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1. REPORT DATE (DD-MM-YYYY) 26-10-2010		2. REPORT TYPE PROGRESS REPORT		3. DATES COVERED (From - To) JULY 26, 2010-Oct. 25, 2010
4. TITLE AND SUBTITLE SIMULTANEOUS EXTRACTION OF LITHIUM AND HYDROGEN FROM SEAWATER		5a. CONTRACT NUMBER N00014-10-M-0234		
		5b. GRANT NUMBER		
		5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Pyoungho Choi		5d. PROJECT NUMBER N/A		
		5e. TASK NUMBER 0001AA		
		5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES) UNIVERSITY OF CENTRAL FLORIDA FLORIDA SOLAR ENERGY CENTER 1679 CLEARLAKE ROAD COCOA, FL 32922-5703		8. PERFORMING ORGANIZATION REPORT NUMBER QUARTERLY PROGRESS REPORT FOR PERIOD 7/26/10 - 10/25/10		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) OFFICE OF NAVAL RESEARCH 875 N. Randolph St. ARLINGTON, VA 22203-1995		10. SPONSOR/MONITOR'S ACRONYM(S) ONR		
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) 0001AA		
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A APPROVED FOR PUBLIC Release. DISTRIBUTION IS UNLIMITED				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT AN electrochemical cell was constructed and tested for Lithium extraction.				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	11	Pyoungho Choi
			19b. TELEPHONE NUMBER (include area code) (321) 638-1436	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Contract Number N00014-10-M-0234
Attachment No. 2

Quarterly Progress Report

Project Title: Simultaneous Extraction of Lithium and Hydrogen from Seawater

Project Period: 7/26/2010 – 7/25/2011

Reporting Period: July 26, 2010 – October 25, 2010

Date of Report: October 26, 2010

Recipient: University of Central Florida

Award Number: N00014-10-M-0234

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Project Objective: The ultimate goal of the proposed research is to demonstrate a novel electrolytic process for extracting Li from seawater, which contains a number of valuable metals (Table1).¹ The technical objectives of this research are to construct an electrolytic cell, develop high capacity lithium ion adsorbing materials, design solid electrolytes conducting Li ion subject to concentration and potential gradients, and evaluate the process energy consumption and Li production costs.

Table 1. Concentrations and amount of dissolved metals ions in the sea, compared with the estimated land reserves.

Element	Concentration (ppm)	Total Oceanic Abundance (tons)	Mineral Reserves in Land (tons)
Na	10,800	1.40×10^{16}	-
Mg	1,290	1.68×10^{15}	2.20×10^9
Ca	411	5.34×10^{14}	-
K	392	5.10×10^{14}	8.30×10^8
Li	0.1780	2.31×10^{11}	4.10×10^6
Ba	0.0210	2.73×10^{10}	1.90×10^8
Mo	0.0100	1.30×10^{10}	8.60×10^6
Ni	0.0066	8.58×10^9	6.70×10^7
Zn	0.0050	6.50×10^9	1.80×10^8
Fe	0.0340	4.42×10^9	1.50×10^{11}
U	0.0330	4.29×10^9	2.60×10^6 - 5.47×10^6
V	0.0190	2.47×10^9	1.30×10^7

Approach: Figure 1 shows the schematic of lithium extraction from seawater by an electrochemical process. Li^+ ion containing seawater is introduced in the anode in which seawater is dissociated to oxygen, protons and electrons, while a lithium extracting solution is fed to the cathode side of the cell. A thin and highly ion-conductive electrolyte is placed between the electrodes. The migration of Li^+ depends on the potential applied between the anode and

cathode. At low potential, i.e., $<1.23\text{V}$, Li^+ ion may migrate to the negative electrode without the water dissociation reactions. At high potential, i.e., $>1.23\text{V}$, Li^+ ions in seawater are forced to diffuse through the electrolyte to the negative side where they combine with hydroxyl ions (OH^-), co-producing H_2 and Li solution from seawater. As the anode, carbon felt or water splitting electrocatalysts will be used. Li -adsorbing materials, e.g., LiMn_2O_4 , will be prepared and coated onto the anode to increase the Li^+ ion adsorption, and subsequent diffusion to the cathode through electrolytes. As the electrolyte, polymer (e.g., Nafion) and Li^+ ion selective LISICON (lithium super ionic conductor) will also be implemented and their role in the transport of Li^+ ions from the anode to the cathode side will be quantitatively analyzed.

An electrolytic cell will be designed and various electrochemical reaction & process parameters will be determined. An overall performance equation will be developed to describe the relation among the potential, current and concentration of Li^+ ions in the anolyte and catholyte. The process will be optimized and a basic cost analysis of the process will be performed.

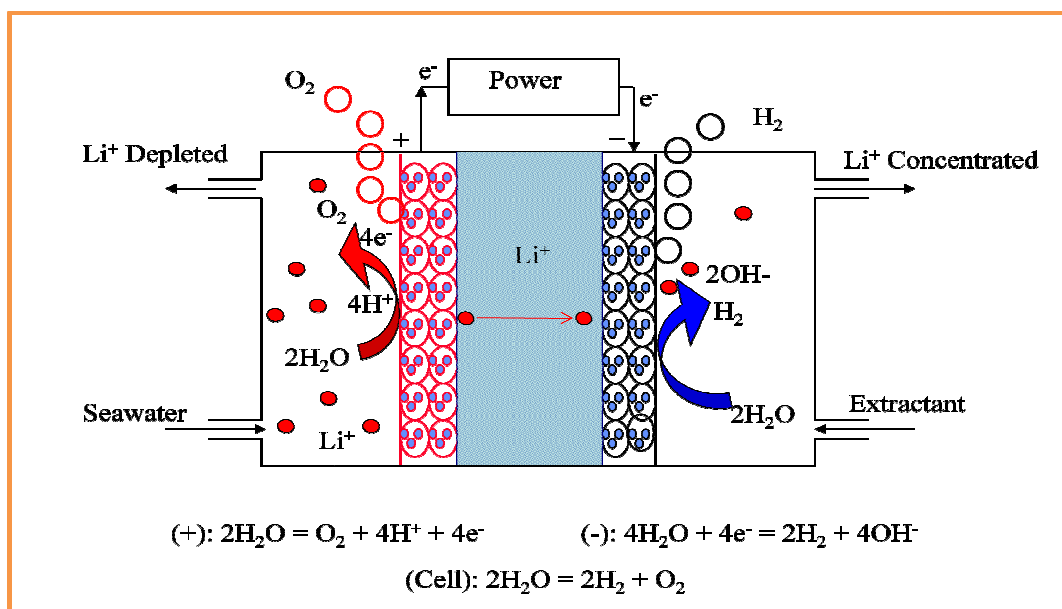


Figure 1. Schematic of the electrochemical process extracting lithium from seawater

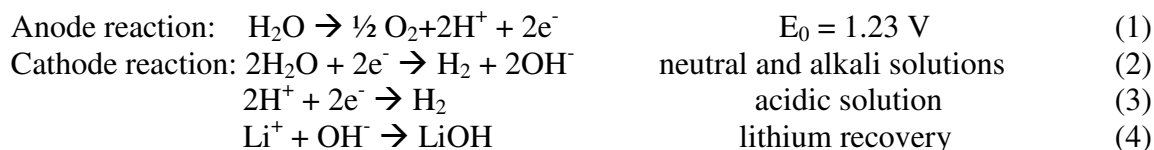


Figure 2 shows structure of LiMn_2O_4 materials.² Lithium atom is in an 8a tetrahedral site in the spinel structure. Acid treatment of the LiMn_2O_4 removes lithium and generates atomic holes, which allow lithium ion to access the site, but not other ions. The mechanism of Li insertion/extraction has been extensively studied.³⁻⁵

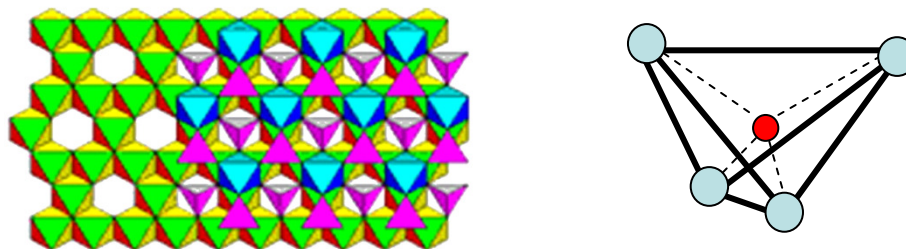
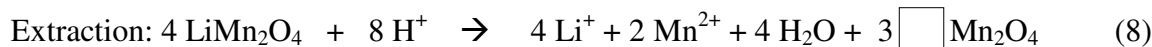
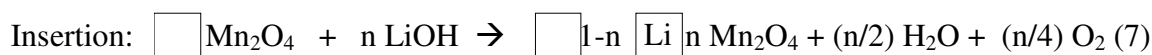
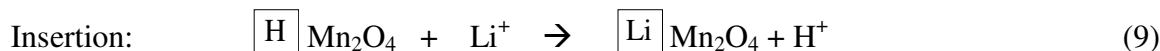


Figure 2. An example of lithium adsorbent, LiMn₂O₄ (Li in 8a tetrahedral site).

For LiMn₂O₄, it proceeds by a redox mechanism which generates oxygen in the insertion as follows:



whereas for Li_{1.33}Mn_{1.67}O₄ and Li_{1.6}Mn_{1.6}O₄, it proceeds mostly by ion-exchange mechanism as



where $\square$ represents a tetrahedral vacant site and n is the number of moles of inserted Li. The manganese oxide adsorbents are very efficient and other ions in seawater do not interfere with Li for the adsorption.

Project Status: A Li⁺ adsorbing material was synthesized using a solid-state reaction and Li⁺ conducting ceramic materials, namely LISICON, were also prepared by a solid-state reaction. As an initial experiment, carbon felt which does not have catalytic activity for water splitting, was used as the anode and cathode. An electrochemical cell was constructed and tested with the materials incorporated. Electrochemical potential was applied between the anode and cathode, and current-potential curves are obtained. A number of electrodes, adsorbents and electrolytes are being prepared, characterized, and tested in the electrolytic cell.

Synthesis of Li⁺ adsorbents: LiMg_{0.5}Mn_{1.5}O₄ was prepared by solid state reaction. Li₂CO₃, Mg(CH₃COO)₂·4H₂O and MnCO₃ were mixed at a 1:0.5:1.5 molar ratio with ball mill machine for 30 min, and calcined at 600°C for 4 hours. Surface area and porosity were analyzed by BET.

Synthesis of LISICON: The 80Li₂S:20P₂S₅ glassy powders were prepared from the mixture of Li₂S and P₂S₅ crystalline powders.⁶ The mixture was mechanically milled. The powders were heated to 230°C and kept at the temperature for 4 hours, and slowly cooled down. A commercially available LISICON film (Ohara, 25.4mm x 25.4mm x 1mm) was also used as an initial experiment.

Construction of Electrolytic Cell: An electrolytic cell was made by incorporating the cell components with a two-pump flow system.

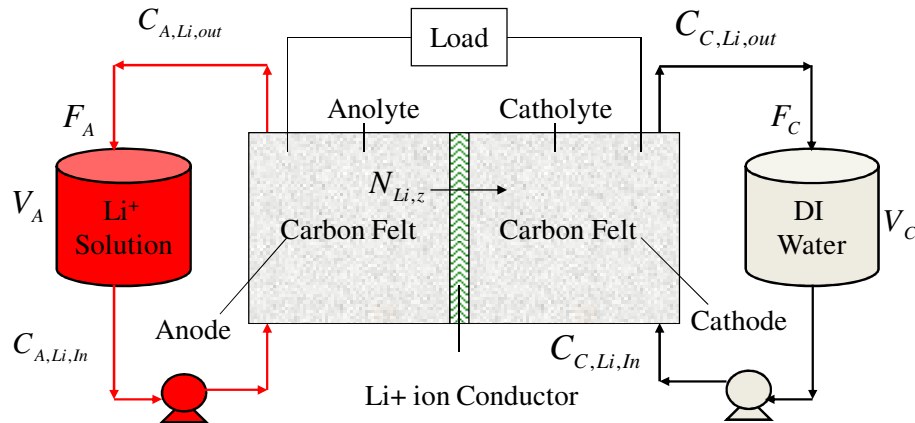


Figure 1 Schematic of electrolytic cell extracting Li^+ ion from seawater or Li-concentrates.

Quantification of Li^+ ion Concentration in Solution: The concentration of Li^+ ion in solution was analyzed by Ion Chromatography. LiNO_3 solution was used to obtain a calibration curve.

Results

BET and porosity of the prepared adsorbents

The specific surface area and pore volume of the prepared sieve1 adsorbent are shown in Table 1. The molecular formula of the sieve1 composed of Li, Mg and Mn are being measured by AAS (Atomic Adsorption Spectroscopy). Also atomic structure and grain size of the adsorbent is being investigated by XRD.

	BET Surface Area, m^2/g	Pore volume cc/g
sieve 1	8.997	0.0375

Li^+ ion calibration by Ion Chromatography

The concentration of Li^+ ion in solution was determined by IC. Figures 2 and 3 show an IC chromatogram of 1 ppm and a calibration curve of Li^+ ions from 0.1ppm to 1ppm, respectively.

Operating Conditions:

- Effluent: 20 mM Methanesulfonic acid, Effluent flow rate=1.0ml/min
- Detection: Suppressed Conductivity
- Suppressor: Cation Self-Regenerating Suppressor (CSRS ULTRA II, 4mm)
AutoSuppression Recycle Mode
- Applied Current: 59 mA
- Injection volume: 25 microliter

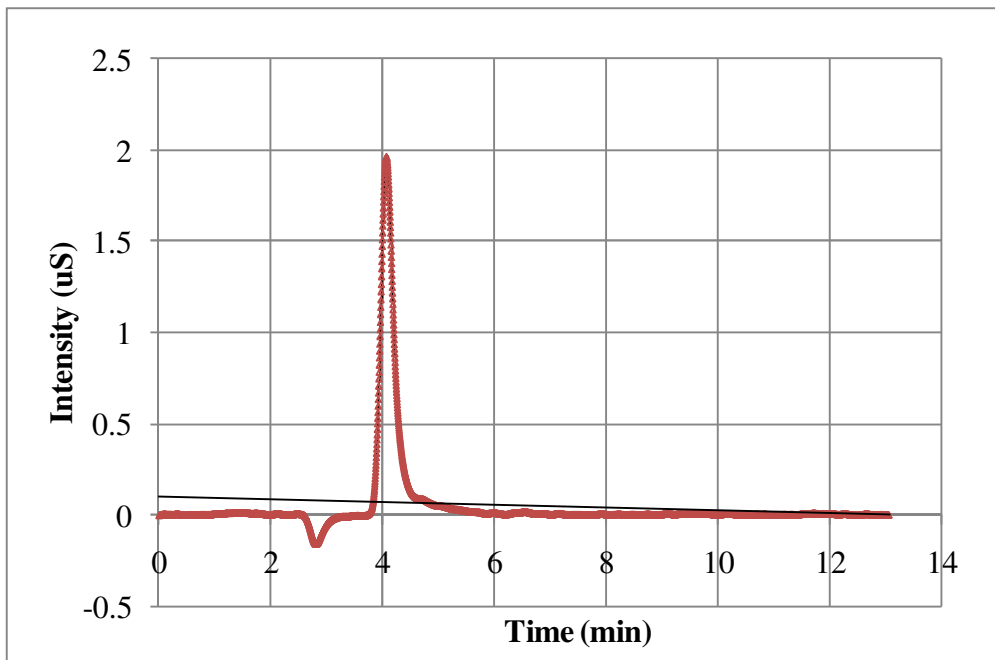


Figure 2. IC chromatogram of 1 ppm Li^+ ion solution

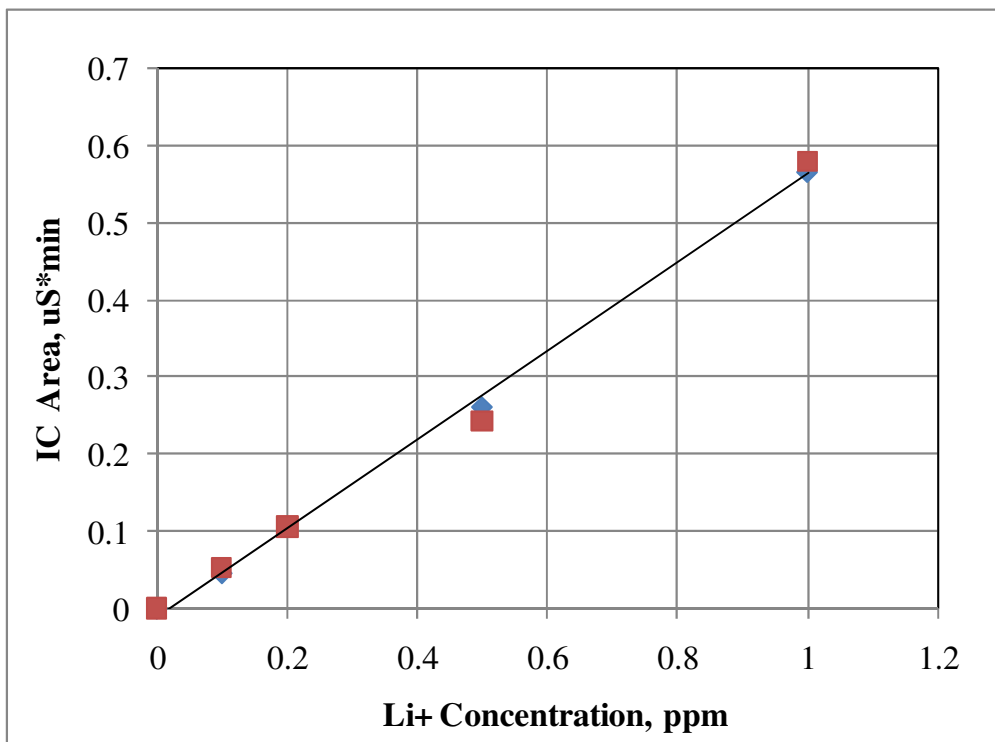


Figure 3. Calibration curve of Li^+ ions from 0.1ppm to 1ppm.

Linear Sweep Voltammetry 1

First, linear sweep voltammetry (LSV) experiment was carried out. The anolyte was 1ppm Li^+ ion solution and catholyte was deionized water. The potential range of 0-3V was scanned and resulting current was obtained. No precious electrode was used and Nafion was used as the electrolyte.

Operating Conditions:

Anode: carbon felt (0.5mm)

Anolyte: 1ppm Li^+ ion solution of 300ml

Anolyte flow rate: 10ml/min

Cathode: carbon felt (0.5mm)

Catholyte: DI water of 100ml

Catholyte Flow rate: 10ml/min

Electrolyte: Nafion

Figure 4 shows the LSV of the electrolytic cell with the operating conditions above. According to the chromatogram, more than 2V is required to generate current density of 1 mA/cm^2 . No gas evolution was observed due to the absence of electrocatalysts for the electrochemical water splitting reactions.

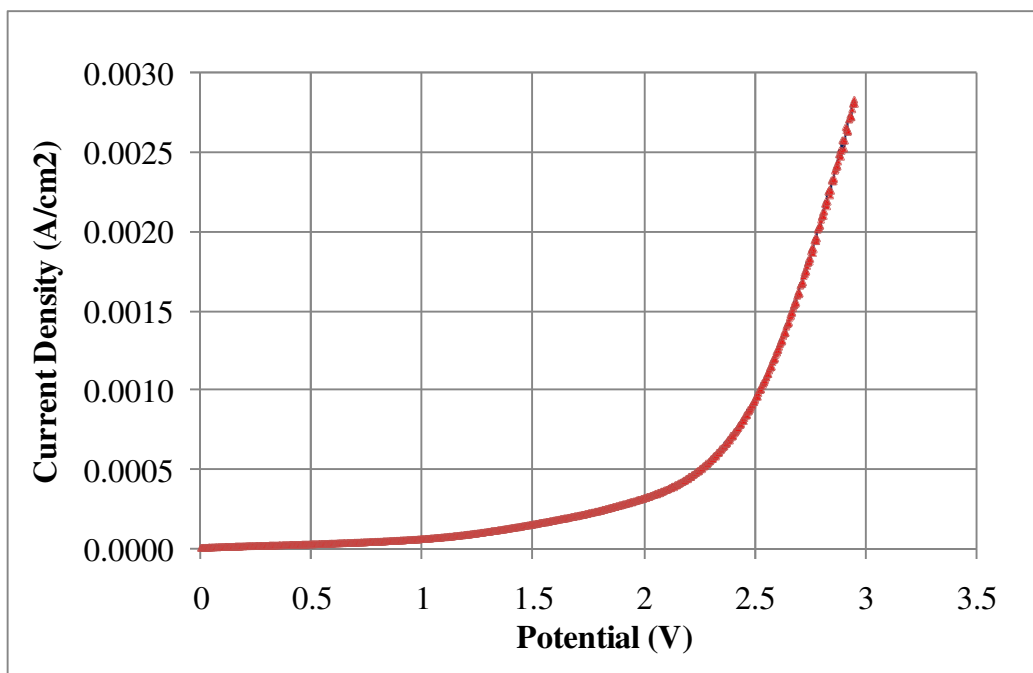


Figure 4. Linear sweep voltammogram of the electrolytic cell.

Galvanostatic Experiment 1

The electrolytic cell current was set at 1 mA/cm^2 and resulting voltage was recorded with time. Anolyte as well as catholyte from the cell was collected every thirty minutes for the analysis of Li^+ ion concentration. As shown in Figure 5, the cell was stable and potential was decreased over time.

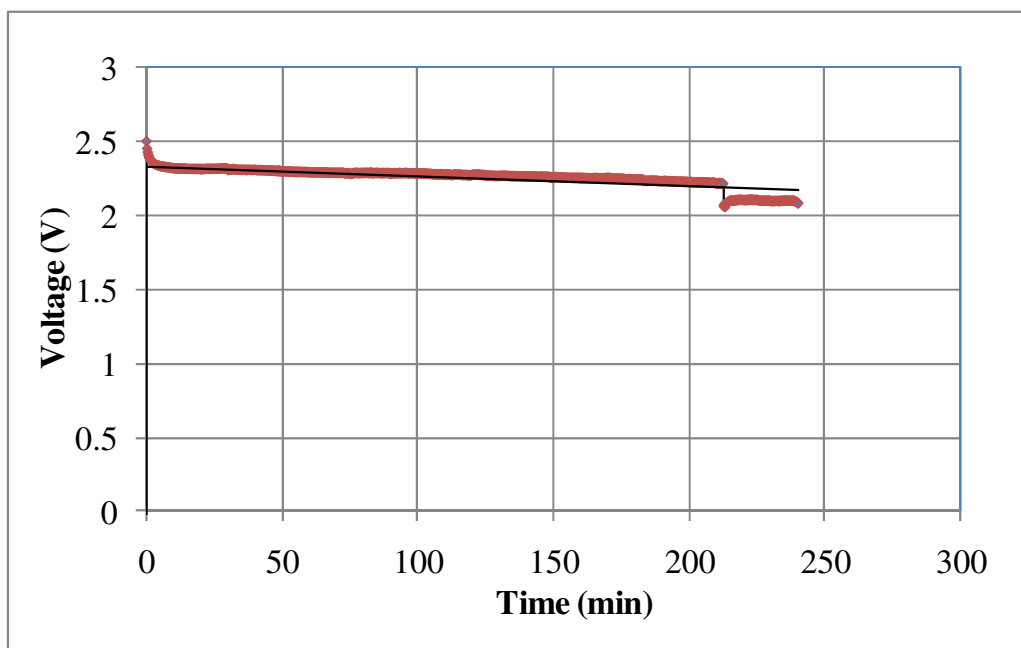


Figure 5. Galvanostatic voltammogram of the electrolytic cell.

The concentration of Li^+ ions in the anolyte and catholyte was determined by IC and shown in Figure 6. The concentration of anolyte decreases because of the diffusion of Li^+ ions to the catholyte under the electrode potential. The diffusion is also assisted by the chemical potential difference, i.e., concentration gradient, across the membrane. The concentration of catholyte was increased with time and higher than that of anolyte due to the lower working volume of the solution. After 2 hours of operation, the concentration of Li^+ ion in the catholyte was 0.76 ppm, while that in anolyte was 0.68 ppm. Thus, the Li^+ ion can be concentrated by the electrolytic cell by employing small volume of catholyte reservoir.

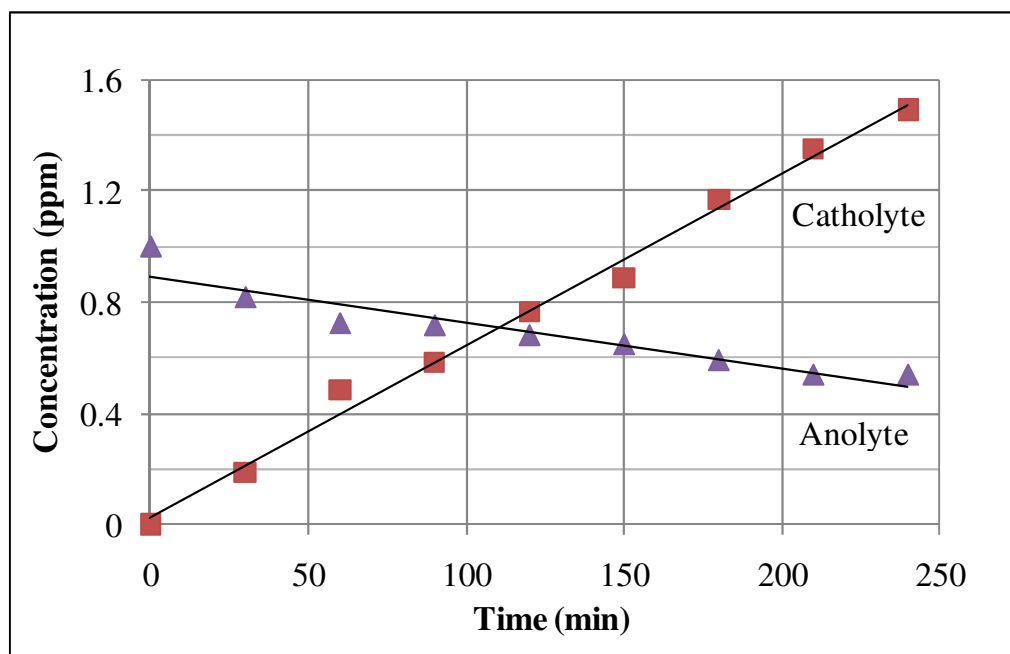


Figure 6. Li^+ ion concentration in the anolyte and catholyte with time.

Linear Sweep Voltammetry 2

LSV experiment employing a lithium superionic conductor (LISICON) was carried out using the Li^+ ion solution. The potential range of 0-3V was scanned and resulting current was obtained.

Operating Conditions:

Anode: carbon felt (0.5mm)

Anolyte: 1ppm Li^+ ion solution of 300ml

Anolyte flow rate: 10ml/min

Cathode: carbon felt (0.5mm)

Catholyte: DI water of 100ml

Catholyte flow rate: 10ml/min

Electrolyte: LISICON (Ohara Inc.)

Figure 7 shows the LSV of the electrolytic cell. The current is relatively low, compared to that of the Nafion membrane. The current density of $0.1\text{mA}/\text{cm}^2$ could be obtained at 1.7V. No gas evolution was observed by the electrochemical water splitting reactions. Figure 8 shows the concentration of catholyte when a galvanostatic experiment was carried out at $0.1\text{mA}/\text{cm}^2$. The Li^+ ion concentration in the catholyte increases to 0.05 ppm after 2 hours of operation.

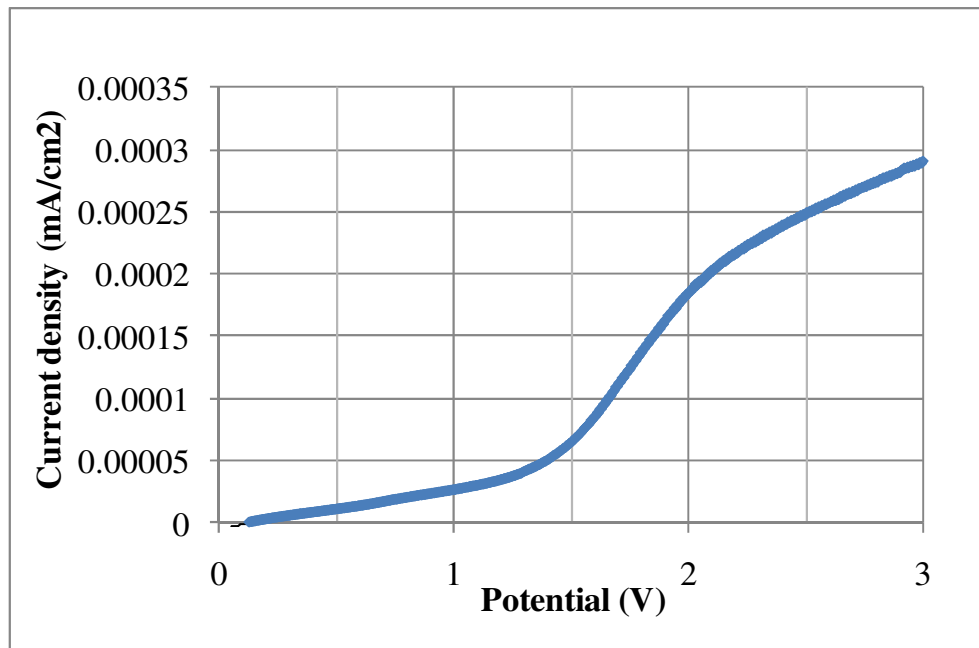


Figure 7. Linear sweep voltammogram of the electrolytic cell.

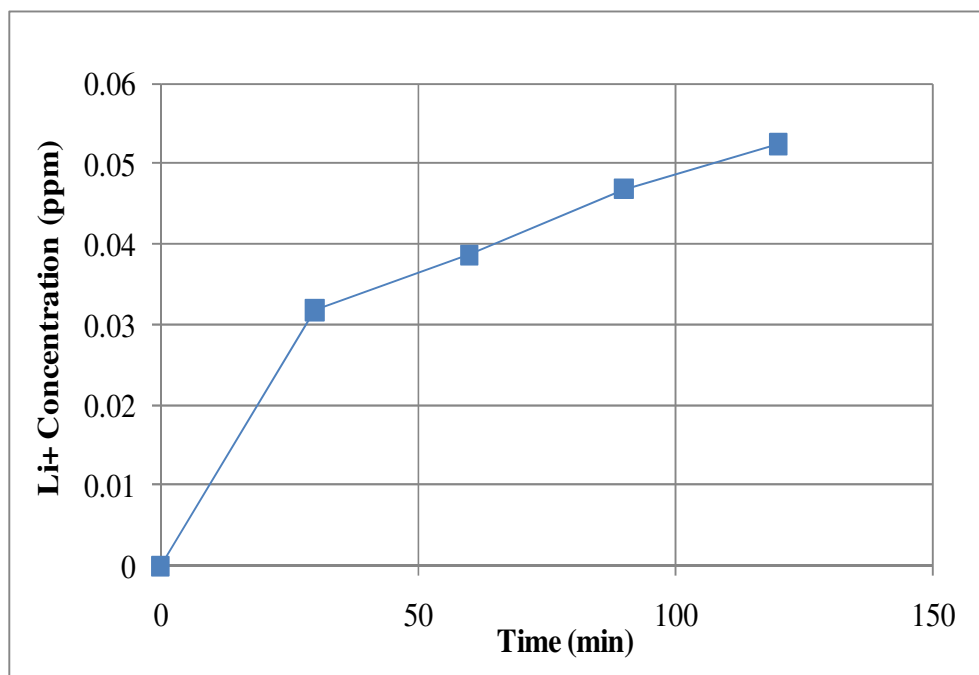


Figure 8. Li⁺ ion concentration in the catholyte with time.

Analysis

A simple analysis is being performed to understand the role of the electrocatalysts, Li^+ adsorbents and conductors in the electrolytic cell.

The basic conservation equations are developed.

Anolyte Reservoir

$$V_A \cdot \frac{dC_{A, \text{Li}}}{dt} = F_A C_{A, \text{Li}, \text{In}} - F_A C_{A, \text{Li}, \text{out}}$$

where V_A is the volume of anode reservoir (seawater tank), F_A is the volumetric flow rate of the working fluid in the anode, $C_{A, \text{Li}, \text{In}}$ and $C_{A, \text{Li}, \text{out}}$ are the concentration of Li^+ ion in the anode side entering and exiting the electrolytic cell, respectively,

Anode Side of Electrolytic Cell

$$F_A C_{A, \text{Li}, \text{In}} - F_A C_{A, \text{Li}, \text{out}} = N_{\text{Li}, z} \cdot A_M$$

$N_{\text{Li}, z}$ is the flux of i in z -direction (across the membrane), and A_M (cm^2) is the geometric area of the MEA.

Electrode Layer

$$\frac{dN_{\text{Li}, z}}{dz} = r_A$$

where r_A is the rate per volume of electrode layer

Li^+ Conducting Electrolyte

If constant chemical potential throughout the electrolyte is assumed,

$$i = -\sigma \frac{d\phi^\alpha}{dz}$$

where σ is the conductivity of the electrolyte and ϕ^α is the potential at the electrolyte phase α .

Cathode Side of Electrolytic Cell

$$F_C C_{C, \text{Li}, \text{In}} - F_C C_{C, \text{Li}, \text{out}} = N_{\text{Li}, z} \cdot A_M$$

Catholyte Reservoir

$$V_C \cdot \frac{dC_{CC,Li}}{dt} = F_C C_{C,Li,in} - F_A C_{C,Li,out}$$

A performance equation will be generated and the effect of the adsorbent, Li⁺ ion conductor and electrocatalyst on the performance of the Li⁺ ion extraction will be quantitatively analyzed.

Plans for Next Quarter:

The planned activities for next quarter include:

- Characterize the prepared adsorbents and glass-ceramic electrolytes
- Prepare electrodes and thin films of Li⁺ ion selective electrolytes
- Incorporate the adsorbents and Li⁺ ion conductor in the electrolytic cell
- Use seawater as the working catholyte solution and characterize the materials and cell
- Optimize the electrochemical Li extraction process (examine the electrochemical cell variables including cell potential, amount of adsorbent, thickness of solid electrolyte, and flow rate of seawater through the cell, etc.)

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