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14. ABSTRACT The goal is to demonstrate a novel electrolytic process for extracting Li from seawater. The technical objectives are to prove the concept of electrolytic process and to develop effective membranes for the diffusion of lithium ion from natural seawater to an extractant. Process variables are potential applied between seawater and fresh water, flow rates, and the ratio of the volume of anolyte to that of catholyte in the flow system.					
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Quarterly Progress Report 2

Project Title: Simultaneous Extraction of Lithium and Hydrogen from Seawater

Project Period: 7/26/2010 – 7/25/2011

Reporting Period: October 26, 2010 – January 25, 2011

Date of Report: January 26, 2011

Recipient: University of Central Florida

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Project Goal:

The goal is to demonstrate a novel electrolytic process for extracting Li from seawater. The technical objectives are to prove the concept of electrolytic process and to develop effective membranes for the diffusion of lithium ion from natural seawater to an extractant. Process variables are potential applied between seawater and fresh water, flow rates, and the ratio of the volume of anolyte to that of catholyte in the flow system.

Project Status:

Li⁺ adsorbing manganese oxides (LiMn_{1.5}Mg_{0.5}O₄) and Li ion-conducting ceramic materials were prepared by solid state reactions. The materials were employed in an electrochemical cell. Natural seawater was introduced as the anolyte and lithium extraction was carried out.

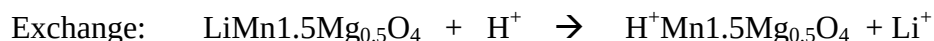
Experimental:

Synthesis of Li⁺ adsorbents:

Lithium adsorbing ion-sieve LiMg_{0.5}Mn_{1.5}O₄ was prepared by solid state reaction. 6.1g of Li₂CO₃, 8.9g of Mg(CH₃COO)₂·4H₂O and 5.6g of MnCO₃ were mixed, ball milled for 2 hours, and calcined at 600°C for 4 hours.

Lithium Extraction from the Adsorbents:

One gram of LiMg_{0.5}Mn_{1.5}O₄ was immersed and stirred in 2 liter of 0.5M HCl solution to exchange lithium with hydrogen and generate space for lithium adsorption. The ion exchange can be written as



Synthesis of LISICON:

The lithium ion-conducting materials were prepared from the mixture of Li₂S and P₂S₅ crystalline powders. The mixture was mechanically mixed using a ball mill apparatus (Retsch

PM100). The powders were heated to 230°C and kept at the temperature for 4 hours, and slowly cooled down. The powders were pressed and calcined to generate 1" diameter disks.

Electrolytic Cell:

An electrolytic cell was made by incorporating the cell components with a two-pump flow system.

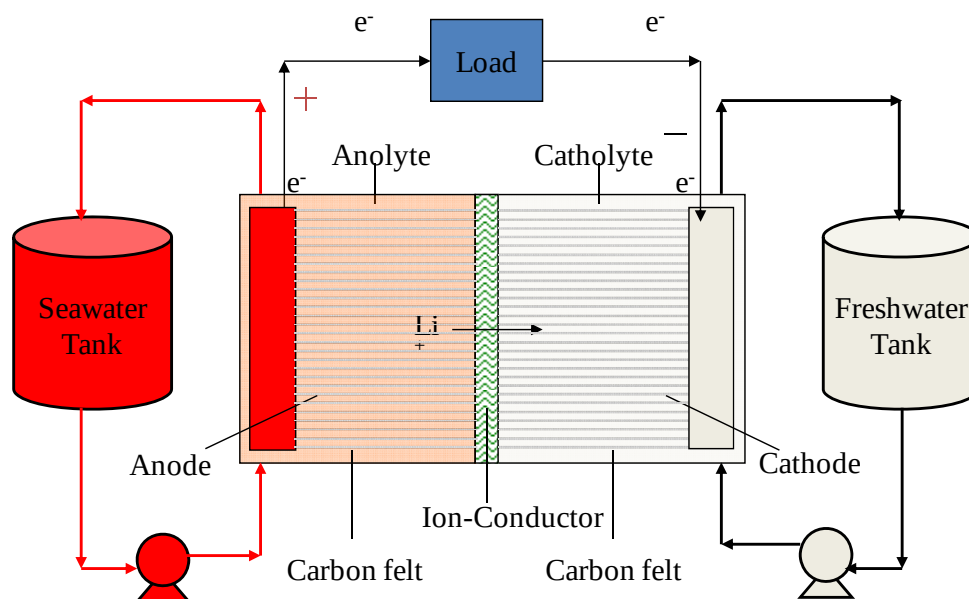


Figure 1. Schematic of electrolytic cell extracting Li⁺ ion from seawater.

Membrane Preparation: The Li adsorbing materials were sprayed on Nafion NRE212. The spraying solution was prepared with 180mg LiMg_{0.5}Mn_{1.5}O₄, 5g methanol, and 1.69g of 5wt.% solubilized Nafion[®] solution (EW1100, supplied by Ion Power). The solution was mixed for 2 hours and sprayed (P=6psig) with an air-sprayer on Nafion. The dimension of sprayed area is 1" x 1".

Ion Chromatography (IC): Ions in seawater diffused from/to the anode and cathode were determined by ion chromatography. Anions were analyzed by Anion Ion Chromatography (Instrument Dionex ICS-1500, Column Dionex AS9-HC; AG9-HC Guard, eluent: 9.00 mM Na₂CO₃, flow rate: 1.25 mL/min, and sample loop was 25 µL). Cations were analyzed by Cation Ion Chromatography (Instrument Dionex DX-500, Cation Column Dionex CS12A; CG12A Guard, eluent: 20.00 mM methanesulfonic acid, flow rate:1.25 mL/min, and sample loop:25 µL)

Results

Linear Sweep Voltammetry 1

Linear sweep voltammetry (LSV) was carried out with the $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -sprayed Nafion membrane. The anolyte was seawater and catholyte was deionized water. Carbon felt is used as anode as well as cathode. The potential was scanned between 0 to 4V and current was measured accordingly.

Operating Conditions:

Anode: carbon felt (0.5mm)

Anolyte: Seawater 300ml

Anolyte flow rate: 10ml/min

Cathode: carbon felt (0.5mm)

Catholyte: DI water of 100ml

Catholyte Flow rate: 10ml/min

Electrolyte: $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ sprayed Nafion

Figure 2 shows the LSV of the electrolytic cell with the operating conditions above. From the chromatogram, more than 3V is required to generate current density of $2\text{mA}/\text{cm}^2$. No appreciable gas evolution was observed due to the absence of active electrocatalysts for the electrochemical water splitting reactions.

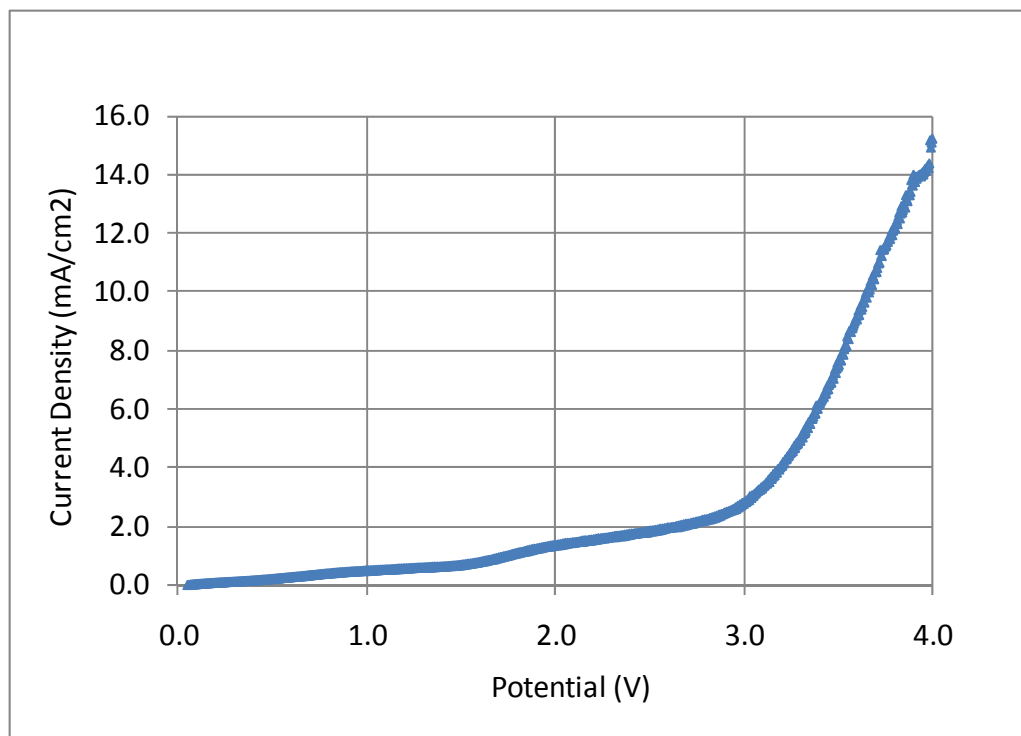


Figure 2. Linear sweep voltammogram of the electrolytic cell.

Potentiostatic Experiment 1

The electrolytic cell potential was set at 3V and current was recorded with time. Anolyte as well as catholyte from the cell was collected (1ml each) every thirty minutes for IC analysis of Li^+ ion concentration. Figure 3 the potentiostatic diagram of the cell. Current density increases as more lithium ions diffuse to the catholyte, which may be attributed to lowered ohmic resistance in the catholyte.

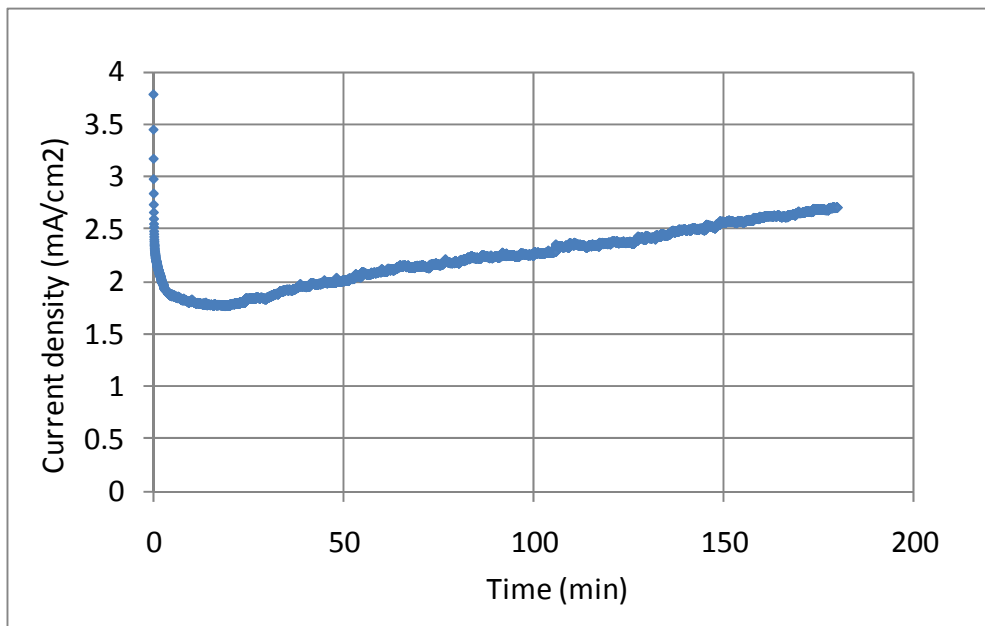


Figure 3. Potentiostatic analysis of the electrolytic cell.

The concentration of Li^+ ions in the catholyte was determined by IC and shown in Figure 4. Due to the low concentration of Li^+ ions in the anolyte (i.e., seawater) compared to 10,800 ppm of Na^+ ions, IC could not distinguish two ions. The Li^+ ion diffusion is assisted by the chemical and electrochemical potential differences, i.e., concentration and potential gradients, across the membrane. The Li^+ ion concentration increases with time and reaches 0.024ppm after three hours of operation. The concentration in the catholyte can be further increased by introducing fresh seawater (i.e., high Li^+ ion concentrate) in the anolyte, reducing the volume of catholyte, and operating longer time. As the membrane ($\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ sprayed Nafion) permits diffusion of seawater solutions from the anolyte to the catholyte, crossover, that other cations (e.g., Na^+ and K^+) and anions (Cl^- and SO_4^{2-}) diffused and were observed in the catholyte. Thus, ion-selective membranes may be favorable to the polymer-based ones.

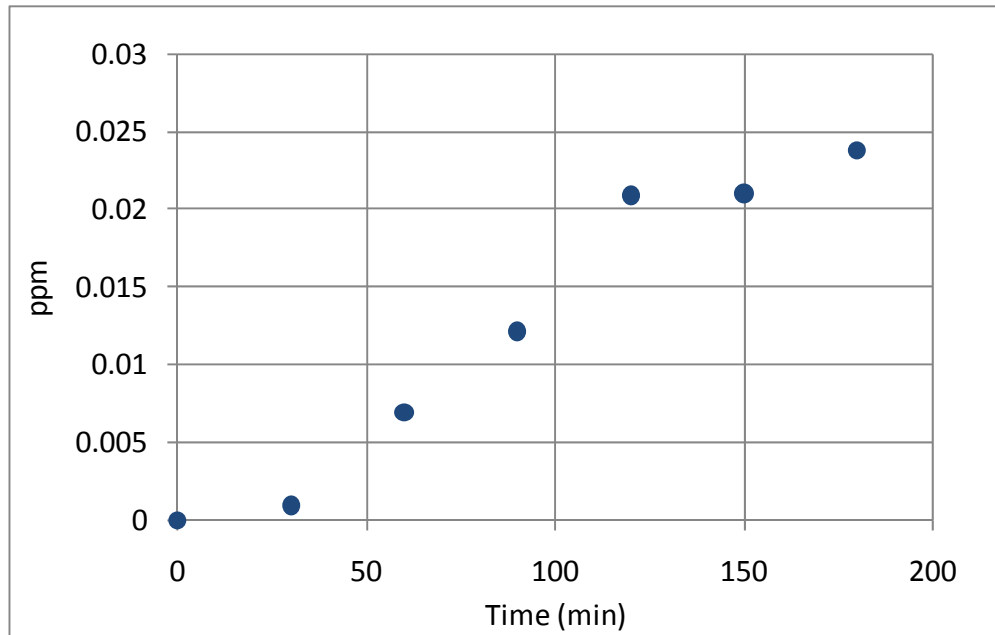


Figure 4. Li⁺ ion concentration in the catholyte with time.

Linear Sweep Voltammetry 2

LSV was carried out using the Li₂S-P₂S₅ glass ceramic membrane. The potential was scanned to 4V at the rate of 50mV/sec.

Operating Conditions:

Anode: carbon felt (0.5mm)

Anolyte: Seawater 300ml

Anolyte flow rate: 10ml/min

Cathode: carbon felt (0.5mm)

Catholyte: DI water of 100ml

Catholyte flow rate: 10ml/min

Electrolyte: Li₂S-P₂S₅ glass ceramic

Figure 5 shows the LSV of the electrolytic cell. The resistivity of the membrane in the cell is $9.25 \times 10^4 \Omega \cdot \text{cm}$, which is the contributions from the seawater in the anolyte, ion conductor, and fresh water in the catholyte.

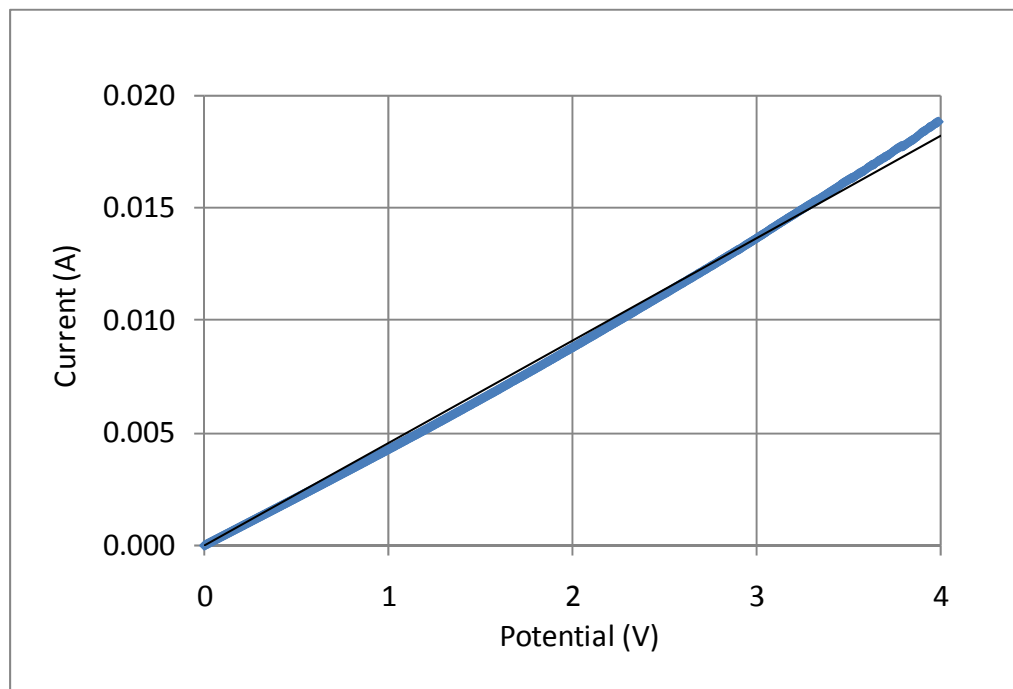


Figure 5. Linear sweep voltammogram of the electrolytic cell.

Potentiostatic Experiment 2

Figure 6 shows potentiostatic analysis of the cell. Current density decreased from 2.1V to 2.05V after 2 hours. Figure 7 shows the Li^+ ion concentration in the catholyte; it increases with time and reaches 0.07ppm after two hours. Compared to $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ sprayed Nafion, the lithium recovery from seawater was improved significantly. Further, the ceramic membrane only allows diffusion of ions but prevents transport of bulk solution. Figure 8 shows the IC chromatogram of catholyte after two hours. An appreciable amount of Li^+ ions is detected. However, other ions, i.e., Na^+ and K^+ , were also observed in the catholyte.

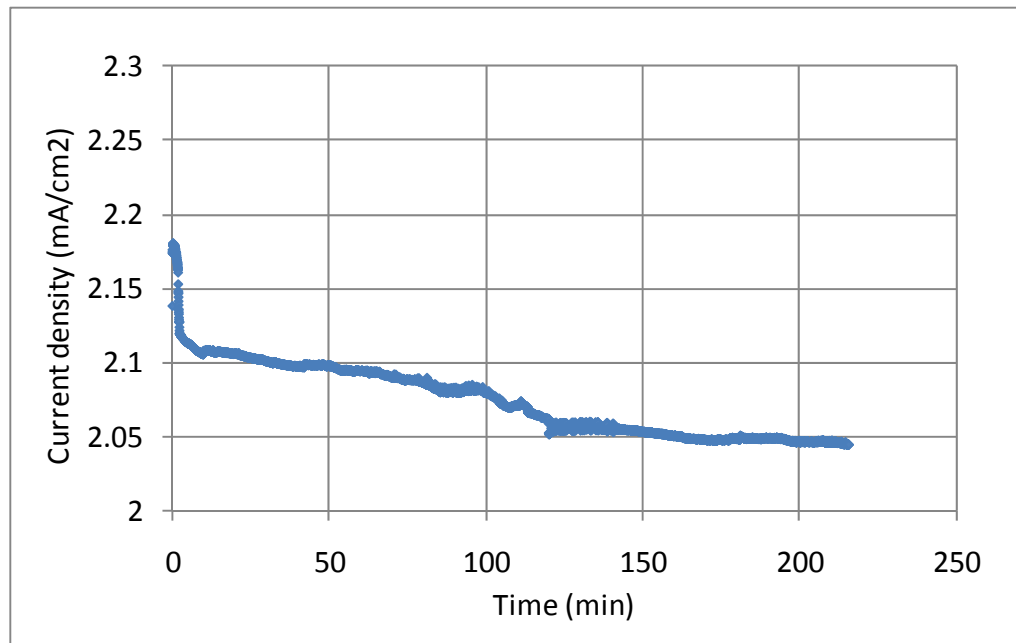


Figure 6. Potentiostatic analysis of the electrolytic cell.

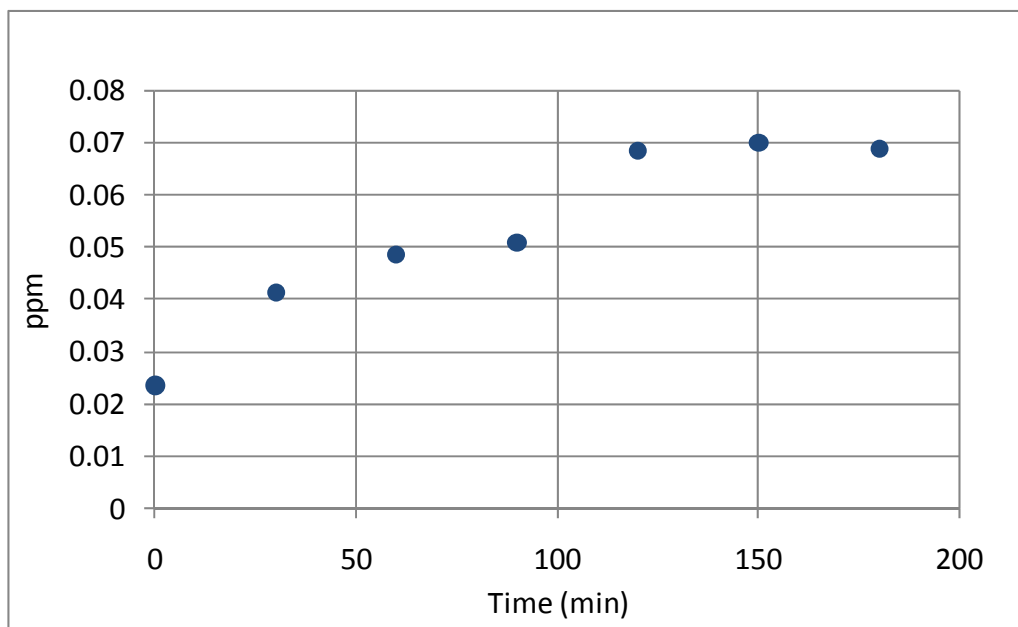


Figure 7. Linear sweep voltammogram of the electrolytic cell.

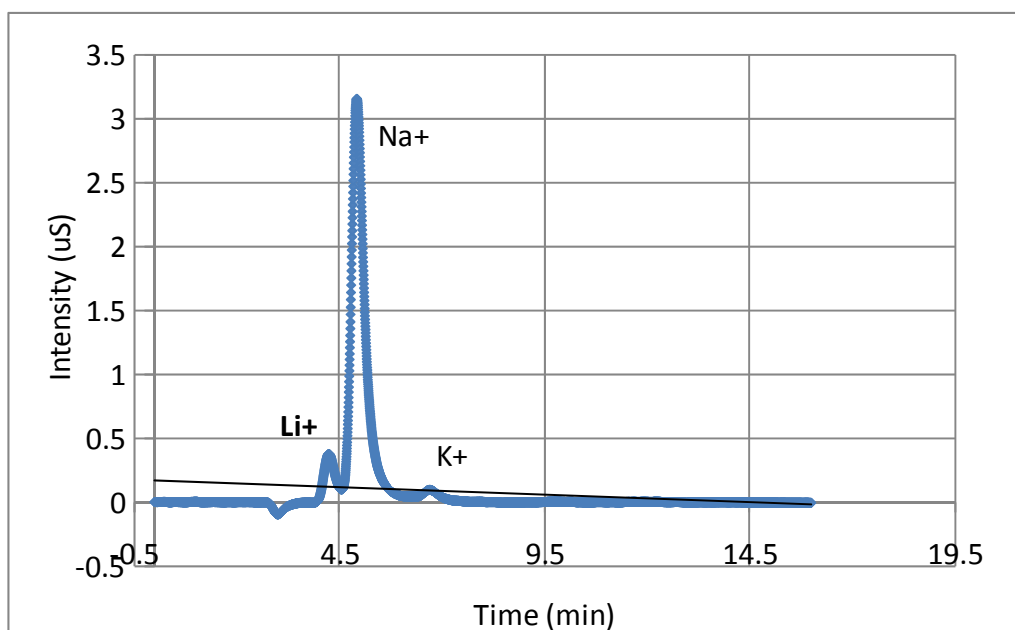


Figure 8. IC chromatogram of catholyte after two hours of operation.

Summary:

An electrochemical process extracting lithium from seawater was investigated. Li ions could be extracted from seawater using an electrochemical process employing solid electrolytes. Li ion conducting ceramic membrane produces high selectivity to lithium ion in the catholyte. Cell resistance should be reduced to increase the diffusion of lithium ions.

Plans for Next Quarter:

The efficiency of lithium extraction should be improved by reducing the cell resistance and lithium ion selectivity of the membrane. The resistance may be reduced by developing thinner membrane, introducing electrolyte in the catholyte, and employing electrocatalysts at the anode and cathode.

The planned activities for next quarter include:

- Prepare thin and dense Li^+ selective membranes
- Investigate the effect of electrolyte (e.g., HCl) in the catholyte
- Prepare electrocatalysts on Nafion or ceramic electrolyte to improve the extraction efficiency
- Measure hydrogen gas production along with lithium extraction during the process employing active electrocatalysts (Figure 9)
- Continuously optimize the electrochemical Li recovery process

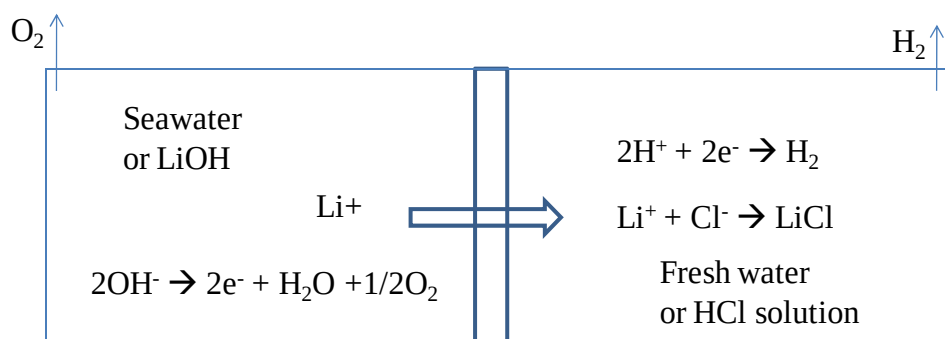


Figure 9. Schematic representation of electrochemical lithium extraction process.

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