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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 cathoyte in the flow system.

15. SUBJECT TERMS

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Final Report

Project Title: Simultaneous Extraction of Lithium and Hydrogen from Seawater

Project Period: 7/26/2010 – 7/25/2011

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1. Background

Lithium is a key component in secondary batteries and its demand has been increasing drastically in recent years. Accordingly, there are concerns on the supply of lithium. Globally, most of the known reserves of minable lithium are concentrated in South America (Bolivia and Chile), Australia, and China. There have been debates as to whether the lithium supplies would meet the surging demand, especially in electric vehicles. Regardless of the debates, stable provision of lithium would stabilize the price of the metal and can increase the energy security of US.

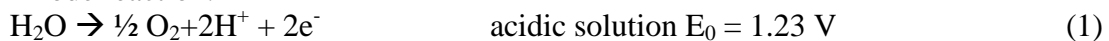
Seawater contains 230 billion tons of lithium which is more than four orders of magnitude higher than lithium contained in all terrestrial mines and salt lakes combined. However, the concentration of lithium in seawater is so low, *i.e.*, 0.17 mg/L, that a new technology to extract the lithium in seawater should be developed [1]. Seawater is also the ultimate source of hydrogen. The production of hydrogen from seawater is technically different from that of fresh water because it contains many cations that interfere with the electrolytic process. Seawater contains salts of less than 35 salinity (g salt/kg solution) and seawater electrolysis (SWE) technology lies between the two well-known technologies, namely, water (or fresh water) electrolysis and the brine electrolysis using a solution containing 350 salinity (g salt/kg solution). While electrolysis of seawater can be carried out either desalination of sea water and followed by the well-established fresh water electrolysis or direct electrolysis of sea water, the latter seems more attractive because the desalination often employs the reverse osmosis process that not only requires additional cost but also causes environmental problems.

Hydrogen Generation by Seawater Electrolysis [2-10]

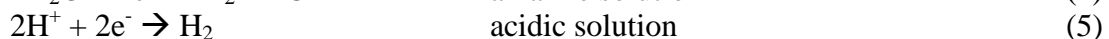
Two main types of industrial electrolysis units are being produced today. They basically differ in the type of electrolyte that is used. The first type of electrolyzers is characterised by the use of a strongly alkaline aqueous solution of 25–35 wt% potassium hydroxide (KOH) to maximise the ionic conductivity, in which the hydroxide ions (OH⁻) are the charge carriers. The reactions that take place in the electrolysis cells. In the second type of electrolyzers the electrolyte is an ion conducting membrane that allows hydrogen ions to be transported from the anode to the cathode side to recombine forming hydrogen. They are known as proton exchange membrane (PEM) electrolyzers.

Figure 1 shows a configuration of the seawater electrolysis. Seawater and fresh water are introduced to the anode and cathode side, respectively. Hydrogen and oxygen are produced at the cathode and anode surface, respectively. At the anode, oxygen as well as chlorine gas can be produced, while the hydrogen is generated at the cathode. The oxygen evolution at the anode is thermodynamically favorable to the chlorine generation

Anode reaction:



Cathode reaction:



However, the kinetics of the chlorine generation is much faster than that of oxygen evolution, i.e., the ratio of exchange current densities of chlorine to oxygen production is in the range of 10^3 - 10^7 . Thus, at high potentials, e.g., > 2.0 V, the chlorine gas may be evolved exclusively. However, the two reactions competitive as the concentration of reacting water molecule is much higher than that of chlorine ions near the electrode surface.

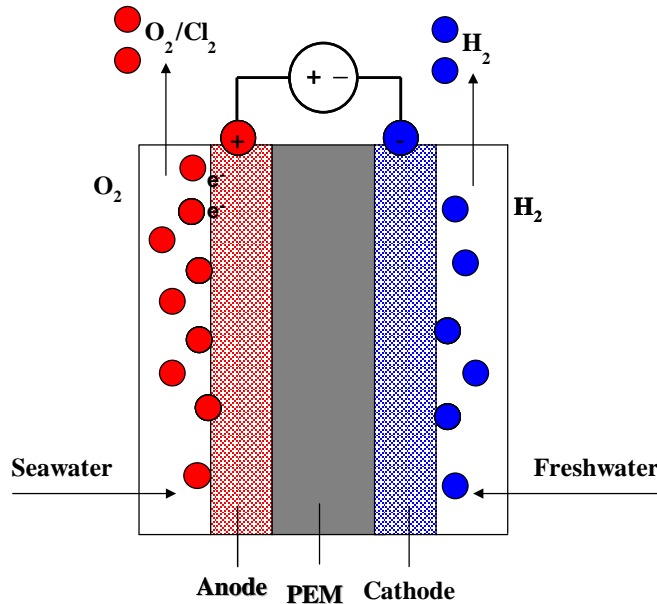


Figure 1. Schematic of electrolytic cell extracting Li^+ ion from seawater.

During the SWE, Ca^{2+} and Mg^{2+} ions may be participate in the following reactions,



which may result in solid deposits of Ca(OH)_2 and Mg(OH)_2 on the cathode surface. The formation of the deposits may inhibit the diffusion of reacting species to the electrode surface and blocks the active site of cathode for the hydrogen generation reaction.

Li Extraction [11-17]

Lithium is currently produced from brine due to its cost advantage over hard rock based process. Several methods such as adsorption, solvent extraction, and co-precipitation have been investigated for the extraction of lithium from seawater. The adsorption method is relatively attractive for the recovery of lithium from seawater because certain materials such as spinel type manganese oxides show extremely high affinity toward lithium ions only. The technology currently developed, however, requires very long time to win Li from seawater and the extraction efficiency is low. Further, it requires a purification step-not cost effective.

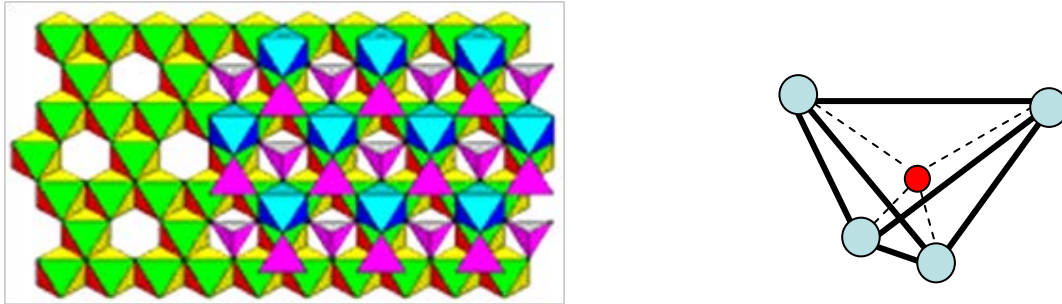


Figure 2. An example of lithium adsorbent, LiMn_2O_4 (Li in 8a tetrahedral site).

2. Goal

Under electrochemical potential, Li^+ ions in the seawater may be made to migrate toward a negative electrode. A lithium selective membrane is placed between the electrodes which allows Li^+ ions to permeate, but blocks the passage of other ions present in the seawater, from reaching the cathode. The ultimate goal of the proposed research is to demonstrate a novel electrolytic process for extracting Li (or other valuable minerals) from seawater. The process may be combined with seawater electrolysis process where electrochemical potential drives the hydrogen generating reactions.

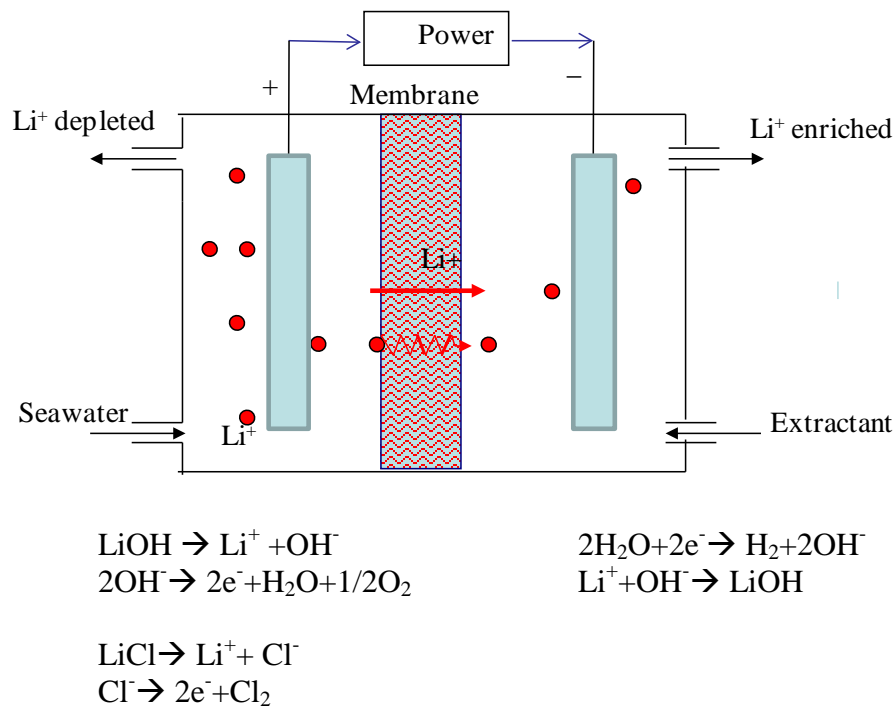


Figure 3. Schematic of the electrochemical process extracting lithium from seawater.

3. Experimental

Synthesis of Li^+ adsorbents: lithium adsorbing ion-sieve $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared by solid state reaction. 6.1g of Li_2CO_3 , 8.9g of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 5.6g of MnCO_3 were mixed, ball milled for 2 hours, and calcined at 600°C for 4 hours.

Synthesis of Lisicon: the lithium ion-conducting materials were prepared from the mixture of Li_2S and P_2S_5 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.

MEA preparation: Iridium (Ir) was used as the anode and Pt/C (Tanaka, 45.5wt.% Pt), or Ir, or Raney-Ni was used as the cathode. MEAs were prepared by spraying the electrode onto diffusion layers using a spraying technique. The catalyst ink was prepared with 180mg catalyst, 5g methanol, water, and 1.54g of 5wt.% solubilized Nafion[®] solution (EW1100, supplied by Ion Power): this gives 30% ionomer in the catalysts layer. The loadings were $3.0\text{mg}/\text{cm}^2$ and $1.5\text{mg}/\text{cm}^2$, for the anode and cathode, respectively. The NRE 212 membrane was “sandwiched” between electrode-coated diffusion layers.

Electrochemical measurement: The electrochemical measurements were carried out in an electrolyzer with a two-pump flow system (Figure 4). Li solutions or seawater was used as the anolyte and deionized water as the catholyte. For lithium extraction, potentiostatic experiments (set potential 2-4V) were carried out, while for seawater electrolysis galvanostatic measurements were made.

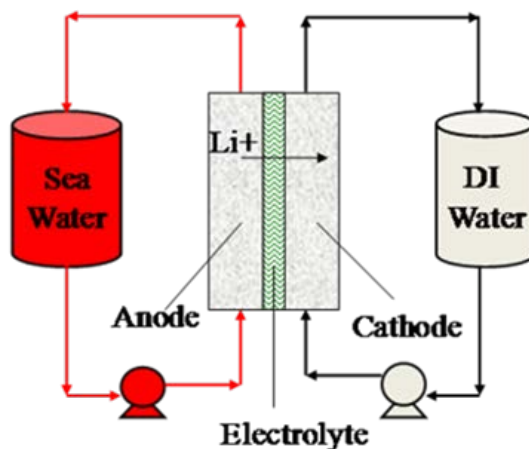


Figure 4. An electrolytic cell extracting Li^+ ion from seawater or Li-concentrates.

Measurement of hydrogen gas produced: Hydrogen and oxygen gases coming out of the cell were collected and the amount was measured volumetrically.

Ion chromatography: 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 Na_2CO_3 , 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).

4. Results & Discussion

IC Calibration of Li⁺ ions in a solution

The concentration of Li⁺ ion in solution was determined by IC. Figure 5 shows the calibration curve of Li⁺ ions from 0.1ppm to 1ppm, respectively.

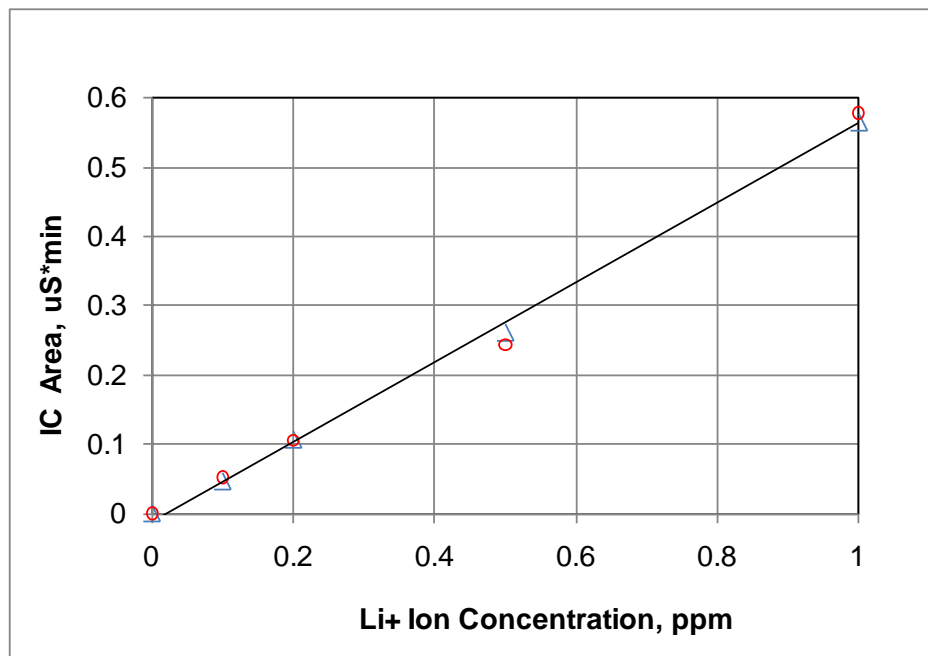


Figure 5. Calibration of lithium ions in solution by IC (Effluent: 20 mM Methanesulfonic acid, Effluent flow rate=1.0ml/min, detection: Suppressed Conductivity, Suppressor: Cation Self-Regenerating Suppressor (CSRS ULTRA II, 4mm), Applied Current: 59 mA, Injection volume: 25 microliter).

A linear relation was observed between the concentration of lithium and IC area over 0.1-1 ppm lithium concentration. Figure 6 shows the IC chromatogram of seawater diluted by 100 times. Due to the high concentration of Na⁺ relative to Li⁺ ions, the Li⁺ ions were not separately distinguished; Li⁺ peak comes out just before the Na⁺ peak.

I. Lithium Extraction Using A Non-Ionselective Polymer membrane

I-1. Li extraction from 1 ppm lithium model solution

Nafion was used as the electrolyte and carbon felt was used as the electrode or current collector. Anolyte is 1 ppm lithium solution and catholyte is deionized water solution. Figure 7 shows linear sweep voltammetry (LSV) of the electrochemical cell; potential was scanned over 0-3V and resulting current was recorded. According to the chromatogram, more than 2V is required to generate current density of 1 mA/cm². No gas evolution was observed due to the absence of electrocatalysts for the electrochemical water splitting reactions.

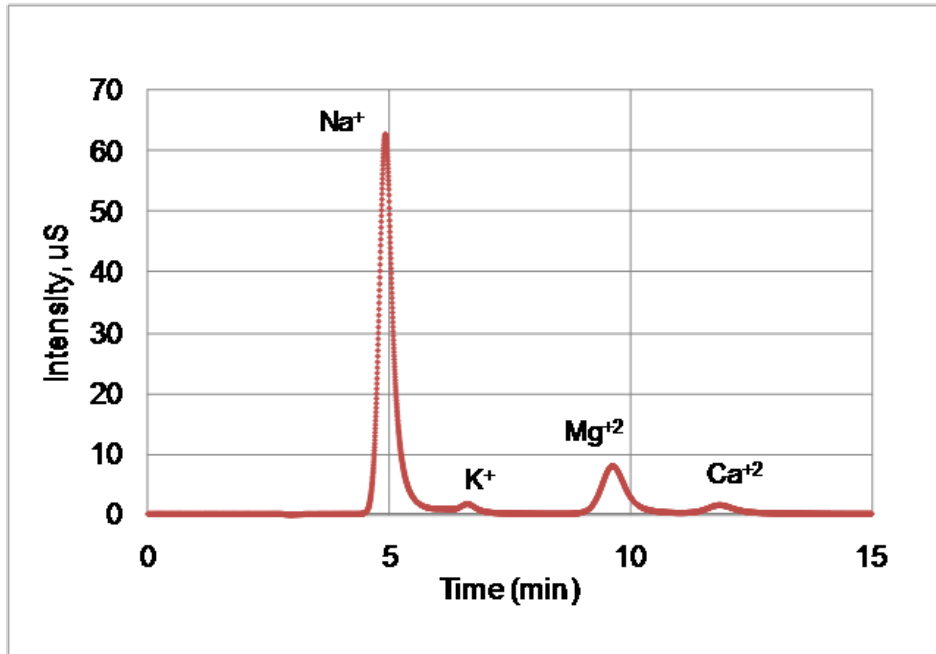


Figure 6. Ion chromatogram of seawater diluted by 100 times.

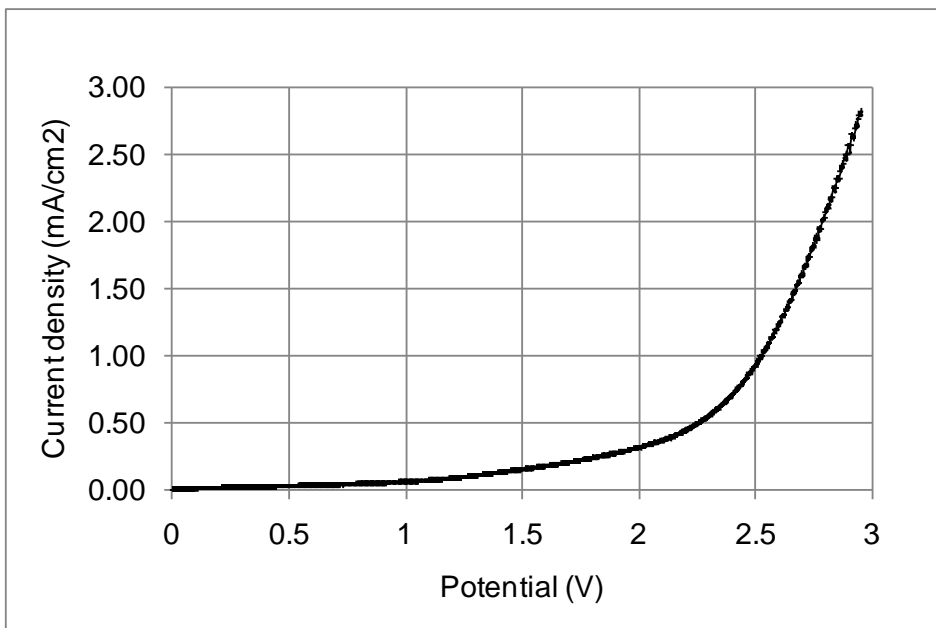


Figure 7. Linear sweep voltammetry of the electrolytic cell (anode: carbon felt (0.5mm), anolyte: 1ppm Li^+ ion solution of 300ml, anolyte flow rate: 10ml/min, cathode: carbon felt (0.5mm), catholyte: DI water of 100ml, catholyte Flow rate: 10ml/min, electrolyte: Nafion).

Figure 8 shows the concentration of anolyte and catholyte with time. The concentration of catholyte was increased with time and it was 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.

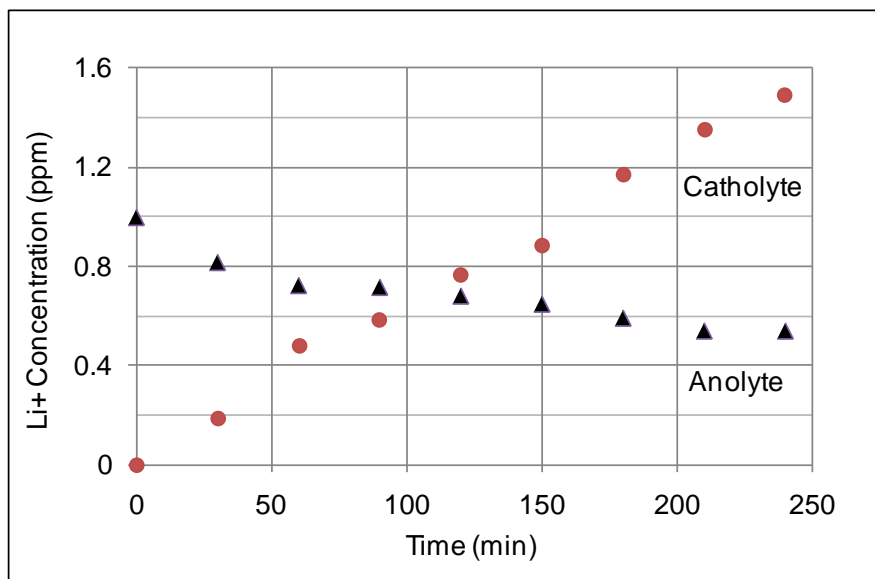


Figure 8. Concentration of anolyte and catholyte with time.

I-2. Lithium extraction from Seawater

Extraction of lithium from seawater using a non ion-selective membrane was carried out. Figure 9 shows the LSV of Nafion incorporated electrolytic cell. Compared to the 1 ppm Li anode solution, higher current densities were observed due to the higher concentration of ions in seawater. The current density was $6.5\text{mA}/\text{cm}^2$ when the applied potential was 3V. No electrochemical production of hydrogen and oxygen was observed. Lithium ions were not separated by the use of the non selective membrane.

I-3. Li extraction in seawater using Nafion sprayed with Li absorbing materials

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. Figure 10 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. 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, that other cations (e.g., Na^+ and K^+) and diffused to the cathode and were observed.

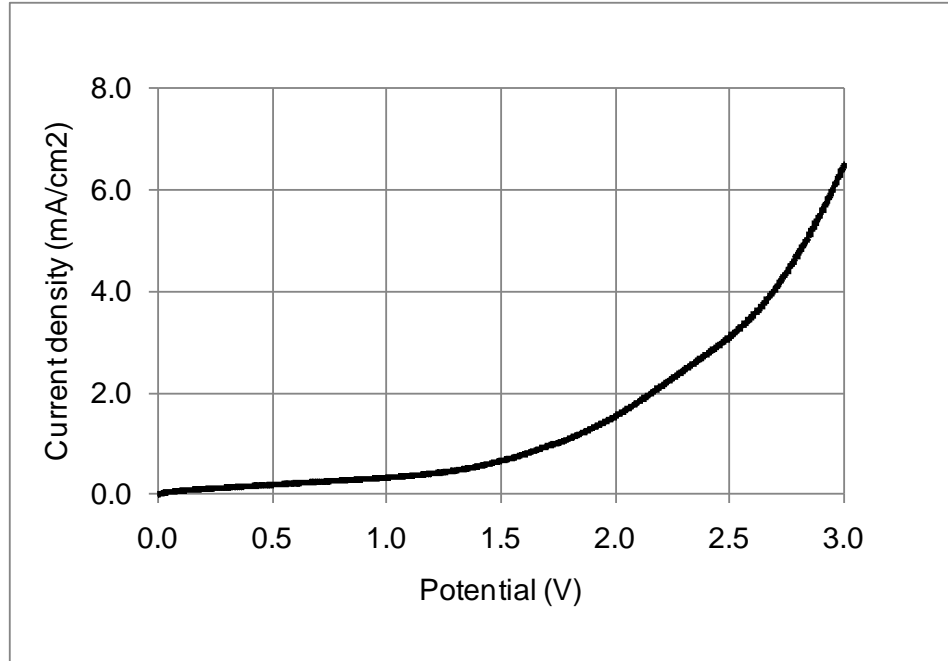


Figure 9. Linear sweep voltammetry of the electrolytic cell (anode: carbon felt (0.5mm), anolyte: seawater of 300ml, anolyte flow rate: 10ml/min, cathode: carbon felt (0.5mm), catholyte: DI water of 100ml, catholyte Flow rate: 10ml/min, electrolyte: Nafion).

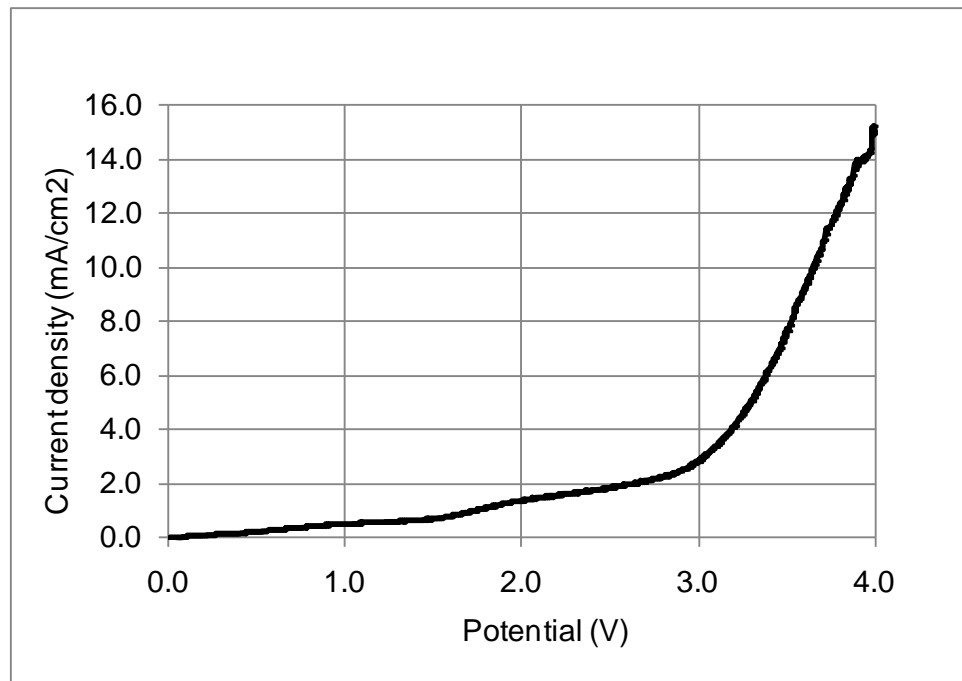


Figure 10. LSV of electrolytic cell with Li-absorber sprayed on Nafion (anode: carbon felt (0.5mm), anolyte: seawater 300ml, anolyte flow rate: 10ml/min, cathode: carbon felt (0.5mm), catholyte: DI water of 100ml, catholyte Flow rate: 10ml/min)

II. Electrolysis of Seawater

II-1. Effect of Cathodes

Iridium was employed as the anode material as it selectively generates oxygen over chlorine in seawater electrolysis. Figure 11 shows the electrochemical activity of various MEAs consisted of Pt, or Ir or Raney-Ni cathodes at $10\text{mA}/\text{cm}^2$. Raney-Ni is inexpensive and is very effective for seawater electrolysis. Figure 12 shows the amount of hydrogen generated at the constant current density. The volume of the hydrogen gas increases with time. The solid line represents the theoretical value calculated from the applied current density based on the assumption that the electrons produced in the reaction 1 contribute to the formation of hydrogen by the reaction 4 or 5.

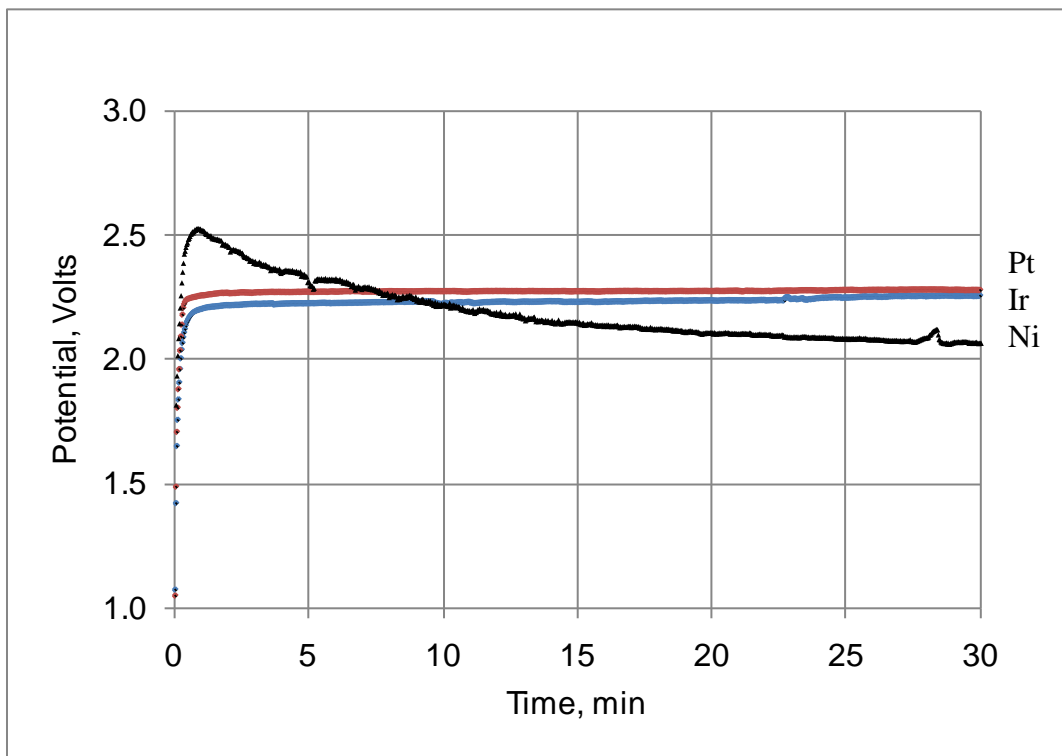


Figure 11. Potential responses to constant current density of $10\text{mA}/\text{cm}^2$ (anode: $3.0\text{mg Ir}/\text{cm}^2$, cathode: Pt, Ir, Ni $1.5\text{mg}/\text{cm}^2$, anolyte: seawater, catholyte: fresh water, and cell temp.: 20°C).

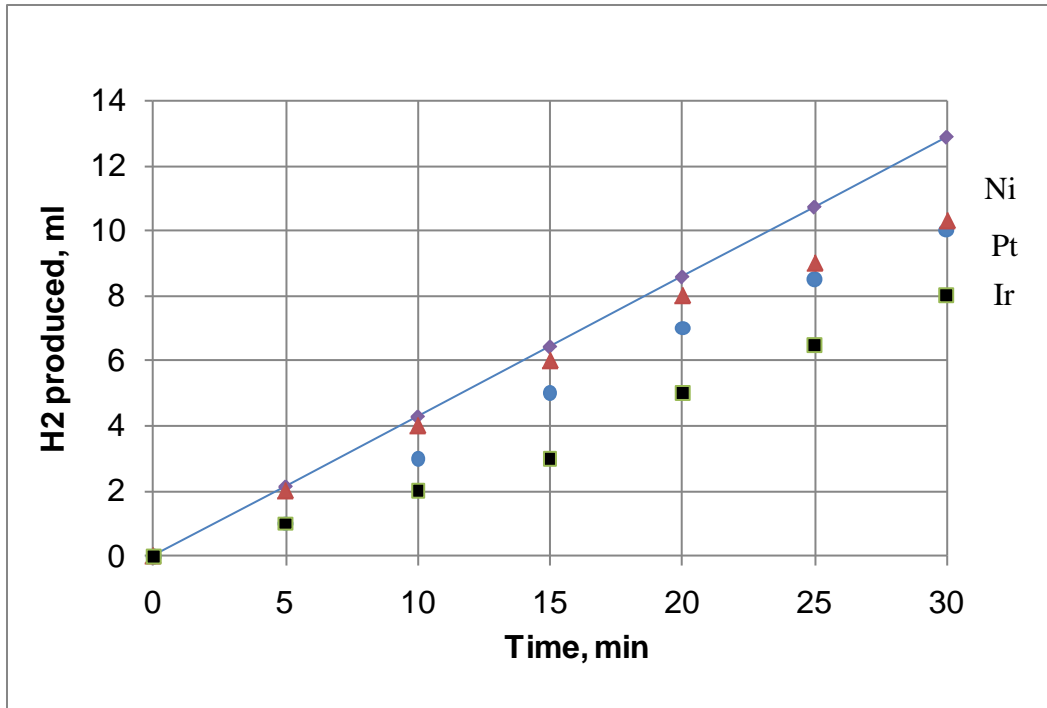


Figure 12. Volume of hydrogen gas produced at 10 mA/cm^2 (anode: 3.0 mg Ir/cm^2 , cathode: Pt, Ir, Ni 1.5 mg/cm^2 , anolyte: seawater, catholyte: fresh water, and cell temp.: 20°C).

Figure 13 shows the potential changes under a constant current density of 100 mA/cm^2 . At the high current density, Ir cathode shows the lowest potential among the electrodes. The electrodes are stable and no increase in resistance or potential was observed during the electrolysis.

Table 1 shows the averaged current efficiency for hydrogen generation at three different current densities. At low current density, Ni and Pt show higher efficiency than Ir does. However, the efficiency is more than 90% at 100 mA/cm^2 for all the cathodes.

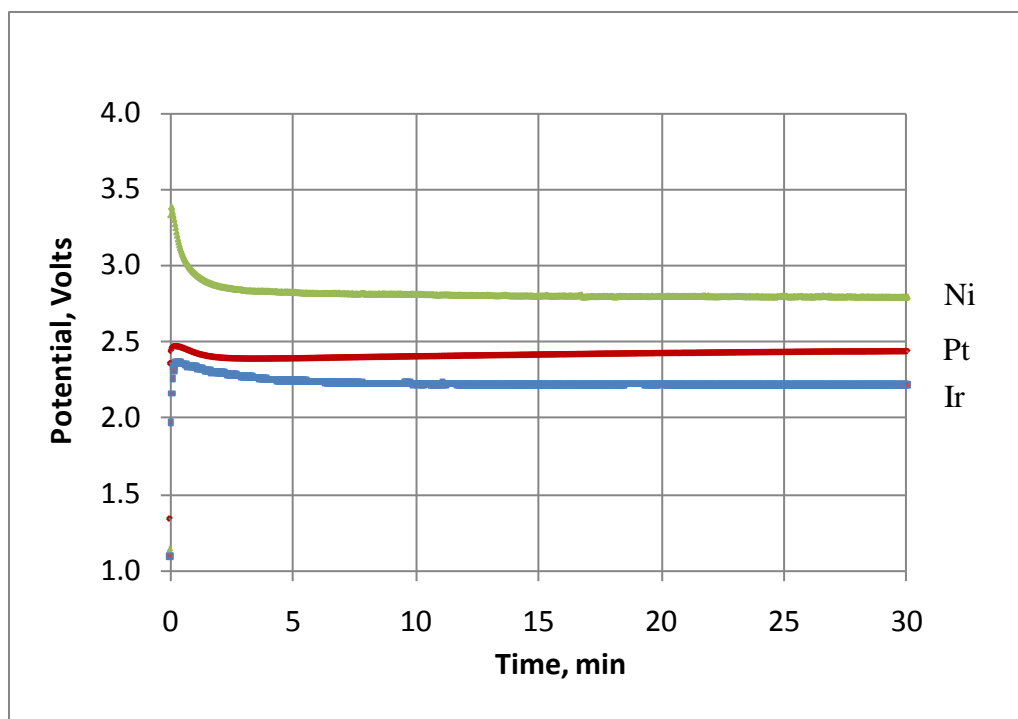


Figure 13. Potential responses at constant current density of 100mA/cm² (anode: 3.0mg Ir/cm², cathode: Pt, Ir, Ni 1.5mg /cm², anolyte: seawater, catholyte: fresh water, and cell temp.: 20°C).

Table 1. Current efficiency for hydrogen generation

| | Averaged Current Efficiency, % | | |
|----|--------------------------------|----------------------|-----------------------|
| | 10mA/cm ² | 50mA/cm ² | 100mA/cm ² |
| Pt | 71.0 | 91.4 | 92.7 |
| Ir | 51.8 | 86.7 | 92.2 |
| Ni | 89.5 | 77.4 | 90.4 |

II-2. Ion Chromatogram Analysis of Catholyte

Due to relatively high Na⁺ concentration in seawater and non-selective diffusion of ions from the anolyte (seawater) to the catholyte (freshwater), the Li⁺ peak was not separately detected.

Table 2 shows the percentage of ions diffused from the anolyte to the catholyte. The amount of Na⁺ ions diffused was less than 0.1% for all the conditions. The rate of ionic diffusion depends on the applied current and electrode materials used. The production of hydrogen by the electrically active metals was not favorable for the diffusion of ions across the membrane.

Table 2. Percentage of Na⁺ diffused to catholyte at 10mA/cm² and 100mA/cm².

| Time | Percentage of Na ⁺ ion diffused to the catholyte @100 mA/cm ² , % | | | Percentage of Na ⁺ ion diffused to the catholyte @10 mA/cm ² , % | | |
|------|---|-------|-------|--|-------|-------|
| | Pt | Ir | Ni | Pt | Ir | Ni |
| 5 | 0.088 | 0.060 | 0.053 | 0.021 | 0.031 | 0.014 |
| 10 | 0.063 | 0.027 | 0.021 | 0.013 | 0.016 | 0.010 |
| 15 | 0.062 | 0.024 | 0.017 | 0.010 | 0.009 | 0.005 |
| 20 | 0.062 | 0.018 | 0.014 | 0.008 | 0.008 | 0.005 |
| 25 | 0.062 | 0.016 | 0.012 | 0.007 | 0.008 | 0.004 |
| 30 | 0.063 | 0.014 | 0.011 | 0.008 | 0.007 | 0.004 |

III. Li Extraction Using Ion-Selective Inorganic Membrane

The extraction of lithium using a lithium selective membrane was carried out. The electrical potential between the anode and cathode was from 2V to 4V.

1. Li extraction from 1 ppm Li solution

The extraction process was performed using a 1 ppm lithium solution as the anolyte and deionized water as the catholyte. Figure 14 shows the concentration of lithium ions in the catholyte as a function of time.

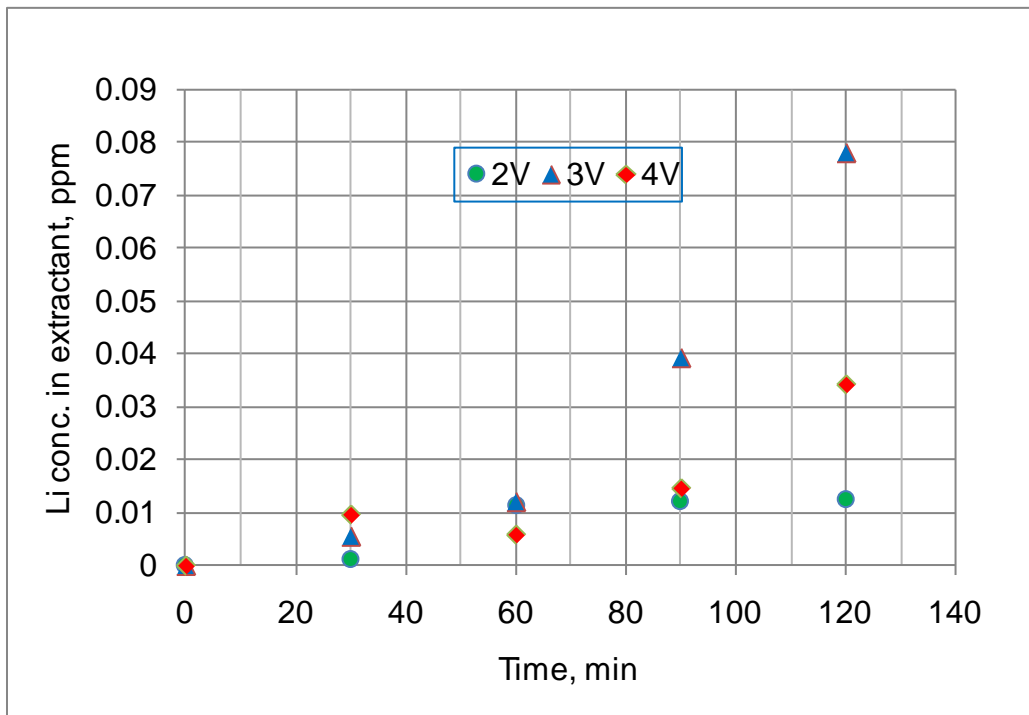


Figure 14. Concentration of lithium ions in the extractant solution with time (anode: carbon, cathode: carbon, anolyte: 1 ppm lithium solution, catholyte: deionized water, and cell temp.: 20°C).

The concentration in the catholyte solution increases with time and reached 0.012ppm, 0.034ppm, and 0.078ppm for 2V, 4V, and 3V potentials. Therefore, the recovery was less than 10% from the 1 ppm lithium solution.

2. Li extraction from seawater

Seawater was used as the anolyte and deionized water as the catholyte. Figure 15 shows the concentration of lithium ions in the catholyte. The concentration increases with time and reaches 0.06ppm after 2 hours for 4V potential application.

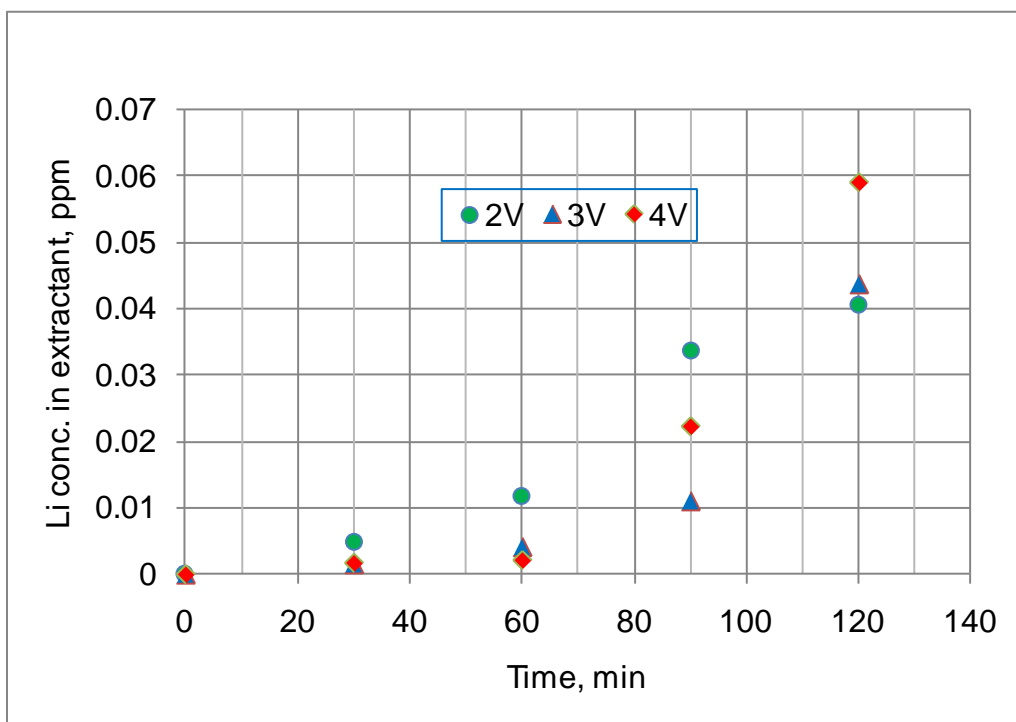


Figure 15. Concentration of lithium ions in the extractant solution with time (anode: carbon, cathode: carbon, anolyte: seawater, catholyte: deionized water, and cell temp.: 20°C).

3. Li extraction from concentrated seawater

Concentrated seawater was prepared from sea salt (Aldrich) by dissolving 80g in 1 liter deionized water, which provides two times of concentrated seawater solution. Figure 16 shows the concentration of lithium ions in the catholyte. The concentration increases with the potential applied. It reaches 0.087 and 0.093 ppm for 3V and 4V potentials, respectively.

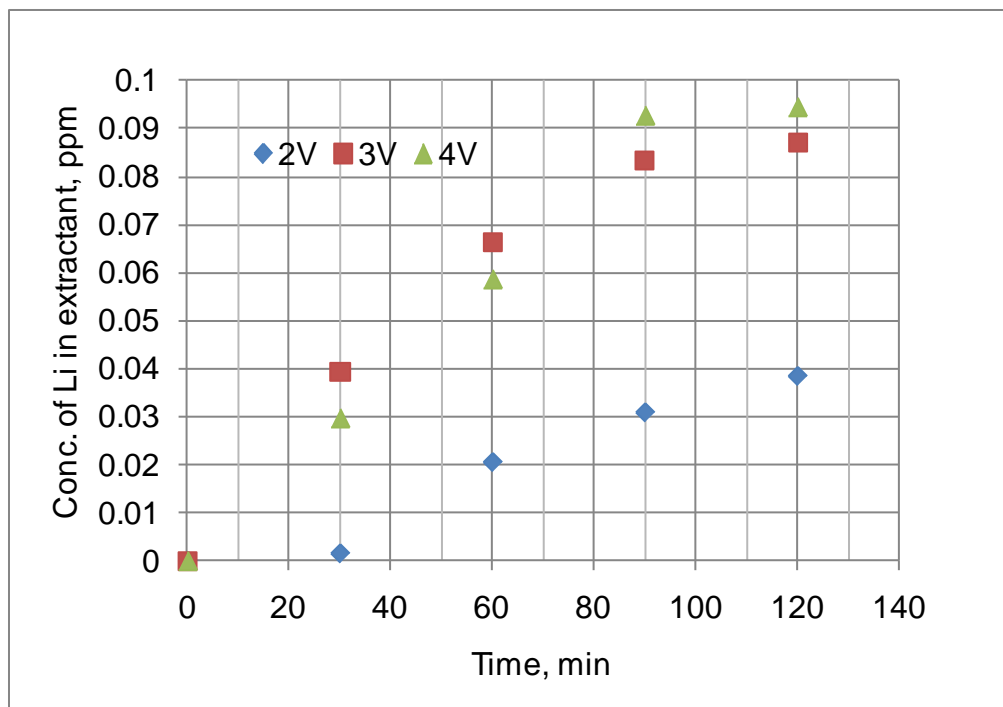


Figure 16. Concentration of lithium ions in the extractant solution with time (anode: carbon, cathode: carbon, anolyte: concentrated seawater, catholyte: deionized water, and cell temp.: 20°C).

5. Conclusions

An electrochemical process was investigated to produce hydrogen and extract lithium. Lithium extraction was performed with a non ion-selective polymer membrane and a lithium-selective membrane. The following conclusions can be drawn from the present investigation.

I. Lithium Extraction Using A Non-Selective Polymer membrane

1. For 1 ppm lithium anolyte, Nafion can be used to extract lithium; the lithium concentration is concentrated through high potential $>2V$ and employing smaller volume in the extraction side of the reservoir.
2. For seawater solution with Nafion membrane, the current density was $6.5\text{mA}/\text{cm}^2$ when the applied potential was 3V with no production of hydrogen and oxygen gases. Lithium ions were not separated from Na ion by the membrane.
3. For seawater solution with a Li absorbing material ($\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$) sprayed Nafion membrane, diffusion of seawater cations (e.g., Na^+ and K^+) was observed. Current density of $2\text{mA}/\text{cm}^2$ could be obtained at 3V. No appreciable gas evolution was observed due to the absence of active electrocatalysts for the electrochemical water splitting reactions.

II. Electrolysis of Seawater

Electrolysis of seawater has been performed to produce hydrogen effectively by employing iridium (Ir) as the anode, and Pt, Ir and Ni as the cathodes in solid polymer membrane electrolyzer.

1. At low current density, i.e., 10 mA/cm², Pt, Ir and Ni cathodes showed similar activity for hydrogen production. However, at high current density of 100mA/cm², the activity of cathode decreases in the order Ir > Pt > Ni.
2. Ions diffuse through the membrane during seawater electrolysis. As the concentration of Na⁺ ion in seawater is much higher than that of lithium, that Li⁺ ion was not separated from Na⁺ by ion chromatography.
3. The diffusion of ions depends on the current density; it increases with the current density (or potential). However, the amount of ions diffused was less than 0.1% for all the cathode (Pt, Ir, and Ni) at 100mA/cm².

III. Li Extraction Using an Ion-Selective Inorganic Membrane

A lithium ion-conducting ceramic membrane produces high selectivity to lithium ion diffusion. The concentration of lithium in the catholyte was analyzed during the extraction.

1. For 1 ppm lithium solution, the concentration of lithium reaches 0.09ppm, which corresponds to 9% recovery from the anolyte.
2. For seawater solution, the concentration of lithium ion reaches 0.06ppm at 4V.
3. For concentrated seawater, the lithium recovery from the anode reaches 0.09ppm at 3-4V.

The results indicate lithium is selectively diffused across the membrane and the concentration of lithium in the catholyte depends on the potential applied and lithium concentration in the anolyte.

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