composition analysis (The determination of the total volume % of saturates, olefins, and aromatics) (e.g. Koehler Instruments \$10 K) (ASTM: D1319)*

Ceramatec is evaluating the need for this equipment and has not yet ordered.

#### **2.5.2 Subtask 5.2 – Upgrading reactor & separation set-up**

*The Recipient shall upgrade the reactor size and install a reactor in the range of 2-10 liters. A data acquisition system to control the variables and monitor output shall be provided.*

A 1.8 liter reactor has been ordered and is due to arrive early in the 8<sup>th</sup> quarter.

#### **2.5.3 Subtask 5.3 – Process runs**

*The Recipient shall obtain at least two samples of Shale Oil in sufficient quantity for the various runs planned and obtain permission to use the samples for the present study. Preferably the Recipient shall obtain samples with different origin which can be evaluated. Shale Oil shall be processed systematically according to the approved testing plan provided in the PMP.*

*Composition of shale oil shall be determined before and after the process. Up to 16 select runs shall also be characterized in terms of the oil character and chemistry.*

*The recipient shall determine the composition of shale oil using ASTM method D-291 for C, H, N elements and method D-1552 for S before and after the process. The samples shall also be analyzed using ASTM D2887 for distillation curve and ASTM D287 for API gravity measurements.*

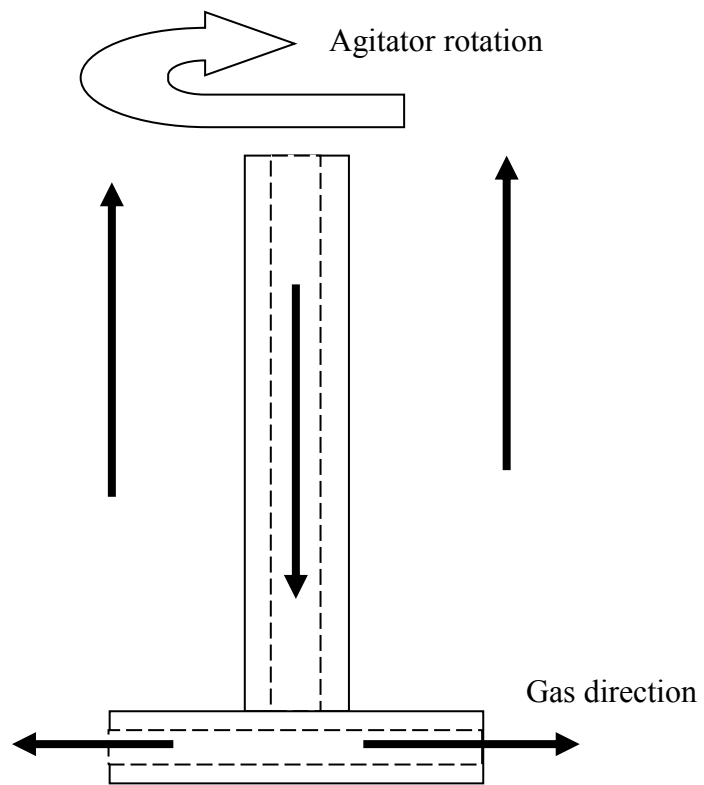
The Shale Oil processing is related to developing the process of treating shale oil, or heavy oil at elevated temperature and pressure in the presence of an alkali metal, either sodium or lithium and also a hydrogen source, either hydrogen gas or methane (natural gas) to form an oil stream with reduced 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. The investigation focus of this task during the 7<sup>th</sup> quarter was on maximizing the liquid phase yields. Also, based on results in budget period 1, all future work will be limited to the utilization of sodium as the alkali metal.

### **Experimental**

Several additional experiments were performed on upgrading of oil shale Exploration Company shale oil (OSEC) and San Joaquin heavy crude oil (SJ) aimed towards parametric optimization. All experiments were performed with using Sodium as an alkali metal, 180 gm (approx.) of oil as raw material unless otherwise specified. Temperature, pressure and modes of operation were varied to maximize the liquid phase yield. 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.

The reactor set up underwent a major improvement. The conventional agitator was replaced with Gas Entrainment Impeller. Under the influence of centrifugal force, the agitator created a vortex in the center which allows for the gas in the header space to travel through the center of the agitator rod. Figure 1 shows the schematic of operation of the agitator. Some of the experiments were performed using the new agitator.





**Figure 1: Principle of operation of gas inducing agitator**

**Table 1: List of Experiments Performed**

| Expt #          | Feed | Oil quantity (g) | Quantity of Na (g) | Upgrading gas | Time (hr) | Pressure (psig) | Temp (°C) |
|-----------------|------|------------------|--------------------|---------------|-----------|-----------------|-----------|
| 1               | SJ   | 180              | 10.6               | H2            | 2         | 1000            | 375       |
| 2               | SJ   | 180              | 10.6               | H2            | 2         | 1000            | 375       |
| 3               | SJ   | 180              | 10.6               | H2            | 2         | 1000            | 375       |
| 4               | OSEC | 304              | 9.54               | CH4           | 2         | 1000            | 250       |
| 5               | SJ   | 180              | 10.6               | H2            | 1         | 1000            | 375       |
| 6               | SJ   | 180              | 10.6               | CH4           | 2         | 1000            | 280       |
| 7 <sup>1</sup>  | SJ   | 180              | 10.6               | H2            | 2         | 1000            | 375       |
| 8               | SJ   | 180              | 10.6               | H2            | 2         | 2000            | 375       |
| 9               | SJ   | 180              | 10.6               | H2            | 2         | 1400            | 375       |
| 10              | OSEC | 250              | 8.76               | H2            | 2         | 2000            | 375       |
| 11 <sup>2</sup> | SJ   | 180              | 10.6               | H2            | 2         | 2000            | 375       |
| 12 <sup>3</sup> | SJ   | 180              | 10.6               | H2            | 2         | 2000            | 375       |
| 13 <sup>4</sup> | SJ   | 180              | 10.6               | H2            | 2         | 2000            | 375       |
| 14 <sup>5</sup> | SJ   | 180              | 10.6               | H2            | 2         | 1500            | 375       |
| 15 <sup>6</sup> | SJ   | 180              | 10.6               | CH4           | 2         | 2600            | 275       |

### **Extractive Separation of Sulfides**

The solid fraction in the reactor as well as centrifuge contains sodium sulfides along with carbonaceous residue. Sodium sulfides can be separated using solvent extraction. Same experimental apparatus was used for solvent extraction. A 5:1 mixture of solvent and solid residue was heated in the closed vessel under nitrogen. Upon cooling the solvent and solids were separated using centrifuge. CHNS contents of the final solids and initial solids were measured. The loss in sulfur content corresponds to sodium sulfides solubilized in the solvent.

### **Results and Discussions**

#### *1. CHNS*

CHNS measurements were performed on raw material samples and product samples. Compositional analysis for SJ raw material samples is shown in Table 2 below and Table 3 lists analysis results for products.

**Table 2: C, H, N, and S Composition of Raw Materials**

| Raw material | C (%) | H (%) | N (%) | S (%) |
|--------------|-------|-------|-------|-------|
| SJ           | 85.70 | 11.27 | 0.76  | 1.54  |

<sup>1</sup> Low beginning pressure (10 psi) to test the effect of suppressing the early reaction

<sup>2</sup> Fast ramping of temperature

<sup>3</sup> Repeat of earlier experiment

<sup>4</sup> Repeat to recover sulfides by methyl formamide solvent extraction

<sup>5</sup> New gas inducing impeller

<sup>6</sup> New gas inducing impeller

**Table 3: C, H, N and S Composition of Products from SJ feedstock**

| Experiment number | C (%) | H (%) | N (%) | S (%) |
|-------------------|-------|-------|-------|-------|
| 1                 | 85.36 | 10.84 | 0.74  | 0.52  |
| 2                 | 86.33 | 12.06 | 0.19  | 0.002 |
| 3                 | 86.53 | 11.88 | 0.18  | 0.03  |
| 4                 | 87.11 | 11.90 | 0.12  | 0.03  |
| 5                 | 85.12 | 11.64 | 0.38  | 0.20  |
| 11                | 85.55 | 12.29 | 0.00  | 0.00  |
| 13                | 84.37 | 11.48 | 0.34  | 0.05  |
| 14                | 84.52 | 12.08 | 0.00  | 0.01  |
| 15                | 83.97 | 12.12 | 0.00  | 0.00  |

As observed from Table 3 above, 99% sulfur and nitrogen removal has been possible with elevated pressured of hydrogen. These experiments also led to higher liquid yields.

## 2. Inductive Coupled Plasma (ICP)

Inductive coupled plasma measurements were performed for selected experiments of SJ feedstock. Table 4 shows the ICP measurements on SJ feedstock and Table 5 shows the ICP measurements on the products of SJ feedstock.

**Table 4: ICP measurements on different SJ feedstocks**

| Element/Feed    | Fe  | Al    | Cr | Cu | Mo | Si    | V   | Zn   | Ni    | Hg | As | Co |
|-----------------|-----|-------|----|----|----|-------|-----|------|-------|----|----|----|
| SJ <sup>7</sup> | 218 | 55.35 | 0  | 0  | 0  | 3.476 | 197 | 9.47 | 331.4 | 0  | 0  | 0  |

**Table 5: ICP measurement of products of SJ feedstock**

| Expt | Fe    | Al    | Cr    | Cu   | Mo    | Si    | V     | Zn    | Ni    | Hg    | As   | Co    |
|------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|------|-------|
| 2    | 0.00  | 55.23 | 1.195 | 0.00 | 1.733 | 0.532 | 1.401 | 3.998 | 7.133 | 0.00  | 0.00 | 1.635 |
| 3    | 0.308 | 96.86 | 3.303 | 0.00 | 3.385 | 1.139 | 2.654 | 6.541 | 11.07 | 0.00  | 0.00 | 1.771 |
| 4    | 0.16  | 103.5 | 2.016 | 0.00 | 0.00  | 1.338 | 0.763 | 8.158 | 10.47 | 0.00  | 0.00 | 2.326 |
| 10   | 0     | 21.72 | 3.957 | 0    | 0.342 | 0.368 | 0.724 | 5.69  | 7.423 | 4.276 | 13.6 | 0.025 |

<sup>7</sup> Reading of zero metal content corresponds to undetectable.

## **2.6 Task 6.0 –Post reactor / pre electrolysis separation steps**

*The Recipient shall set up a reactor and centrifugal separator to separate the sodium / lithium sulfide salts and heavy metals from the upgraded shale oil. Individual separation schemes shall be designed for the removal of salts, heavy metals and metal mercaptides shall be identified. The separated products including the upgraded oil, metal mercaptides, metal polysulfides shall be chemically analyzed for efficiency of separation. The separated oil shall be analyzed for CHNS content, metals content, API gravity and boiling point distribution. Further an industrially suitable separation that can be economically scaled up shall be identified and designed*

### **2.6.1 Subtask 6.1-Separations Experimental set up**

*The recipient shall assemble an experimental set up that shall include a reactor assembly to treat the upgraded oil (Task 5.0 above) with H<sub>2</sub>S and the balance of apparatus as described in PMP.*

### **2.6.2 Subtask 6.2-Separation of metal Salts**

*The recipient shall implement four different separation schemes with the following variables and parameters:*

*H<sub>2</sub>S partial pressure*

*H<sub>2</sub> partial pressure*

*Operating temperature*

*Operating pressure*

*The operating procedure for these separation schemes is detailed in PMP. The preferred separation technique shall be chosen upon investigation of the proposed schemes.*

### **Sodium Sulfide Separation**

Over the past several months, methylformamide has been concluded to be a good solvent for dissolution of model sodium sulfides for electrolysis section. In this quarter, work was performed to extract sodium sulfides formed in the upgrading reactor. 5:1 ratio was mixed in the reactor and the mixture was heated to 200 °C. Upon cooling, the solvent was separated from the remaining solids by centrifugation. The solids were analyzed by CHNS. IN experiment number 13, approximately 90% sulfur was removed (4.28% beginning sulfur content to 0.42% final sulfur content in the solid phase).

### **2.6.3 Subtask 6.3-Separation of metal mercaptides**

*In order to separate the oil soluble mercaptides the mixture shall be subjected to acid treatment using dilute mineral acids. The acid treated mixture shall be separated and the acidic aqueous phase shall be analyzed using CHNS analyzer.*

## 2.6.4 Sub-task 6.4 - Design

*The overall separation scheme shall be designed to include H<sub>2</sub>S recycle loop to the separation reactor, sulfur recycle, purge and chosen separation scheme.*

## 2.7 Task 7.0 - Electrolysis development

*To reduce the overall cost of the upgrading process, an electrolysis process will be developed to regenerate sodium or lithium from the respective polysulfide. The process will feature ceramic ion conductive membranes developed at Ceramatec. The energy cost to regenerate the alkali metals from the polysulfide is expected to be about half that of producing the metals from their respective chlorides.*

### 2.7.1 Subtask 7.1 – Membrane fabrication

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

#### **Ionic Conductivity Measurement of NaSICON GY**

Given the impressive performance results of sodium recovery test cell *Na\_molten\_20110504* (see Long Term Test Results in Section 2.7.4), we decided to measure the ionic conductivity of NaSICON GY samples, whose outer surfaces have also been grounded down to remove the outer zirconia-rich layer. Two specimens of the material were prepared by pressing and sintering NaSICON GY powder into 8 mm thick and 0.5 inch in diameter parts. Then, one millimeter of material was removed on each of the outer surfaces to remove the zirconia rich skin. XRD analysis of the samples confirmed that the composition of the outer surfaces was pure phase NaSICON GY material. Finally, 3.5 mm in diameter overlapping gold electrodes were sputtered on both sides of the membrane. The ionic conductivity of the samples was measured by AC Impedance Spectroscopy. Our target was to measure the conductivity from room temperature up to 150°C. However, the material turned out to be so conductive that the resistance of the samples, at temperatures over 75°C, was too low for the instrument to properly resolve the measurement. Figure 2 shows the AC impedance scans for one of the samples at room temperature [A], at 50°C [B], and at 75°C [C]. Figure 3 displays the measured ionic conductivities for the two specimens. The average activation energy and intercept, from the measured data, are equal to 0.284 eV and 184778 S-K/cm, respectively. These samples are approximately one order of magnitude more conductive than previously reported data in 2008 (see Figure 3). At this time is unknown whether this large increase in the measured conductivity is entirely due to the elimination of the zirconia skin or whether other unknown factors might play a role. Figure 3 also shows the ionic conductivity prediction from 75°C up to 130°C using the calculated intercept and activation energy. The predicted ionic conductivity, at the preferred cell operating temperature of 130°C, is equal to 124 mS/cm.

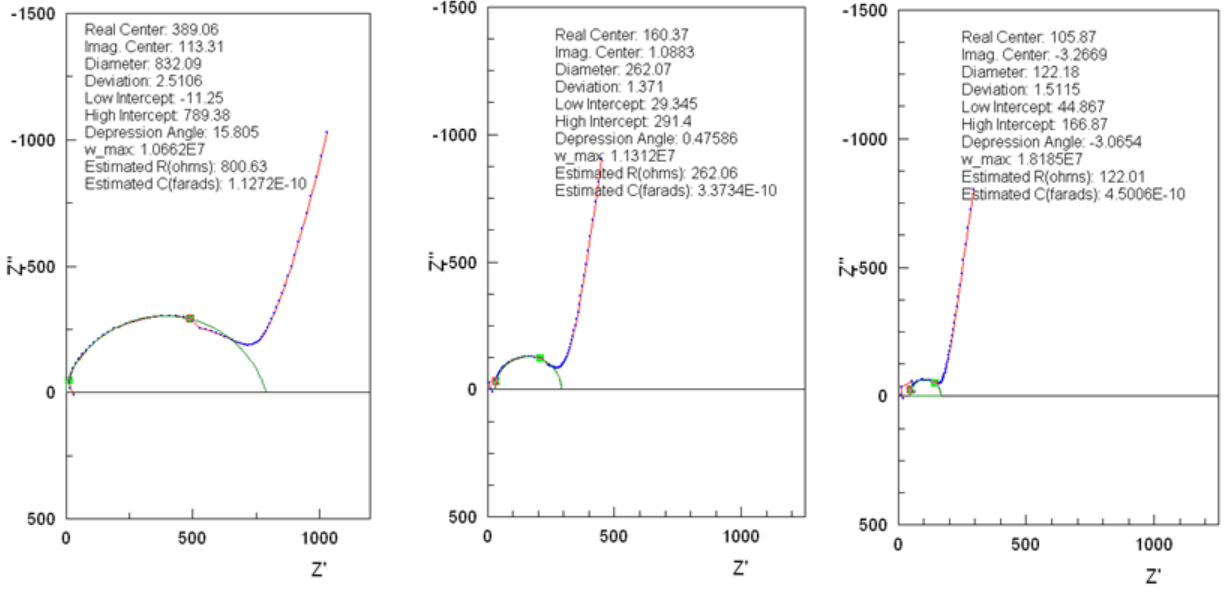


Figure 2: AC Impedance Spectroscopy scans of NaSICON GY sample at room temperature [A], 50°C [B], and 75°C [C]

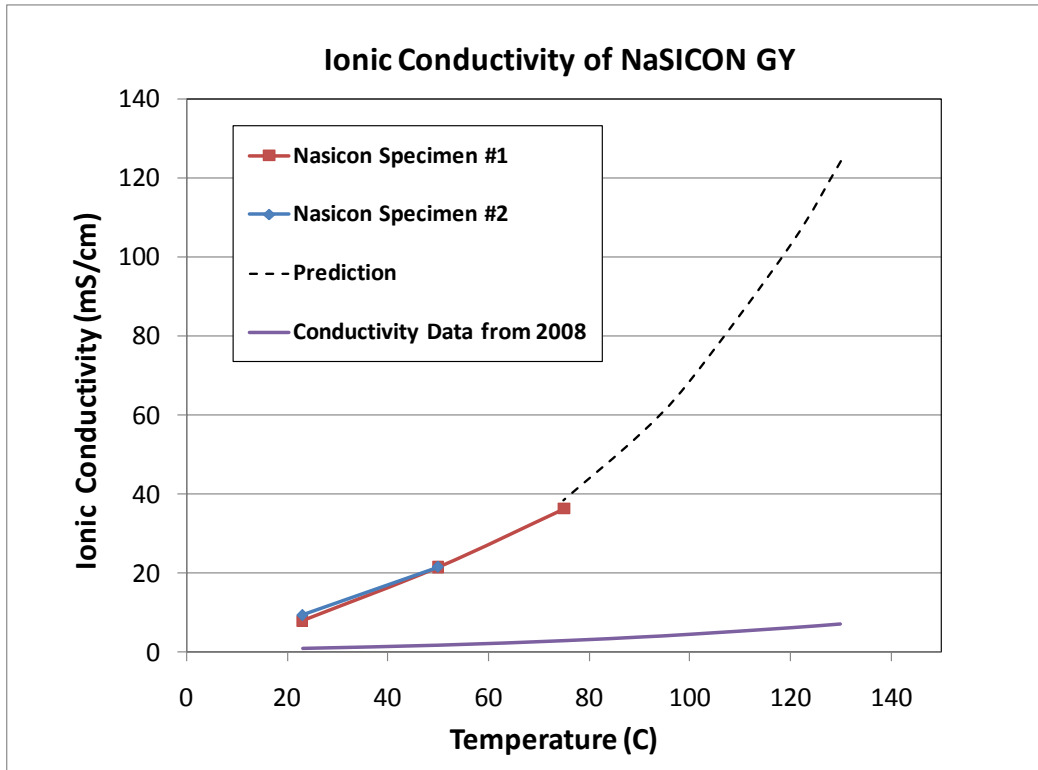


Figure 3: Measured and predicted ionic conductivity of NaSICON GY versus temperature

### **2.7.2 Subtask 7.2 – Seal testing**

*The Recipient shall down select an optimum seal approach based on the knowledge acquired during the seal testing effort in Phase 1 of the project. The seal shall have the best metal polysulfide and alkali metal compatibility in the temperature range of interest. Further testing shall be conducted to understand the long term performance of the seal.*

Two new glass powders (ASF1098 and BNL115BB-N) have been acquired from Asahi Glass Corporation in an effort to develop a seal between alumina and NaSICON that is chemically inert to solutions of sodium hydroxide in organic solvents. The two new glass compositions do not contain silica, which we believe reacts with sodium hydroxide. The basic compositions of both of them are boron oxide, zinc oxide, and bismuth oxide. The Coefficients of Thermal Expansion (CTE) of ASF1098 and BNL115BB-N are 5.3 and 7.3 ppm, respectively. Unfortunately, all the attempts made to bind alumina to NaSICON disks with these glasses have been unsuccessful. The NaSICON disks tend to delaminate from the alumina during the firing step. In the next quarter, we will try to use these materials to form a chemically resistant coating over our standard silica based glass seal, rather than using them as sealants themselves.

### **2.7.3 Subtask 7.3 – Cell design and set-up**

*The Recipient shall improve and scale-up the existing cell design based on the operational knowledge acquired during Budget Period I of the project. The cell shall be easily scalable and shall incorporate all the features necessary to recuperate the alkali metal from the anode compartment on a continuous or semi-continuous basis. A comparative study between designs using tubular and planar membranes shall be conducted to determine the most favorable cell geometry. The design shall have all upstream equipment necessary to process the molten alkali polysulfide salts coming from the separation step of the oil upgrade process. The design shall have all downstream equipment needed to recuperate sulfur from the outlet anolyte stream.*

### **Expansion of the Electrolysis Laboratory**

We have expanded our Electrolysis Laboratory by adding a new glove box (Figure 4[A] and [B]). The glove box will be dedicated exclusively to run electrolysis cells (up to three simultaneously). In addition, we have installed a new PSA based gas drying system to maintain very low moisture content inside the glove boxes. The system has been piped to allow a maximum of three glove boxes for future expansions (Figure 5).



Figure 4: . Front of view of new 41ft<sup>3</sup> Plas-Lab acrylic glove box [A]. Side panel with feed through connections for heaters AC power, cells DC power, and type T thermocouples [B].

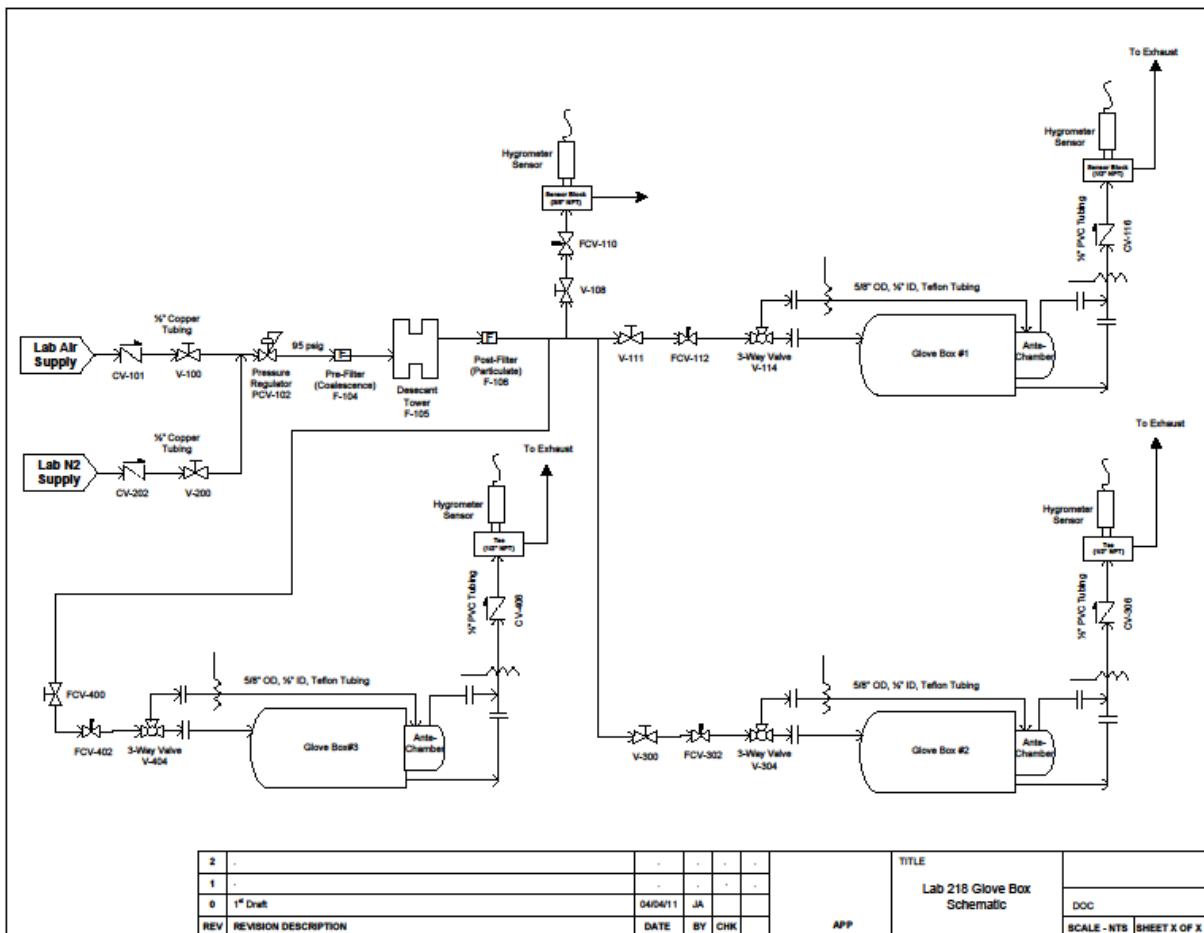
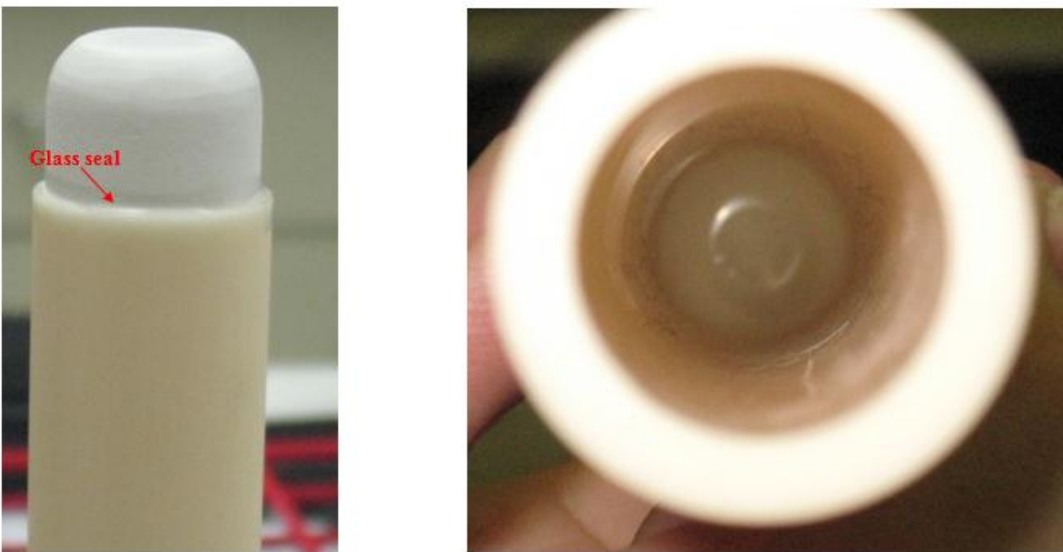


Figure 5: Schematic of the new gas drying system installed in the Electrolysis Laboratory

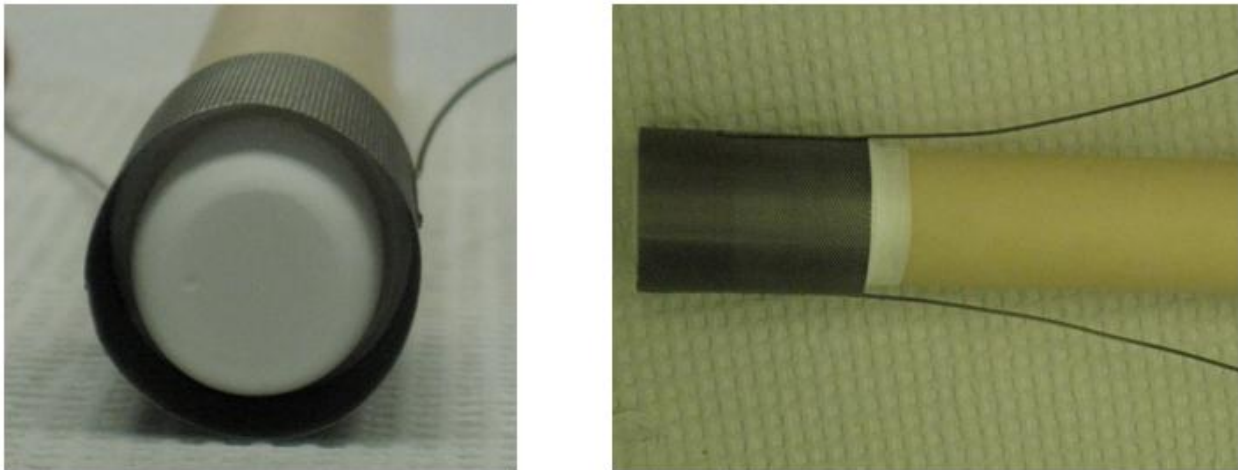


## Electrolysis Test Cell Design

In this quarter we have assembled a cell using a NaSICON GY tube with a closed-end cap. The NaSICON part was sealed to a 1" OD alumina tube using our standard glass seal material. Figure 6[A] and [B] shows two photographs of the outside and inside sides of the NaSICON-alumina tube assembly. The seal was hermetic to the helium leak tight check test. Then, a cylindrical coaxial anode electrode made of Titanium expanded mesh was attached to the alumina tube. A spacer made of PTFE tape was used to set a 3.5 mm gap between the electrode and the NaSICON solid electrolyte tube. Two Titanium wires were spot welded to the mesh as current collectors. Figure 7 shows the cell assembly. In this arrangement, the active area of the cell is approximately equal to  $6.7 \text{ cm}^2$ . The cell will be tested during the next quarter.



**Figure 6: Outside [A] and inside [B] sides of the NaSICON-alumina tube assembly sealed with the standard glass seal material**



**Figure 7: Bottom [A] and side [B] views of the tubular electrolytic cell**

## **Study of Anolyte Solvents**

Four new organic solvents have been identified and tested as potential anolytes for the sodium recovery cells. These solvents were Dimethylsulfoxide (DMSO), 1-Ethyl-3-Methylimidazolium tetrafluoroborate (ionic liquid), 1,3-Cyclohexanediol, and 1,4-Butanediol. The adequacy of these solvents was studied in terms of their stability in the presence of sodium metal, sodium polysulfide solubility, and ionic conductivity.

Table 6 lists the results of the tests. For comparison purposes, we have also included the solvent currently used in the sodium recovery test cells (MF). Clearly the only solvent out of the four studied, which is comparable to MF, is DMSO. The two polyalcohols tested, although they have good sodium sulfide solubility, have extremely low ionic conductivities. On the other hand, the ionic liquid has high ionic conductivity but very low solubility. Despite the fact that the conductivity of DMSO is roughly half than MF (see Figure 8), DMSO is less reactive with sodium metal. Based on these results, we decided to assemble and test a sodium recovery test cell using  $\text{Na}_2\text{S}_4$  dissolved in DMSO as anolyte system. The test results have been reported in Subtask 2.7.4.

**Table 6: Properties of the anolyte solvents studied**

| <b>Solvent</b>      | <b>Na<sub>(m)</sub> Stability</b> | <b>Na<sub>2</sub>S<sub>4</sub> Solubility<sup>+</sup><br/>(% wt.)</b> | <b>Ionic Conductivity<sup>++</sup><br/>(mS/cm)</b> |
|---------------------|-----------------------------------|---|--|
| 1,4-Butanediol      | Very slow reaction                | 4.4   | 0.0009   |
| Ionic Liquid        | Very slow reaction                | 0.14  | 13.47  |
| 1,3-Cyclohexanediol | Very slow reaction                | 10.7  | 0.01   |
| DMSO                | Slow reaction                     | 14.3  | 5.43   |
| MF                  | Fast reaction                     | ~15-20  | 15   |

<sup>+</sup> Solubility measured at room temperature. <sup>++</sup> Ionic conductivity of saturated  $\text{Na}_2\text{S}_4$  solution measured at room temperature

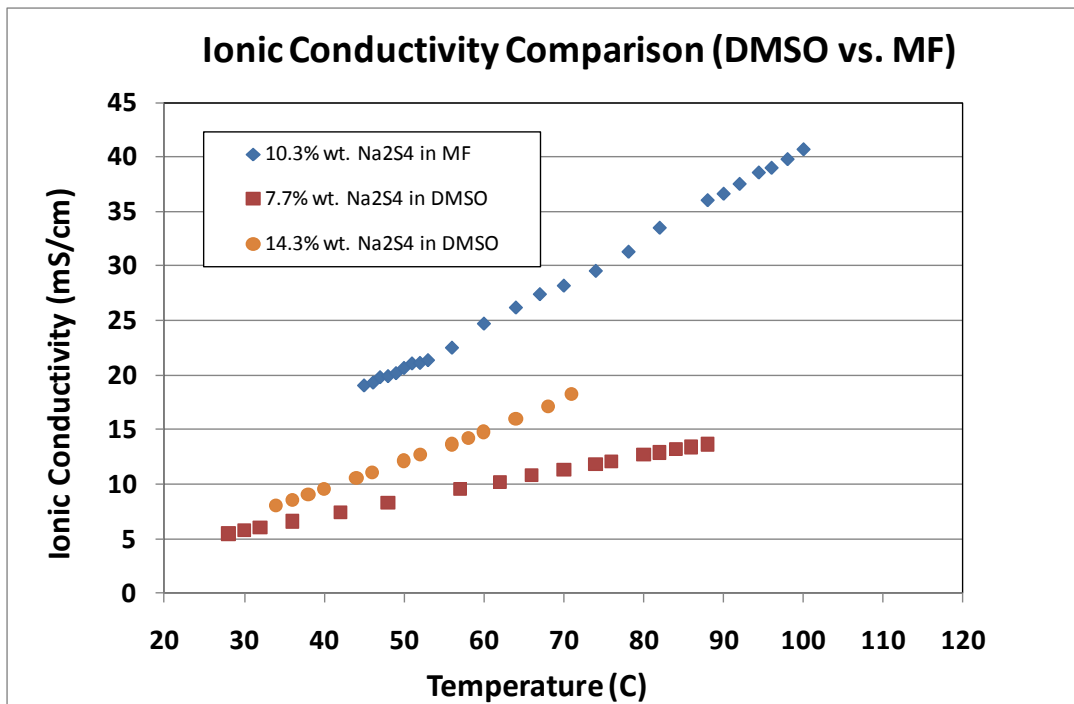


Figure 8: Ionic conductivity comparison between solutions of Na<sub>2</sub>S<sub>4</sub> in MF and in DMSO

#### 2.7.4 Subtask 7.4 – Cell operation

*The Recipient shall assemble and operate cells of different designs under various conditions including variation of the current density, electrode gap, temperature, electrolyte composition, and alkali metal. All tests in Budget Period 2 shall be conducted with cells using membranes of planar geometry. The cells shall be able to operate from a variety of polysulfide sources, including potentially impure alkali polysulfide mixtures synthesized from processed shale oil samples. A large number of different test condition combinations shall be conducted as defined in the test matrix of the PMP. Cell operation shall be monitored and streams composition characterized to determine the cell's efficiency.*

#### Sodium Metal Production Test Cell Results

A study was started to investigate the production of sodium metal via electrolysis of anhydrous sodium hydroxide at low temperature. The first step was to find a stable organic solvent to dissolve the sodium hydroxide. The desired properties of the anolyte solvent need to be high solubility, high ionic conductivity, high boiling point, and non-reactivity with sodium hydroxide. A number of solvents were screened out. We found out that solvents from the amide group, which were useful with the sodium polysulfide recovery cells, react with NaOH. Other solvents such as glymes and sulfoxides, although stable in the presence of NaOH, were only able to dissolve a very small amount of caustic. At the end, only two solvents (1,2-propanediol and ethylene glycol), out of the group screened, seemed to meet the requirements. Figure 9 shows the ionic conductivity of the anolyte solutions versus temperature. Both solutions are approximately 12%wt. in NaOH. As shown in the figure, the solution in EG is approximately 3.5 times more conductive than in 1,2-propanediol at a temperature of 100°C.

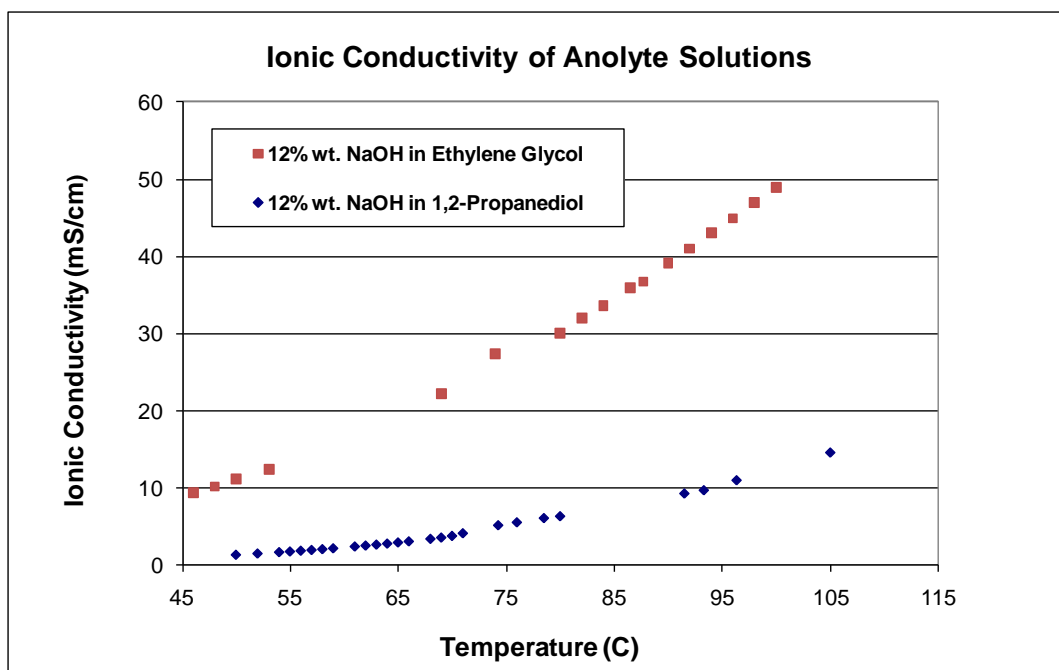


Figure 9: Ionic conductivity comparison of NaOH solutions in Ethylene Glycol and 1,2-Propanediol

In this reporting period, four sodium production test cells have been assembled and run (Table 7). The test cells are of similar design as the sodium recovery test cells used to recover sodium from sodium polysulfides. The anolyte consists of a solution of NaOH in EG and the catholyte is molten sodium metal. 1” inch in diameter, 0.5 mm and 1 mm thick NaSICON GY membranes were used. Platinized titanium and graphite were tested as anode electrodes. A cell’s temperature operating range of 120-140 °C was covered. The first two runs of the set were conducted at constant voltage between 5 and 6 VDC, while the last two were conducted at constant current density between 30 and 100 mA/cm<sup>2</sup>.

Table 7: Sodium production test cells assembled and run during the reporting period

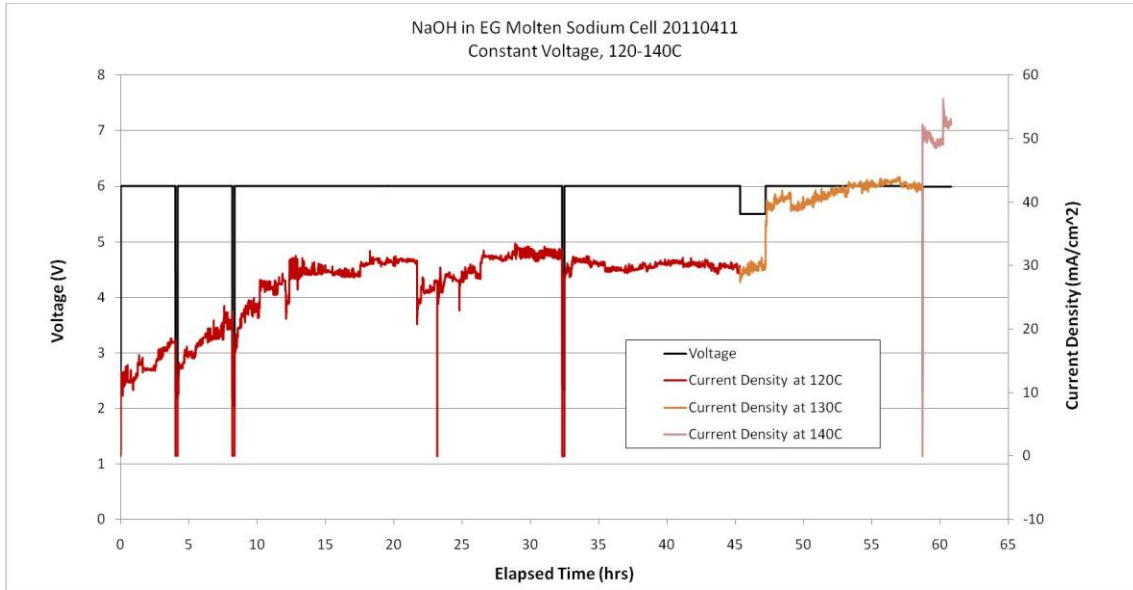
| Cell ID#                   | Anolyte                          | Anode Electrode  | Membrane  | Catholyte | Cathode Electrode                   | Seal Type          | Operating Conditions   |
|----------------------------|----------------------------------|--|---|-----------|-------------------------------------|--------------------|--|
| NaOH_EG_Molten_Na 20110406 | 11.2% w/w NaOH in Ethyleneglycol | Platinized Ti Mesh, 28.6 mm diameter, 3 mm from membrane.                                | NaSICON GY (1 mm thick)                                 | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=120±2C<br>Anolyte agitation, 500 rpm<br>Constant Voltage=5-6 VDC                         |
| NaOH_EG_Molten_Na 20110411 | 9.49% w/w NaOH in Ethyleneglycol | Graphite with Teflon shielded Ti connecting wires, 25.4 mm diameter, 5 mm from membrane. | NaSICON GY (1 mm thick), Same membrane used in 20110406 | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=120-140±0.1C<br>Anolyte agitation, 500 rpm<br>Constant Voltage=6 VDC                     |
| NaOH_EG_Molten_Na 20110418 | 6.5% w/w NaOH in Ethyleneglycol  | Graphite with Teflon shielded Ti connecting wires, 25.4 mm diameter, 5 mm from membrane. | NaSICON GY (0.5 mm thick)                               | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=130-140±0.1C<br>Anolyte agitation, 500 rpm<br>Constant Current=50-100 mA/cm <sup>2</sup> |
| NaOH_EG_Molten_Na 20110420 | 6.5% w/w NaOH in Ethyleneglycol  | Graphite with Teflon shielded Ti connecting wires, 25.4 mm diameter, 5 mm from membrane. | NaSICON GY (0.5 mm thick)                               | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=130±0.1C<br>Anolyte agitation, 500 rpm<br>Constant Current=30-50 mA/cm <sup>2</sup>      |

Figure 11 displays cell voltage versus run time at 50, 75, and 100 mA/cm<sup>2</sup> for Test Cell *NaOH\_EG\_Molten\_Na\_20110418*. The cell was started at 100 mA/cm<sup>2</sup> with the voltage reading around 4.5 V. However within six hours into the test, the voltage started to increase very quickly reaching the 6 V cut-off value in 9 hours. Then, the current was reduced to 75 mA/cm<sup>2</sup>. Similarly, the voltage remained relatively constant for an initial 9-10 hour period until it started a quick increase with a similar slope as the previous current density level. Finally, the current was further decreased to 50 mA/cm<sup>2</sup>. This time the voltage started to increase right from the beginning after the change though at a slower rate than the two previous instances. The test was finished after 40 hours of total operation. Post-test evaluation of the membrane and electrodes did not provide a clear cause that could explain the quick polarization of the cell. Similar results were obtained with the test of cell *NaOH\_EG\_Molten\_Na\_20110420* (Figure 12) at even lower current densities (30-56 mA/cm<sup>2</sup>).

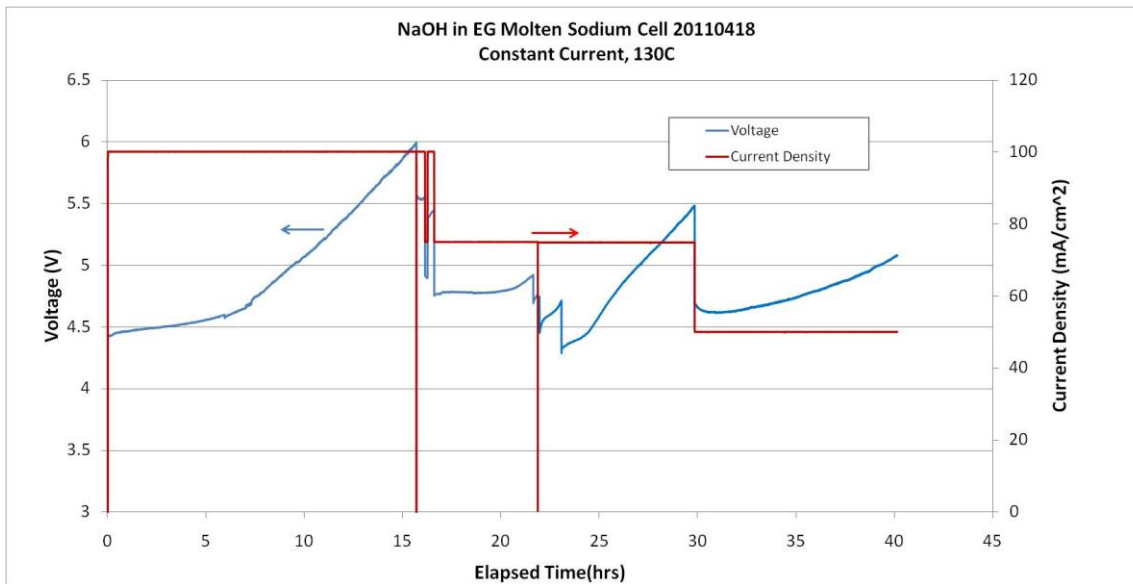
The effect of temperature on cell's performance was studied during test cell run *NaOH\_EG\_Molten\_Na\_20110411* at a constant voltage of 6 VDC. Figure 10 shows a current density increase of approximately 10 mA/cm<sup>2</sup> per every 10°C increase in temperature within the range 120-140°C. At 140°C, the measured current density was approximately 50 mA/cm<sup>2</sup>. This current density increase is due to the decrease in the overall resistance of the cell. Since the ionic conductivity of the anolyte solution, in this case, is significantly higher than that of the Na-SICON membrane, the resistance due to the latter component dominates the total resistance of the cell. Therefore, the observed increase in current density was mostly due to the decrease in the ionic conductivity of the membrane with temperature.

We have observed very fast degradation of the silica-boria glass material, which is used to seal the anode and cathode compartments, in our test cells. Figure 13 shows pictures of this seal for Test Cell *NaOH\_EG\_Molten\_Na\_20110411* before the test [A] and after 60 hours of operation [B]. Even though the seal was still leak tight after the test, the seal surface shows a rough and porous texture versus the glassy and smooth texture prior to the test. Our hypothesis is that sodium hydroxide reacts with the silica in the glass, creating pores in the structure. We have identified alternative silica-free glass compositions that will be tested in the future.

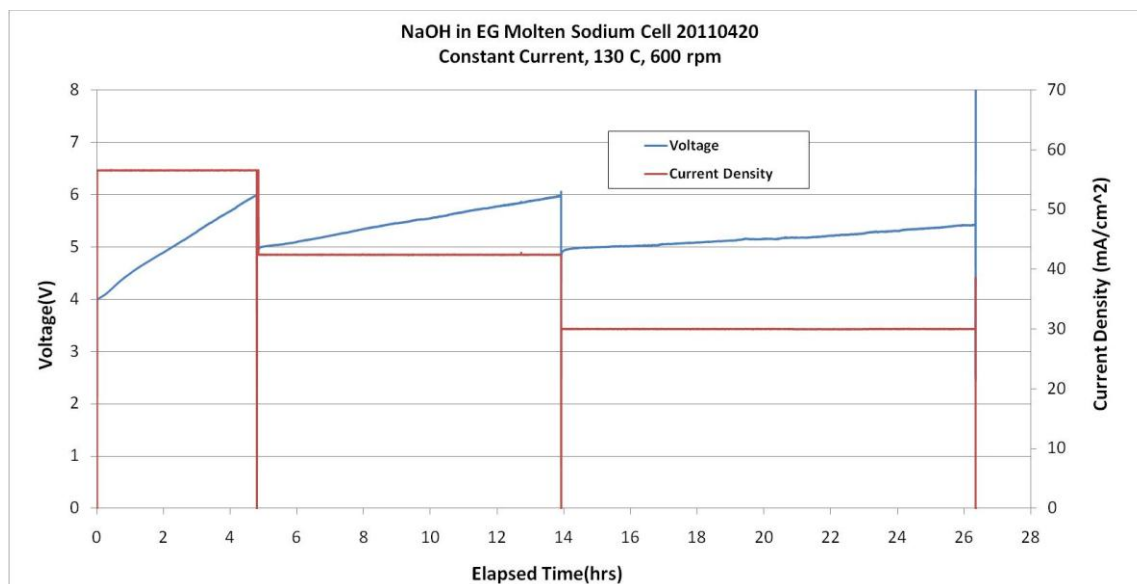
As a conclusion of these tests, we have proved that sodium metal can be produced from sodium hydroxide, dissolved in an organic solvent, at low temperature. We need to understand the cause(s) of the quick cell polarization observed in the tests. Finally, a seal that is resistant to NaOH needs to be found.



**Figure 10: Cell current density and voltage versus elapsed time at constant voltage (6 V) for Test Cell *NaOH\_EG\_Molten\_Na\_20110411*. Cell was run at temperatures of 120°C, 130°C, and 140°C**



**Figure 11: Cell voltage and current density versus elapsed time at constant current density (50, 75, and 100 mA/cm<sup>2</sup>) for Test Cell *NaOH\_EG\_Molten\_Na\_20110418***



**Figure 12: Cell voltage and current density versus elapsed time at constant current density (30, 42, and 50 mA/cm<sup>2</sup>) for Test Cell *NaOH\_EG\_Molten\_Na\_20110420***



**Figure 13: Glass seal before [A] and after [B] run of cell *NaOH\_EG\_Molten\_Na\_20110411***

## **Sodium Recovery Test Cell Results**

In these test cell runs DMSO is used as Anolyte. Test Cell *Na\_molten\_20110421* was assembled using an anolyte consisting of 7%wt. Na<sub>2</sub>S<sub>4</sub> dissolved in DMSO (Table 8). The cell was run at a temperature of 130°C. Figure 14 shows the current density and the cell voltage for this run. In run 1, the cell was operated in constant voltage mode for approximately 5 hours, initially at 5V and then at 4.5V. During this period, the current density passed through the cell varied between 60 and 90 mA/cm<sup>2</sup>. In run 2, the cell was operated in constant current mode at 50 mA/cm<sup>2</sup>. The voltage stayed relatively constant below 4 V for over 30 hours. However after this period, the cell started polarizing very quickly, reaching the 6V cutoff voltage within the next 12 hours. We noticed that there was a significant amount of solids that had precipitated out of the anolyte solution. The anolyte solution was filtered and the solids analyzed by XRD. In addition, the ionic conductivity of the filtered anolyte was measured from room temperature up to 90°C. XRD analysis confirmed that the solid precipitate was mostly sodium sulfate, whose solubility in DMSO is very limited. The sulfate anion SO<sub>4</sub><sup>-2</sup> is formed by the oxidation of the sulfoxide group S=O in the DMSO molecule. Unfortunately, DMSO is not electrochemically stable, within the voltage operating window, and it competes with the oxidation of the polysulfide ions. In this oxidation process DMSO is decomposed. To make things worse, the precipitation of sodium sulfate removes sodium ions from solution, which in turn reduces the ionic conductivity of the remaining anolyte. Figure 15 compares the ionic conductivity of the anolyte solution prior to the test and after Run 2. Basically, the conductivity dropped by a factor of three. Figure 16 shows that the overall cell resistance more than doubled after the test. Sadly, the main conclusion of the study is that despite the excellent physical properties of DMSO, including its low reactivity with sodium metal, this solvent is not electrochemically stable and therefore not suitable to be used in sodium recovery cells.

**Table 8: Properties of sodium recovery test cell *Na\_molten\_20110421***

| Cell ID#           | Anolyte                                | Anode Electrode                 | Membrane                            | Catholyte | Cathode Electrode                   | Seal Type          | Operating Conditions   |
|--------------------|--|---------------------------------|-------------------------------------|-----------|-------------------------------------|--------------------|--|
| Na_molten_20110421 | Na <sub>2</sub> S <sub>4</sub> in DMSO | Platinized Ti mesh (1.1" diam.) | NaSICON GY (1 mm thick, 0.8" diam.) | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=130C<br>Anolyte agitation<br>Cte Current=50 mA/cm <sup>2</sup> |



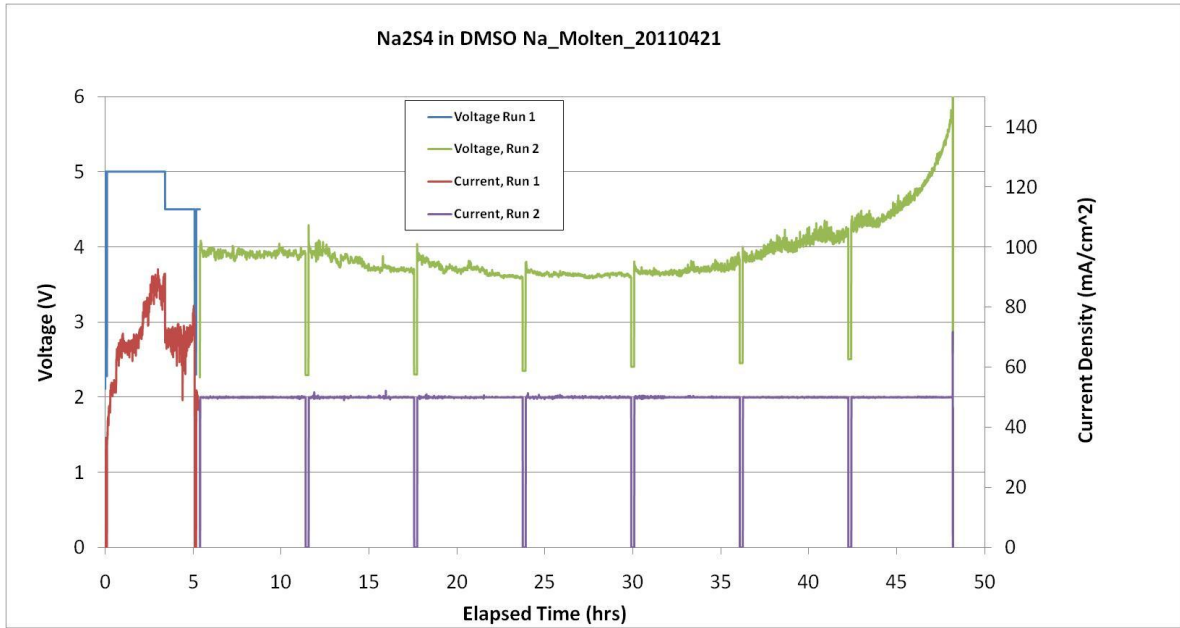


Figure 14: Current density and cell voltage for sodium recovery Test Cell *Na\_molten\_20110421*

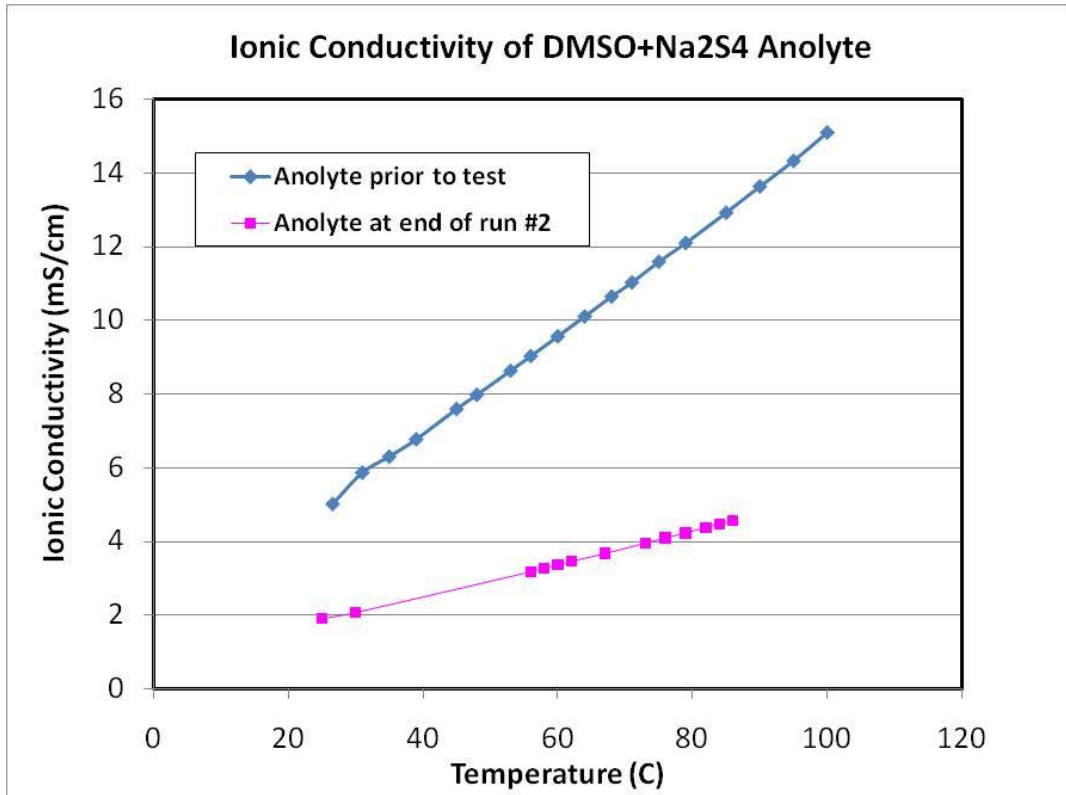


Figure 15: Ionic conductivity of anolyte solution for sodium recovery Test Cell *Na\_molten\_20110421* prior to test and at end of Run #2

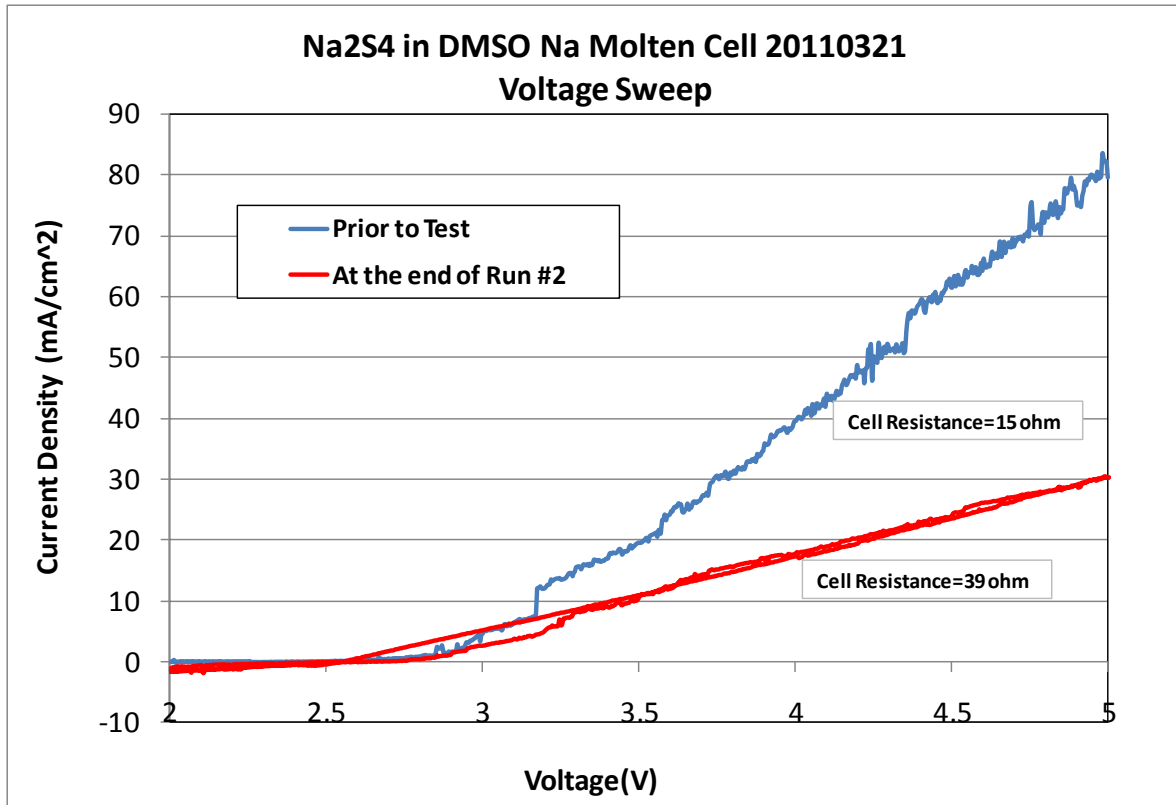


Figure 16: Voltage sweep of sodium recovery Test Cell *Na\_molten\_20110421* prior to test and at end of Run #2

### Long Term Test Cell Results

Two cells have been operated as long term tests during this reporting period. Table 9 summarizes the properties of these cells. Sodium polysulfide ( $\text{Na}_2\text{S}_4$ ) is periodically added to the anolyte in the cells to replenish the sodium as the ions are transported and reduced to sodium metal in the cathode. Cell *Na\_molten\_20110311* was started in March and completed 458 hours (19 days) of run time before failure on the anode side of the NaSICON membrane. On the other hand, cell *Na\_molten\_20110504* has been in continuous operation for 1422 hours (59 days) at a constant current density of  $60 \text{ mA/cm}^2$ . Figure 17 shows the cell voltage and the Open Circuit Voltage (OCV) during the test. Figure 18 takes a closer look at the data for the first 475 hours of operation. It can be observed the decrease in the cell's voltage after each addition of sodium sulfide. This is due to the increase in the ionic conductivity of the anolyte. Table 10 compares the performance of the two cells during the tests. The main difference between cell *Na\_molten\_20110504* and any other cell tested in the past is that the first has been assembled with a NaSICON membrane, whose outer skins (zirconia rich layer) have been removed by grinding. In Section 2.7.1, we reported an order of magnitude increase in the ionic conductivity of NaSICON samples, without the zirconia layer, as compared to membranes that had the skin. In this case, we think that this is the main reason why the operating voltage of cell *Na\_molten\_20110504* was approximately one volt lower than cell *Na\_molten\_2011031*, despite the fact that the membrane in the latter cell was 0.5 mm thinner. Operating the cell at a full 1 V lower, for the same current density, is very advantageous from the stand point of membrane and

other cell components reliability since it reduces the chance of undesired oxidation reactions and corrosion. This could explain why the NaSICON membrane in cell *Na\_molten\_2011031* failed due to corrosion (see Figure 19) only after 19 days of operation, whereas the membrane in cell *Na\_molten\_20110504* is still in perfect condition after two months of run time under similar operating conditions.

The cell's Nernst potential or OCV (Open Circuit Voltage) varied during the test between 2.1 and 2.3V with an average around 2.2V. Since the temperature is kept very uniform  $130 \pm 0.1^\circ\text{C}$ , the OCV variations are mostly due to the change in the sodium polysulfide composition and concentration in the anolyte solution. So after each addition of fresh  $\text{Na}_2\text{S}_4$  to the anolyte the OCV drops and then slowly increases during the run as richer sulfur polysulfide molecules are formed.

A sensor confirmed high levels of hydrogen sulfide (>200 ppm) near the electrolysis cell inside the glove box. We are currently investigating the potential reaction mechanisms that would explain the formation of hydrogen sulfide within the anolyte. Since we run all our experiments under a dry nitrogen atmosphere, we don't expect that the reaction of water with sodium sulfide is the main reaction path. One hypothesis is that hydrogen sulfide could be formed as a product of a decomposition/oxidation reaction of the anolyte solvent itself with sodium sulfide. Aging of the anolyte solvent is evident as the test goes on and it is manifested as an increase in viscosity and in the reduction of the ionic conductivity. This also explains the slow but steady increase in the cell operating voltage as shown in Figure 17. After replacing the anolyte at approximately 700 hours run time, the voltage decreased to a value similar to that of the beginning of the test. This is also a proof of the good condition of the membrane since little or no over potential due to the NaSICON solid electrolyte has been measured.

**Table 9: Summary of sodium recovery test cells tested in long-term mode during the reporting period**

| Cell ID#           | Anolyte                              | Anode Electrode                 | Membrane                              | Catholyte | Cathode Electrode                   | Seal Type          | Operating Conditions   |
|--------------------|--------------------------------------|---------------------------------|---------------------------------------|-----------|-------------------------------------|--------------------|--|
| Na_molten_20110311 | Na <sub>2</sub> S <sub>4</sub> in MF | Platinized Ti mesh (1.1" diam.) | NaSICON GY (0.5 mm thick, 0.8" diam.) | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=140-160C<br>Anolyte agitation<br>Cte Current=50-150 mA/cm <sup>2</sup> |
| Na_molten_20110504 | Na <sub>2</sub> S <sub>4</sub> in MF | Platinized Ti mesh (1.1" diam.) | NaSICON GY (1 mm thick, 0.8" diam.)   | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=130C<br>Anolyte agitation<br>Cte Current=60 mA/cm <sup>2</sup>         |

**Table 10: Summary of performance of sodium recovery test cells run in long-term testing mode during the reporting period**

| Cell ID            | Total Run Time | Avg. Current Density | Avg. Voltage | Number of Na <sub>2</sub> S <sub>4</sub> Additions | Total Na <sub>2</sub> S <sub>4</sub> Added | Na Recovered |                   | Notes   |
|--------------------|----------------|----------------------|--------------|--|--|--------------|-------------------|---|
|                    | Hours (days)   | mA/cm <sup>2</sup>   | V            |  | grams                                      | grams        | % out of Na added |   |
| Na_molten_20110311 | 458 (19)       | 68                   | 4.12         | 16   | 400.4                                      | 54.3         | 51.3              | Cell failed after 458 hours of operation due to corrosion on anode side of membrane |
| Na_molten_20110504 | 1422 (59.2)    | 60                   | 3.13         | 38   | 563.3                                      | 125          | 83.9              | Cell is still in operation with membrane in excellent condition                     |

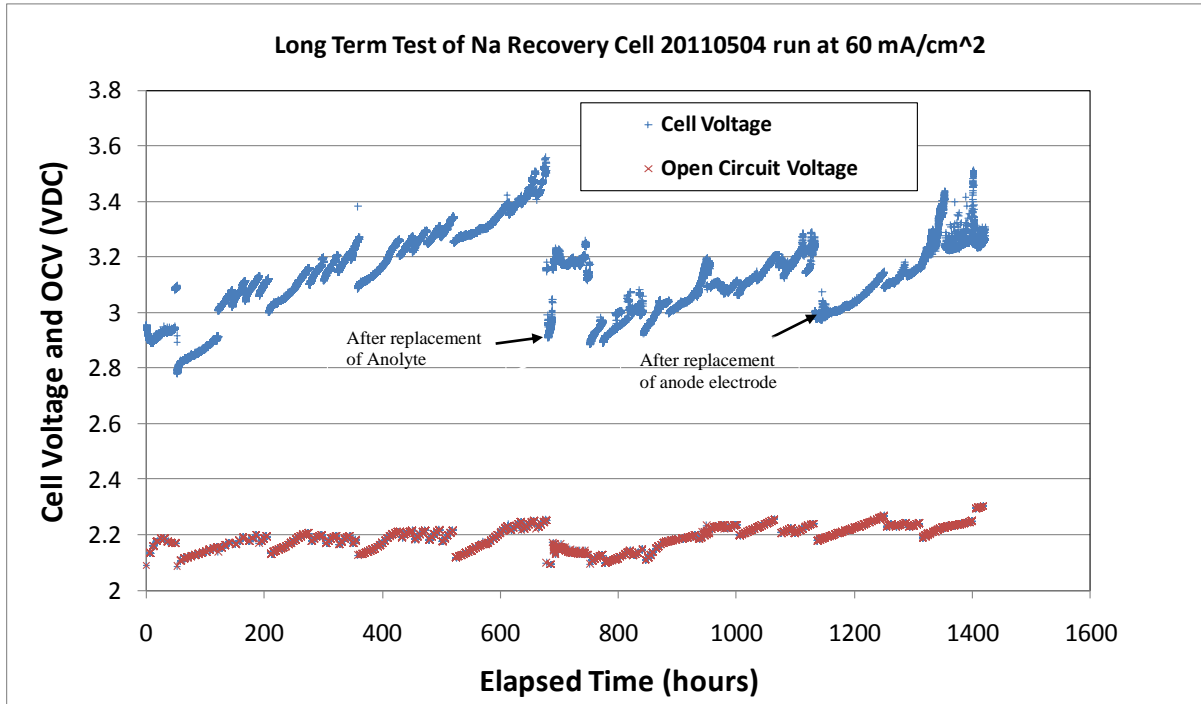


Figure 17: Cell voltage at 60 mA/cm<sup>2</sup> and Open Circuit Voltage (OCV) versus run time for sodium recovery cell *Na\_molten\_20110504*. Run time includes time periods for OCV measurements (no current).

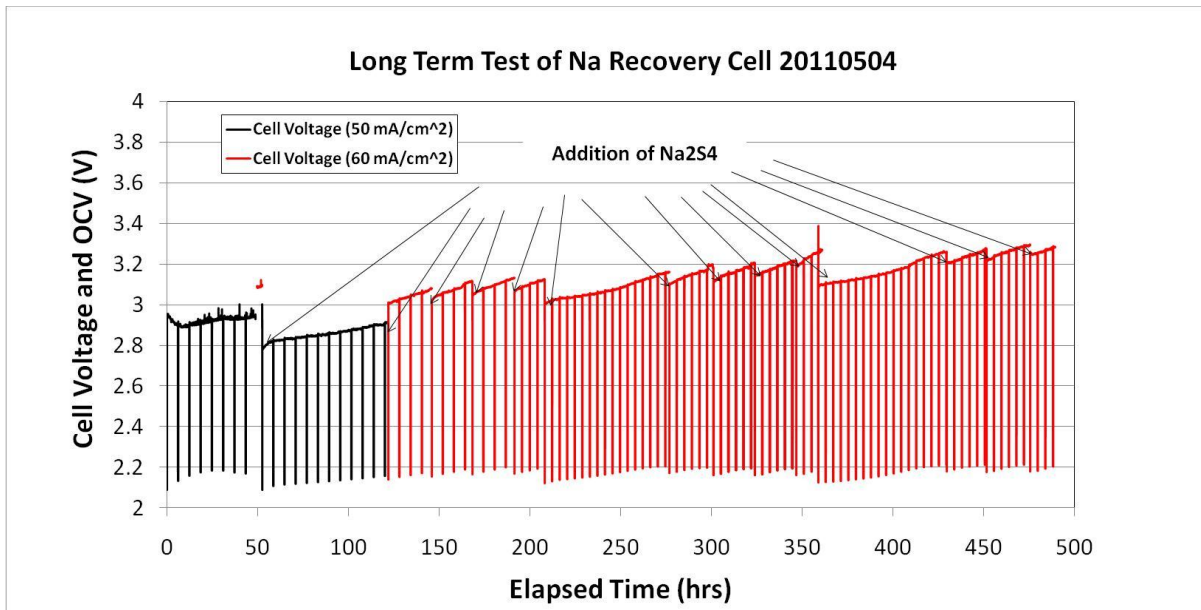
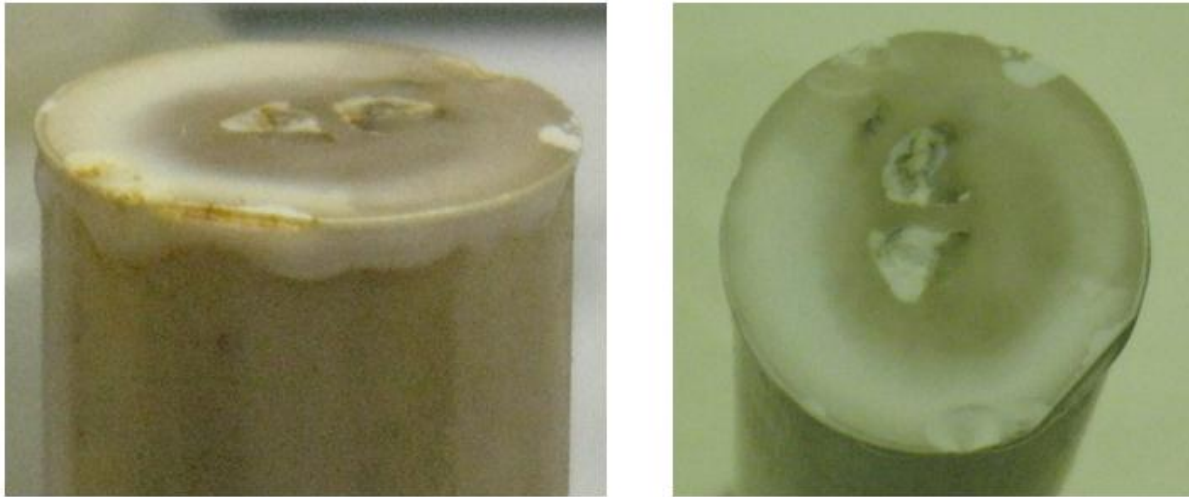


Figure 18: Cell voltage and Open Circuit Voltage (OCV) during first 475 hours of test for sodium recovery cell *Na\_molten\_20110504*. Run time includes time periods for OCV measurements (no current).



**Figure 19: Side [A] and top [B] views of the NaSICON membrane of sodium recovery cell *Na\_molten\_03112011* after 458 hours of operation**

### **Sodium Recovery Test Cells Results using Salts from Upgraded Oil Samples**

For the first time in this project, we have assembled a test cell with an anolyte containing sulfide salts from an OSEC upgraded oil sample (DL04138). A total of 300 g of OSEC shale oil sample was treated with 10.6 g of sodium metal in a hydrogen atmosphere (1500 psig H<sub>2</sub>) at a temperature of 375°C. After the upgrading reaction, a total of 49.24 g of solids were separated by centrifugation from the upgraded oil phase. The solids were repetitively washed with mineral oil and centrifuged to remove any remains of oil. Table 11 lists the C, H, N, and S composition of the solid phase. The high C and H content of the solids is an indication of the organic nature of the sulfide salts contained in the solids. The unaccounted mass in the CHNS analysis (23.3%) is mostly made by sodium and oxygen. Assuming that the composition of oxygen in the solids is similar to that of crude oil (~1% wt.), then a total of 11 g of sodium would be present in the solids. This represents an error of 4% over the total amount of sodium initially added to the reaction process. The error is small enough to conclude that most of the sodium added ended up in the solid phase. Finally, the solids were mixed with the anolyte solvent (MF), in a ratio of 1 to 5, and became completely dissolved in it. A test cell using this anolyte was assembled and run at 130°C in constant voltage mode.

Table 12 summarizes the conditions of all three runs with this test cell. Figure 20 shows the cell voltage and the current density versus elapsed time for the runs. During run #1, the cell was operated at 5 V for approximately 16 hours, resulting in a noisy current density profile averaging around 30 mA/cm<sup>2</sup>. At the end of this first period, the cell was stopped and we discovered that a large amount of black solid material had accumulated and filled the space between the anode electrode and the NaSICON membrane (Figure 23-[A]). After removing the solids, the cell was restarted and run at 4.5 V. The current density initially reached 66 mA/cm<sup>2</sup>, but it decreased down to 1 mA/cm<sup>2</sup> over the following 19 hours. Post-run analysis of the cell showed that the titanium wire current collector had almost completely detached from the platinized titanium electrode. This caused a very high contact resistance at the electrode, which explains the low meas-

ured current density. For run #2, we replaced both the electrode and the NaSICON membrane and run the cell at 4.5V for 12 hours and at 5V for the remaining of the test. During the run the current was interrupted every 4 hours of operation for 30 minutes to measure the Open Circuit Voltage (OCV). Similarly to the previous run, the current density quickly decreased from a value of 40 mA/cm<sup>2</sup>, at the beginning of the test, down to a value of 7 mA/cm<sup>2</sup> towards the end. An interesting observation is that immediately after each current interruption period, to measure the OCV, the current density would jump to a high value but then very quickly (within minutes) decrease to half of the peak current density value. This is characteristic of a capacitive double layer effect, where the electrode surface gets quickly polarized after the voltage driving force is been reestablished. So during the rest periods, the charge is dissipated and therefore the electrode resistance decreases. The double layer effect is consistent with the existence of a non-conducting layer over the electrode surface. Eventually, the cell reached a pseudo steady state operating regime with an average current density of 7 mA/cm<sup>2</sup>. As Figure 20 shows, run 2 was continued until 123 hours of total cell operation were achieved. Disassembly of the cell showed once again a deposit of solid material on the electrode surface. The platinized titanium electrode was replaced with a graphite electrode in run 3. In addition, a new NaSICON membrane was used. Cell performance for run 3 was almost identical to run 2. The test was ended after 209.5 hours of total cell operation. During that time, a total of 4.22 grams of sodium metal were recovered from the anolyte solution. Figure 21 shows the sodium recovery profile versus cell run time for the three runs. This amount of sodium recovered represents 39.6% of the total added to the oil in the upgrading reactor. Figure 23-[B] displays a picture of the graphite electrode covered on a thin non-conductive carbon like deposit. The ionic conductivity versus temperature of the anolyte solutions prior to the test, at the end of run 1, and at the end of run 3 are plotted in Figure 22. For comparison purposes, the conductivity of an anolyte consisting of 10.3 % wt. Na<sub>2</sub>S<sub>4</sub> in MF has been added to the plot. The data shows that the electrical resistance of the electrolyte more than tripled between the beginning of the test and the end of run 3. This is mostly due to the removal of the sodium ions out of the anolyte solution.

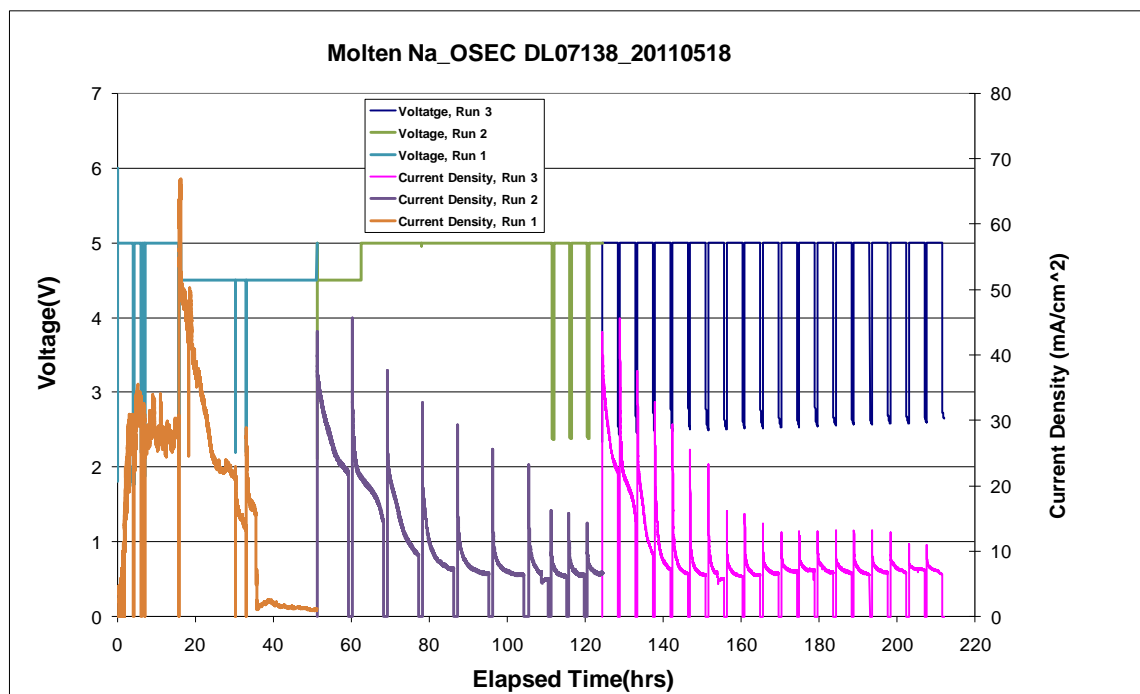
As a final conclusion, this run has demonstrated that sodium can be recovered from an anolyte containing dissolved organic sulfide salts. However, the oxidation of the organic counter ion resulted in the formation of insoluble solids on the anode electrode surface, which in turn significantly increased the resistance of the cell. Therefore, it is desirable to transform the sodium organic sulfide salts into inorganic sodium sulfide salts prior to the electrolysis process to prevent the precipitation of insoluble salts.

**Table 11: Composition (percent) of the solids fraction**

| Sample                            | C     | H    | N    | S    | Na+O  |
|-----------------------------------|-------|------|------|------|-------|
|                                   | %     | %    | %    | %    | %     |
| OSEC DL07111<br>(Solids Fraction) | 63.90 | 9.59 | 0.66 | 2.50 | 23.35 |

**Table 12: Sodium recovery test cells, using sulfide salts from processed oil samples, assembled and tested during the reporting period**

| Cell ID#                             | Anolyte                    | Anode Electrode                 | Membrane                              | Catholyte | Cathode Electrode                   | Seal Type          | Operating Conditions                                     |
|--------------------------------------|----------------------------|---------------------------------|---------------------------------------|-----------|-------------------------------------|--------------------|--|
| Molten Na_OSEC_DL0738_20110524 Run 1 | 20.4 %wt. OSEC salts in MF | Platinized Ti mesh (1.1" diam.) | NaSICON GY (1 mm thick, 0.8" diam.)   | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=130C<br>Anolyte Agitation<br>Cte Voltage=5 V |
| Molten Na_OSEC_DL0738_20110524 Run 2 | 20.4 %wt. OSEC salts in MF | Platinized Ti mesh (1.1" diam.) | NaSICON GY (0.5 mm thick, 0.8" diam.) | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=130C<br>Anolyte Agitation<br>Cte Voltage=5 V |
| Molten Na_OSEC_DL0738_20110524 Run 3 | 20.4 %wt. OSEC salts in MF | Graphite (1.1" diam.)           | NaSICON GY (0.5 mm thick, 0.8" diam.) | Molten Na | Molten Na, Ti rod current collector | Silica-Boria Glass | Temperature=130C<br>Anolyte Agitation<br>Cte Voltage=5 V |



**Figure 20: Cell voltage and current density versus elapsed time for sodium recovery test cell *Molten Na\_OSEC DL07138\_20110518***

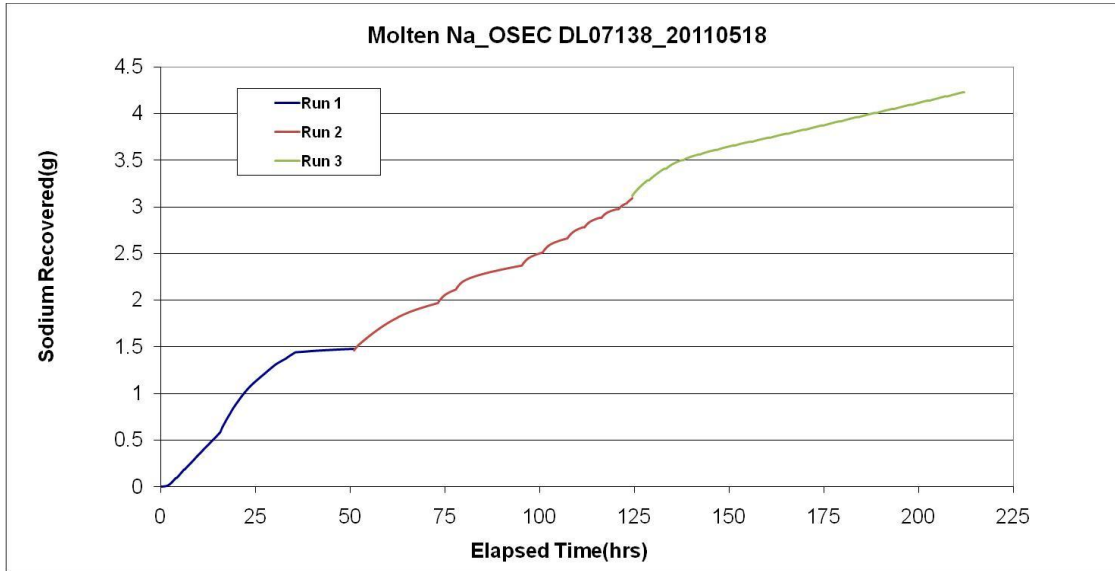


Figure 21: Total sodium recovered during operation of test cell *Molten Na\_OSEC DL07138\_20110518*

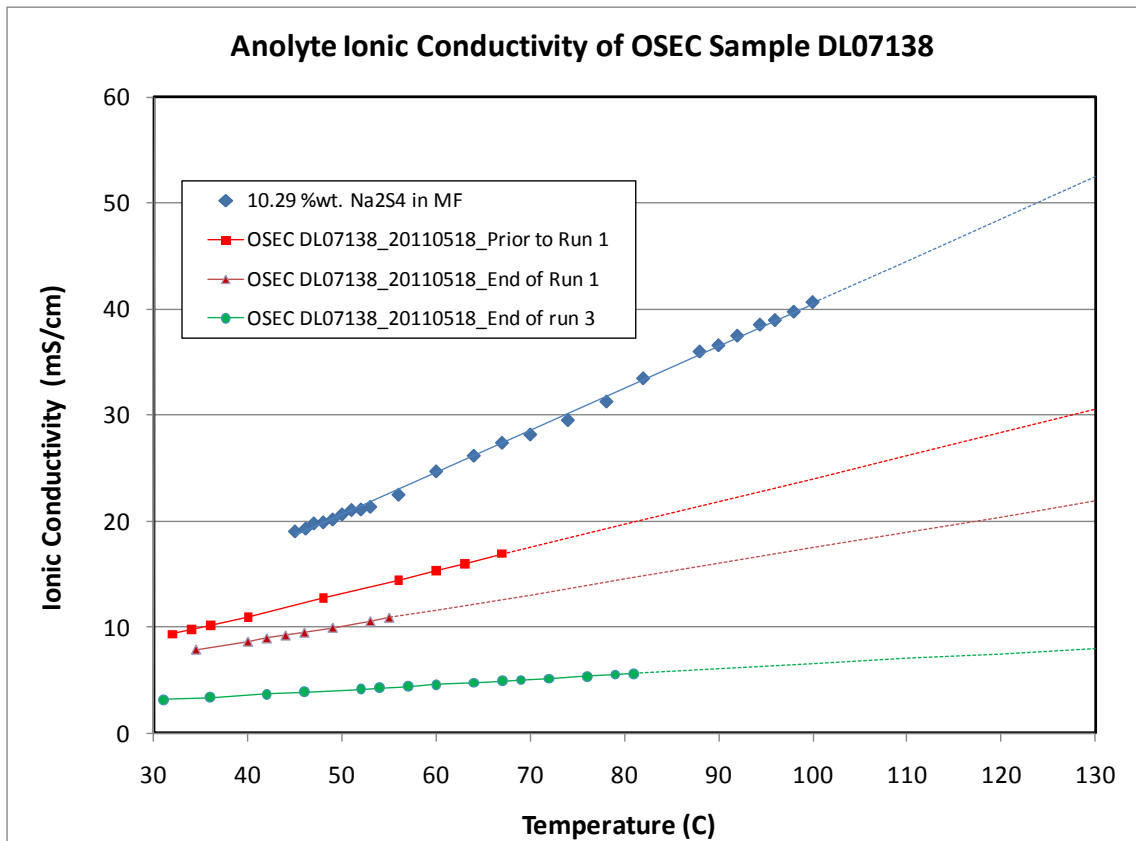
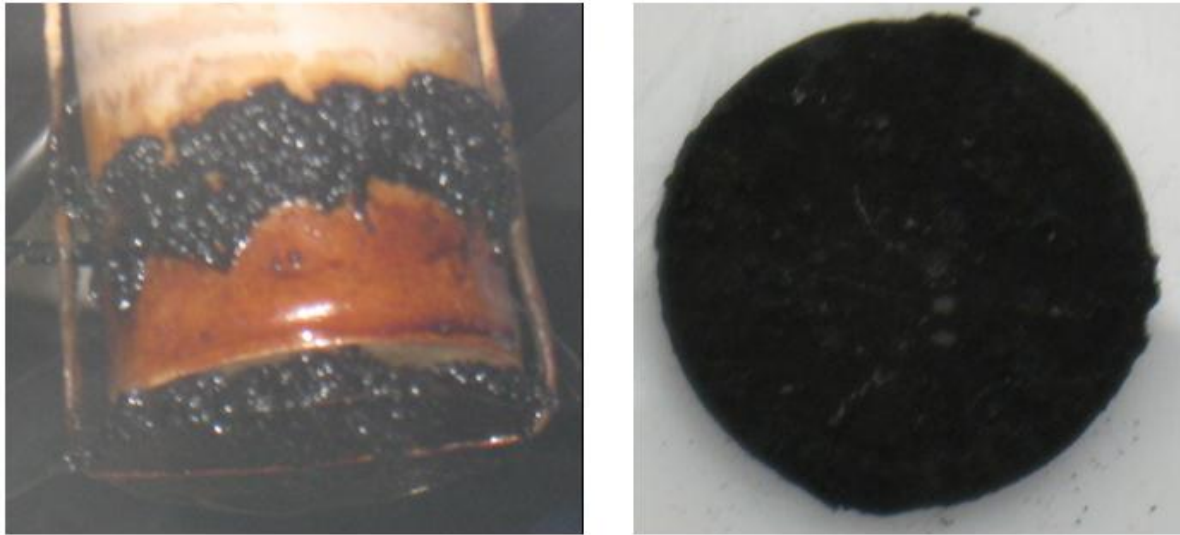


Figure 22: Ionic conductivity of anolyte solution versus temperature for test cell *Molten Na\_OSEC DL07138\_20110518* during the test runs





**Figure 23: Solid material accumulated between the NaSICON membrane and the Ti electrode at the end of run 1[A]. Graphite electrode at the end of run 3 [B]**

## **2.8 Task 8.0 – Modeling and Economic Analysis**

### **2.8.1 Subtask 8.1 – Model Upgrading process**

*The Recipient shall model the upgrading process constructed in Budget Period 1. The design model of separation scheme of Task 3 shall be added to the overall model of upgrading process. The process model shall also take into account the performance comparison with current commercial hydrotreating processes.*

### **2.8.2 Subtask 8.2 – Model Electrolysis process**

*The Recipient shall analyze data from Task 7.0 above and the exiting Budget Period 1 performance model shall be updated and improved. The inputs of the model shall be coupled with the outputs of the upgrading process model to quickly analyze the effect of changes in the value of upstream variables. The model shall contain enough detail to be able to provide accurate cell's performance predictions that shall be used for future optimization and scale-up activities.*

### **Make-up Sodium Production Process**

A process model for the production of sodium metal from sodium hydroxide through a low temperature electrolysis process has been proposed. This sodium production process can be implemented as an alternative to directly purchasing sodium to make up for the metal losses experienced in the sodium recovery process. Figure 24 shows a schematic of the overall process. Anhydrous sodium hydroxide is fed into a stirred tank, where it is mixed with recycled anolyte coming from the electrolysis cells. The anolyte solution is then preheated to the electrolysis cell



- The recycled anolyte and the sodium hydroxide streams are introduced into the anolyte mixing tank at ambient temperature conditions.
- Anolyte, molten sodium and gas streams exit at the temperature of the cell.
- The anolyte solution is preheated to the cell's temperature using some of the Joule heating released within the cell. The remaining heat can be exported to another process.

Table 13 displays the process streams mass flow rates for the three different type of oil feedstocks. From the process energy balance, it has been estimated that approximately only 33% of the energy released within the electrolysis cell, due to Joule heating, is needed to preheat the anolyte solution. The remaining 66% could be exported to the reaction step of the oil upgrading process to heat-up the oil in the main reactor.

**Table 13: Mass balance for the electrolytic sodium make-up production process**

| Type of Oil | Make-up Na Produced | NaOH Consumed | Inlet Anolyte Stream | Recycled Anolyte Stream | Oxygen  | Water   |
|-------------|---------------------|---------------|----------------------|-------------------------|---------|---------|
|             | ton/day             | ton/day       | ton/day              | ton/day                 | ton/day | ton/day |
| Shale Oil 1 | 12.90               | 22.44         | 219.92               | 197.47                  | 4.49    | 5.05    |
| Shale Oil 2 | 5.88                | 10.22         | 100.20               | 89.98                   | 2.04    | 2.30    |
| Heavy Oil 1 | 11.77               | 20.47         | 200.61               | 180.14                  | 4.09    | 4.61    |

### 2.8.3 Subtask 8.3 – Preliminary cost analysis

*The Recipient shall incorporate the cost models for equipment procurement and installation from Subtasks 8.1 and 8.2 into an updated preliminary cost model.*

#### **Preliminary Cost Analysis for the Make-up Sodium Production Process**

##### ***a. Process Operating Costs***

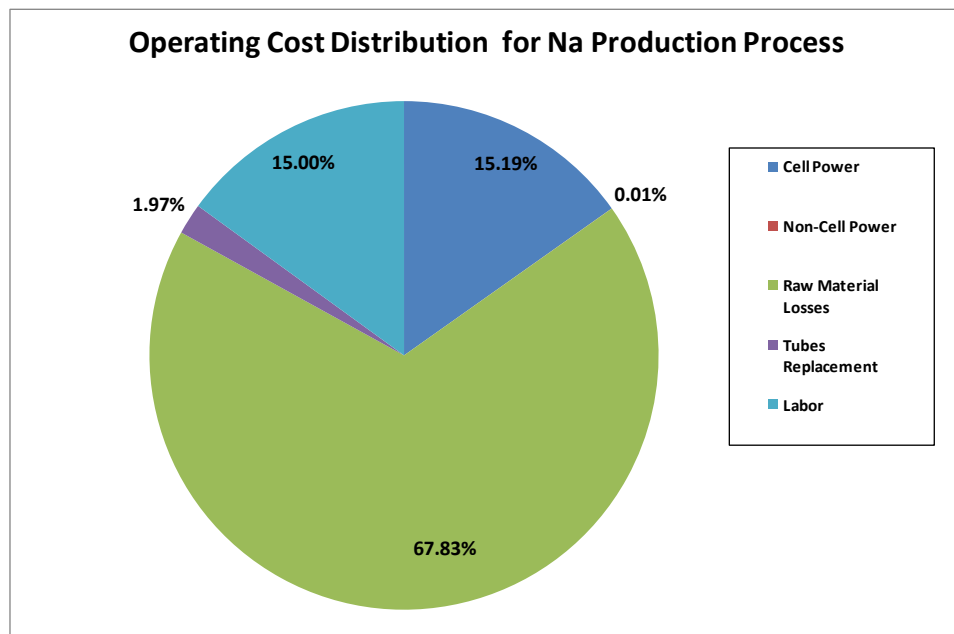
An operating and capital cost estimation study for an electrolytic process to produce sodium metal from sodium hydroxide has been conducted. These cost estimates were conducted based on 25,000 barrels of oil per day upgrading plant, assuming that 5% of the sodium needed cannot be recovered and need to be replaced. An optimum current density of 50 mA/cm<sup>2</sup>, to operate the electrolysis cells, has been found by minimizing the sum of the cost of electrical power and the cost of the NaSICON material.

To estimate the process operating costs, we have identified and focused on the largest cost contributors. These include cost of raw materials (sodium hydroxide), electrical power, membrane replacement, and labor costs. The electrolysis electrical power costs have been subdivided into cell and non-cell costs. The non-cell items include the electrical costs associated with electrolyte and sodium metal pumping, and anolyte mixing in the anolyte stirred tank. An electricity cost of 6.59 cents per kw-h has been used in the calculation of the electrolysis cost. It has been assumed that the energy needed to preheat the anolyte solution, before it enters the cells, is recovered from the heat released within the cells. We have assumed that the expected life of the ionic conductive membranes (e.g. tubes) in the cells is 18 months. Membrane replacement includes raw materials and fabrication costs, but not the removal of the old and installation of the

new membranes. In the raw material losses group we have included the loss of anolyte solvent at a rate of 20% loss per year based on the total anolyte inventory. Labor costs have been calculated as a 15% flat rate of the total operating costs. Table 14 shows the contribution from each of the categories and the total operating costs of the sodium production process. The percent cost distribution is shown in a pie chart (Figure 25). We have not included other costs that might quantitatively contribute to the overall costs such as non-membrane maintenance and repairs, general plant utilities, equipment depreciation, taxes, etc. The cost of raw materials (sodium hydroxide) accounts for 67.8% of the total cost, whereas total electrical power accounts for 15.2%. Therefore, sodium production costs are ultimately dominated by the cost of anhydrous sodium hydroxide and not so much by the cost of electrical power or the cost of the NaSICON membranes.

**Table 14: Operating costs (in dollars per kg of sodium) for an electrolytic sodium production process, where the cells are operated at the optimum current density and temperature conditions**

| Cell Power | Non-Cell Power | Raw Material Losses | Tubes Replacement | Labor    | Total    |
|------------|----------------|---------------------|-------------------|----------|----------|
| \$/kg Na   | \$/kg Na       | \$/kg Na            | \$/kg Na          | \$/kg Na | \$/kg Na |
| 0.300      | 0.000          | 1.341               | 0.039             | 0.296    | 1.977    |



**Figure 25: Operating costs distribution for the sodium production process**

## ***b. Capital Estimation Costs***

The estimation of the capital costs of an electrolytic sodium metal production plant, operating at the optimum conditions, has been conducted. This estimation covered the cost of the main pieces of equipment, raw materials, equipment installation, installed piping and fittings, instrumentation and controls, basic plant facilities, and the cost of electrical installations. Indirect costs such as engineering and supervision, construction expenses, contractor fees, or contingencies were not considered at this time. Equipment sizing was based on a sodium metal production rate equivalent to 5% of the sodium requirements (loses) for a 25,000 barrels per day oil upgrading facility. Costing of standard pieces equipment such storage and mixing tanks, heat exchangers, filters, pumps, and others was done based on general engineering rules of thumb and order of magnitude scaling factors.

The electrolysis cells were priced based on the cost of their materials of construction after a basic design was proposed. Raw materials included fresh anolyte solvent and enough sodium to prime the electrolysis cells. The costs of equipment installation, instrumentation+controls, installed piping+fittings, electrical installations, and service facilities were calculated as percentages of the total capital of purchased equipment. The percentages used are approximations based on ordinary chemical processing plants. Table 15 shows the total plant capital cost for the three different types of oils considered. The columns showing the total cost in terms of dollars per kilo of sodium produced and in dollars per barrel of oil upgraded reflect the total capital investment of the plant divided by an expected plant life of 15 years. Figure 26 displays the capital cost distribution among the different categories as a percentage of the total cost for Shale Oil #1.

Similarly to the sodium recovery plant costs, reported in the January-March Quarterly Report, the two priciest pieces of equipment in the plant are the electrolysis cells and electrical transformers-rectifiers. It should be kept in mind that this cost estimation is very preliminary and a large error (>50%) is expected.

**Table 15: Total capital costs for an electrolytic sodium production facility sized to produce 5% of the total sodium metal requirements of a 25,000 barrel per day oil upgrading plant**

| <b>Type of Oil</b> | <b>Total Capital Costs</b> |          |            |
|--------------------|----------------------------|----------|------------|
|                    | MM\$                       | \$/kg Na | \$/bbl oil |
| Shale Oil 1        | 5.755                      | 0.081    | 0.042      |
| Shale Oil 2        | 4.831                      | 0.150    | 0.035      |
| Heavy Oil 1        | 5.611                      | 0.087    | 0.041      |

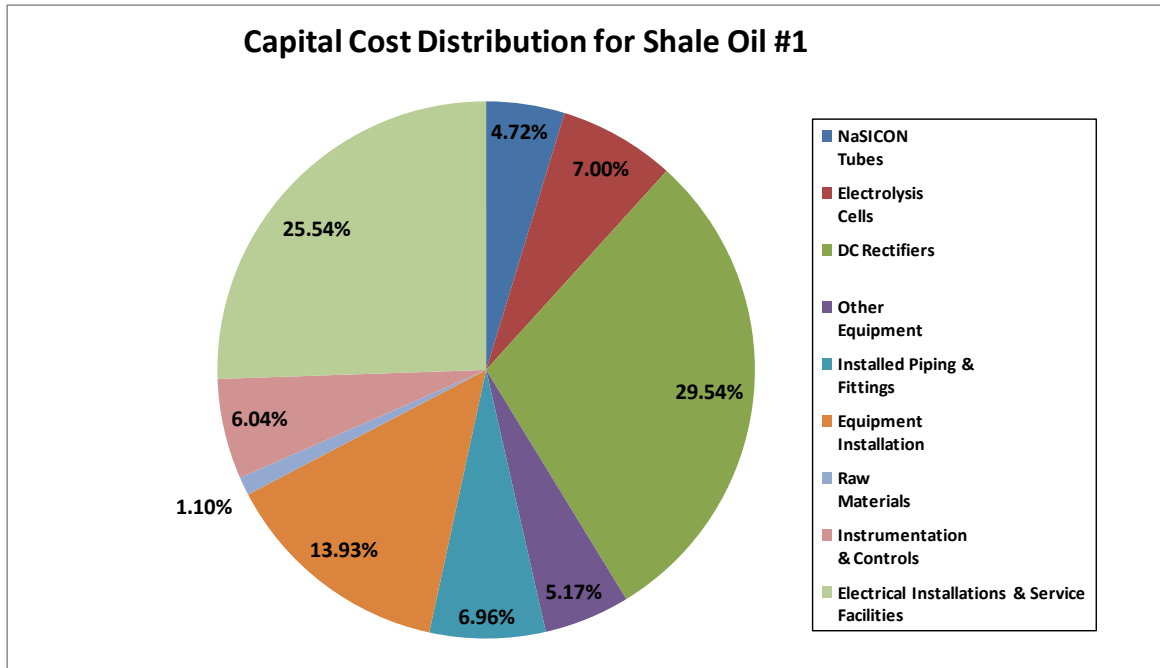


Figure 26: Capital costs distribution for an electrolytic sodium production facility sized to produce 5% of the total sodium metal requirements of a 25,000 barrel per day oil upgrading plant

#### 2.8.4 Subtask 8.4 – Pilot plant cost estimate

*The Recipient shall estimate the costs for equipment procurement and installation based on knowledge obtained in earlier tasks.*

The 7<sup>th</sup> quarterly report is presently submitted

### 3. CONCLUSION

Our conclusion at this point is that high levels of both sulfur and nitrogen can be removed from shale oil or heavy oil with the process tested. Nitrogen removal has been less successful with Shale Oil 2 which of the three oils was the least controlled prior to receipt in terms of storage in air and subject to ambient thermal cycles. Both methane and hydrogen are effective in removal of sulfur, nitrogen, heavy metals, and increasing API gravity.

#### 4. COST STATUS

The corrected monthly costs of the 6<sup>th</sup> quarter are shown in Table 16, along with the projected costs stated in the Project Management Plan and the monthly costs of the 7<sup>th</sup> quarter are shown in Table 17, along with the projected costs stated in the Project Management Plan.

**Table 16: Project revised costing profile for the 6<sup>th</sup> Quarter**

|                              |     | Jan-11    |           | Feb-11    |            | Mar-11    |            | Q6         |            |
|------------------------------|-----|-----------|-----------|-----------|------------|-----------|------------|------------|------------|
|                              |     | Projected | Actual    | Projected | Actual     | Projected | Actual     | Projected  | Actual     |
| Direct Labor                 |     |           | 25,511.93 |           | 19,790.29  |           | 25,991.27  |            | 71,293.49  |
| Benefits                     | 32% |           | 8,163.82  |           | 6,332.89   |           | 8,317.21   |            | 22,813.92  |
| Overhead                     | 41% |           | 10,459.89 |           | 8,114.02   |           | 10,656.42  |            | 29,230.33  |
| Total Burdened Labor         |     |           | 44,135.64 |           | 34,237.20  |           | 44,964.90  |            | 123,337.74 |
| Direct Materials / Spec Test |     |           | 31,202.93 |           | 26,913.53  |           | 38,574.26  |            | 96,690.72  |
| Equipment                    |     |           |           |           | 59,498.10  |           |            |            | 59,498.10  |
| Travel                       |     |           |           |           |            |           | -          |            | -          |
| Subtotal                     |     |           | 75,338.57 |           | 120,648.83 |           | 83,539.16  |            | 279,526.56 |
| G&A                          | 29% |           | 21,848.19 |           | 34,988.16  |           | 24,226.36  |            | 81,062.71  |
| Total monthly                |     | 67,115.12 | 97,186.76 | 60,237.08 | 155,636.99 | 70,063.18 | 107,765.52 | 197,415.39 | 360,589.27 |

**Table 17: Project costing profile for the 7<sup>th</sup> Quarter**

|                              |     | Apr-11     |            | May-11    |            | Jun-11    |            | Q7         |            |
|------------------------------|-----|------------|------------|-----------|------------|-----------|------------|------------|------------|
|                              |     | Projected  | Actual     | Projected | Actual     | Projected | Actual     | Projected  | Actual     |
| Direct Labor                 |     |            | 25,179.91  |           | 29,743.90  |           | 27,035.16  |            | 81,958.97  |
| Benefits                     | 32% |            | 8,057.57   |           | 9,518.05   |           | 8,651.25   |            | 26,226.87  |
| Overhead                     | 41% |            | 10,323.76  |           | 12,195.00  |           | 11,084.42  |            | 33,603.18  |
| Total Burdened Labor         |     |            | 43,561.24  |           | 51,456.95  |           | 46,770.83  |            | 141,789.02 |
| Direct Materials / Spec Test |     |            | 26,116.28  |           | 27,626.47  |           | 29,029.52  |            | 82,772.27  |
| Equipment                    |     |            | 31,637.50  |           |            |           |            |            | 31,637.50  |
| Travel                       |     |            | 1,240.50   |           | 893.83     |           | 3,419.61   |            | 5,553.94   |
| Subtotal                     |     |            | 102,555.52 |           | 79,977.25  |           | 79,219.96  |            | 261,752.73 |
| G&A                          | 29% |            | 29,741.10  |           | 23,193.40  |           | 22,973.79  |            | 75,908.29  |
| Total monthly                |     | 291,122.91 | 132,296.62 | -         | 103,170.65 | -         | 102,193.75 | 291,122.91 | 337,661.02 |

Our costs in the 7th quarter were lower than the projection because there was a lag in ordering equipment. Much of the equipment has been ordered but our larger reactor which is due in next quarter has not been charged to the program.

Figure 27 shows a plot of the total monthly costs and the initially projected costs versus time and Figure 28 shows the cumulative monthly costs versus time. Also shown in Figure 28 is the fraction of actual over planned cumulative expenses.

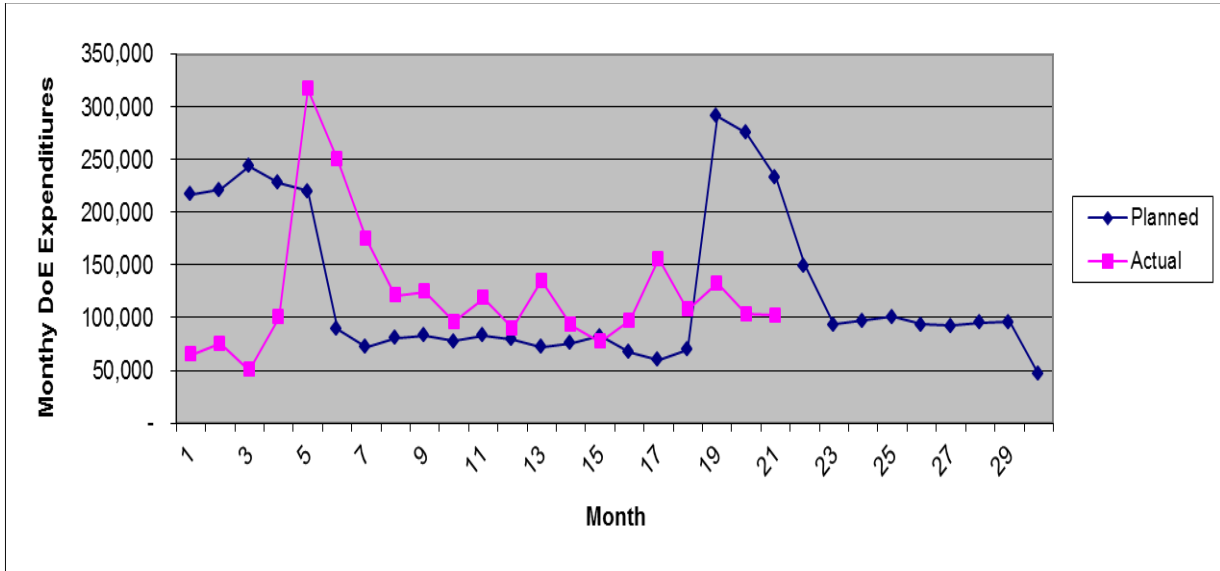


Figure 27: Projected and actual monthly costs over time

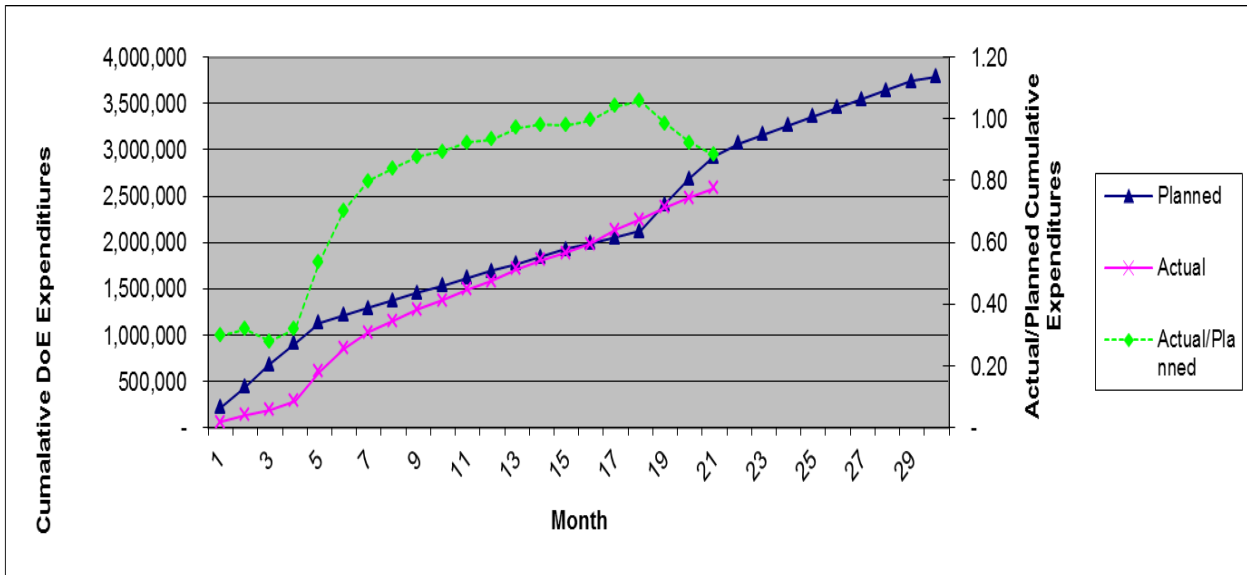


Figure 28: Projected and actual cumulative costs over time



## 5. MILESTONE STATUS

New milestones need to be set for the current Budget Period.

**Table 18: Milestone log for 6<sup>th</sup> 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            | 3/31/11          | 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            | 3/31/11          | 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           | 1/4/11             | 3/18/11          | A preliminary cost model was completed and reviewed internally. Adjustments were recommended by the reviewers and additional cases suggested for updated cost models. |

## 6. ACCOMPLISHMENTS

- Electrolysis of sodium sulfide at temperatures of molten sodium have begun and are showing very encouraging results.
- Reactor tests with methane have continued with encouraging results
- Process models of both the reactor and electrolysis processes have begun which will lead to the preliminary cost model.
- Liquid yields from the reactor process have increased during the quarter and late in the quarter a change was made to the reactor impellor to improve gas phase liquid phase interaction.
- Electrolysis of Na<sub>2</sub>S<sub>4</sub> has exceeded 1500 hours at the target current density and temperature.
- For the first time, assembled a NaSICON tube for utilization in the electrolysis process of this application.
- Began developing process for generation of make-up sodium using sodium hydroxide as a feed.

## 7. PROBLEMS OR DELAYS

Reactor is due in next quarter. The bottoms drain in backordered so we will receive it with a plug in the meantime.

## 8. PRODUCTS

No products to report at this time.

## 9. LIST OF APPENDICES

None

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