COLORADO SCHOOL OF MINES

MEGN 570 ELECTROCHEMICAL SYSTEMS ENGINEERING

Final Project
Electrochemical Recovery of Lithium from Natural Salt Ponds

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I. Introduction

We have spent the past Spring 2020 semester studying electrochemical systems, and much of our focus has been on the PEMFC and Li-ion battery. The potential (no pun intended) of the former and the ubiquity of the latter in providing electrical power for our individual consumer needs and our nation's industrial needs have no doubt informed Dr.DeCaluwe's decision to place these two electrochemical systems under the spotlight of this course. My final project will focus on an electrochemical method of recovering lithium from natural salt pond water, for the purpose of generating the lithium required for Li-ion batteries. Specifically, I will be studying the impacts on the current and molar flux at the cathode of an electrochemical lithium recovery system when various unwanted cations are present.

Currently, about 83 percent of lithium is sourced from brine lakes and salt ponds [4] and the extraction process involves pumping Li-containing freshwater into a series of ponds that concentrate the Li through evaporation over a period of 1-2 years [2]. Given the extremely long period of time required to capture Li via passive evaporation, and the worldwide movement towards electrification of the power grid and electric vehicle technology (which will both require Li-ion batteries in large supply), more efficient methods of Li extraction are warranted.
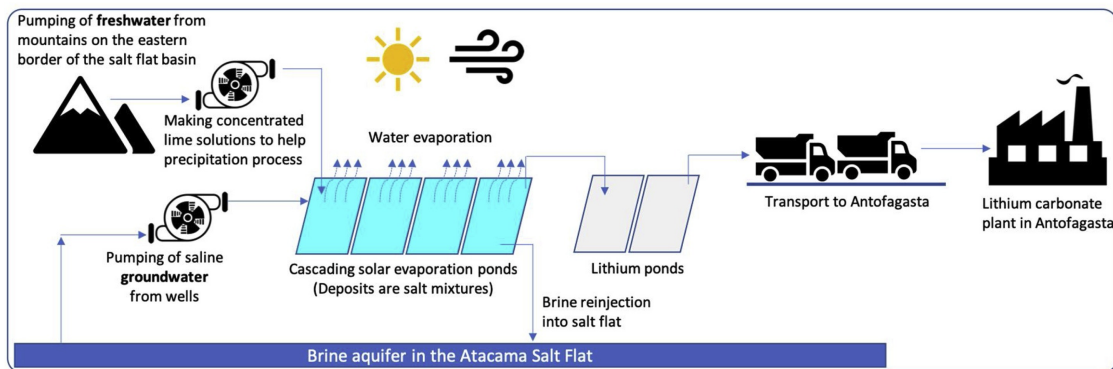

Figure 1: Passive evaporation for Li recovery (Image source: [2]).

An electrochemical method to recover lithium from brine water has been proposed by many scientists [1,3,4], but often the analyses are performed in a laboratory using LiCl dissolved in water to simulate brine, ignoring the effects of other cations which are present in real brine waters or only the impact of Na^+ [3,4]. This study will consider the impact of other cations on the molar flux of Li^+ ions, which is directly related to how much lithium can be recovered using an electrochemical recovery system.

II. Model Formation

The lithium capture process consists of four steps:

1. Negative current is applied to cathode, and lithium ions flow to the cathode

2. The brine is replaced with a recovery solution

3. Positive current applied to the cathode, releasing ions into the recovery solution

4. The recovery solution is exchanged with new brine, process repeats
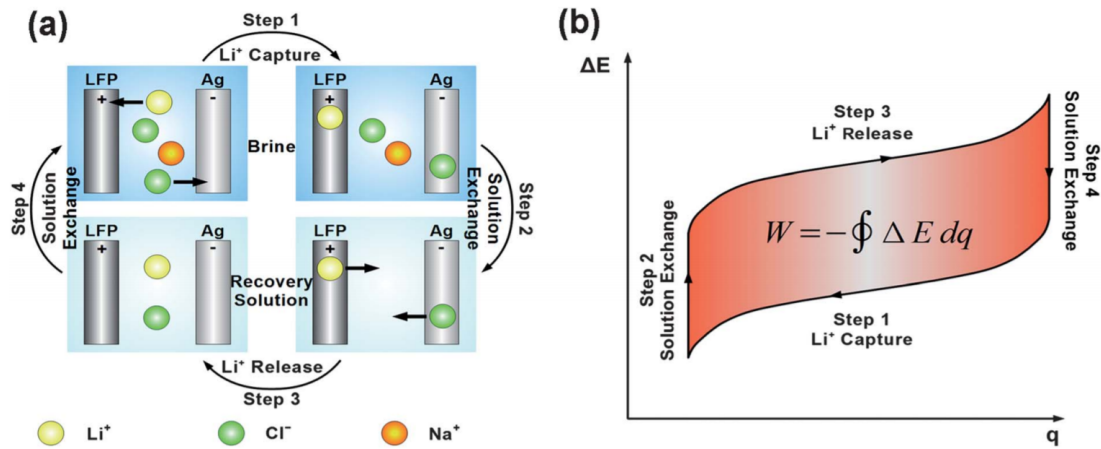
This is depicted below:

Figure 2: Diagram of electrochemical Li recovery process (Image source: [4]).

I will only be considering step 1, the thermodynamically favored step of lithium intercalation at the cathode, with no external current applied ($i_{ext} = 0$). I have chosen FePO$_4$ as the cathode material, which is also a common Li-ion battery material (the same property is desired for both applications: energetically favorable intercalation of Li$^+$ ions)

I wish to calculate the molar flux of Li^+ for three cases:

1. only lithium cations present in the brine

2. lithium and sodium cations present in the brine

3. lithium, sodium, and calcium cations present in the brine

These calculations will be for electro-diffusion only, and will ignore any convection terms. This model development is largely inspired by our homework assignment 5.

The chemical reaction which describes this step at the cathode is the following (reduction of Li$^+$) reaction:

$$FePO_{4,cathode} + Li^+_{brine} + e^-_{,cathode} \longrightarrow LiFePO_{4cathode} \tag{1}$$
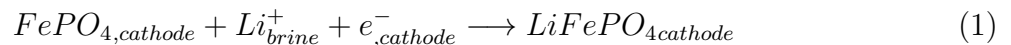
I calculate the molar flux of each species k using the following formula discussed in Lecture 22:

$$N_k = -D_{k,eff}\nabla X_k \frac{C_{k_i nt}}{X_{k_i nt}} - D_{k,mig}\nabla\phi \tag{2}$$

With no external current applied, $i_{ext} = 0$ and our double layer current is equal to the faradic current. This current originates from the diffusion of each species due to a concentration gradient and electric potential gradient present within the cathode.

Coding all of the variables in the previous section, and using mass action kinetics to calculate the faradaic current density:

$$i = F\sum_k z_k N_k \tag{3}$$

Case 1: Brine/electrolyte properties, Li^+

The concentration of the brine is assumed constant at 5 mM (natural brine concentration [1]).

The temperature is $30°C$.

The electrolyte is simplified as LiCl, dissolved in water. In Case 2 and Case 3, I will include the presence of other cations, chiefly Na^+ and Ca^{2+}. In Case 1, I will consider the charged species Li^+ as the sole cation being transported through the liquid electrolyte in the cathode.

The brine is LiCl, dissolved into water, with the following conditions:

- **Node 1**

- $X_{Li^+} = 0.03$

- $X_{Cl^-} = 0.03$

- $X_{solvent} = 0.94$

- Electric Potential $\phi_1 = 0.9V$

- **Node 2**

- $X_{Li^+} = 0.06$

- $X_{Cl^-} = 0.06$

- $X_{solvent} = 0.88$

- Electric Potential $\phi_1 = 0.5V$

The distance between the nodes is 30 microns, and the average diameter of the solid active material particles is 5 microns. The cathode porosity (electrolyte volume fraction) is 40 percent, and the tortuosity is characterized by a Bruggeman coefficient of -0.5.

Case 2: Brine/electrolyte properties, Li^+, Na^+

- **Node 1**

- $X_{Li^+} = 0.0003$ (Li:Na ratio in brine 1:100 [4])

- $X_{Na^+} = 0.03$

- $X_{Cl^-} = 0.03$

- $X_{solvent} = 0.9397$

- Electric Potential $\phi_1 = 0.9V$

- **Node 2**

- $X_{Li^+} = 0.0006$

- $X_{Na^+} = 0.06$

- $X_{Cl^-} = 0.06$

- $X_{solvent} = 0.8794$

- Electric Potential $\phi_1 = 0.5V$

Case 3: Brine/electrolyte properties, Li^+, Na^+, Ca^{2+}

- **Node 1**

- $X_{Li^+} = 0.0003$ (Li:Na ratio in brine 1:100 [4])

- $X_{Na^+} = 0.03$

- $X_{Ca^{2+}} = 0.03$

- $X_{Cl^-} = 0.03$

- $X_{solvent} = 0.9097$

- Electric Potential $\phi_1 = 0.9V$

- **Node 2**

- $X_{Li^+} = 0.0006$

- $X_{Na^+} = 0.06$

- $X_{Ca^{2+}} = 0.06$

- $X_{Cl^-} = 0.06$

- $X_{solvent} = 0.8194$

- Electric Potential $\phi_1 = 0.5V$

III. Results

Summary of results

- Molar flux of lithium decreases when other cations are included in model

- Current density is highest in Case 3, and lowest in Case 2

- Zero current is achieved at the same electric potential difference for all three cases

- Chlorine ion flux appears unaffected by presence of additional cations
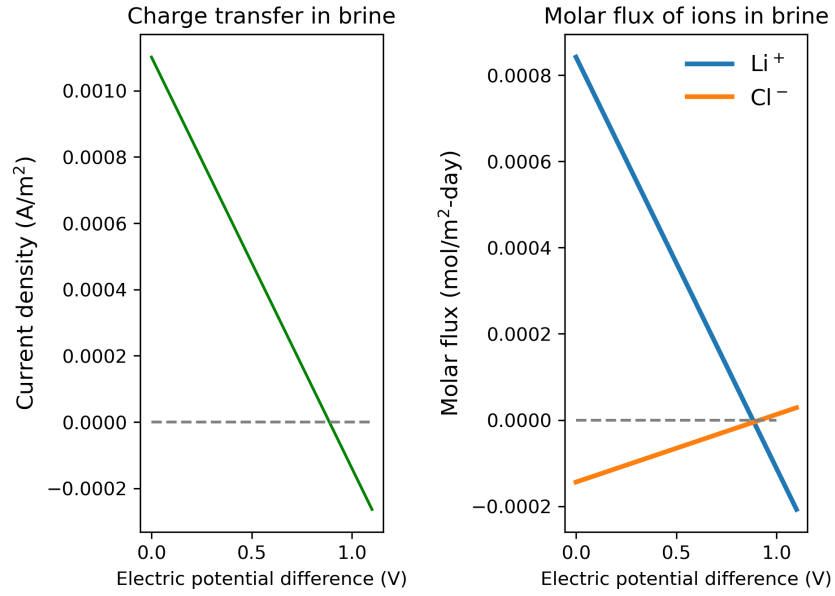
Case 1, Li^+

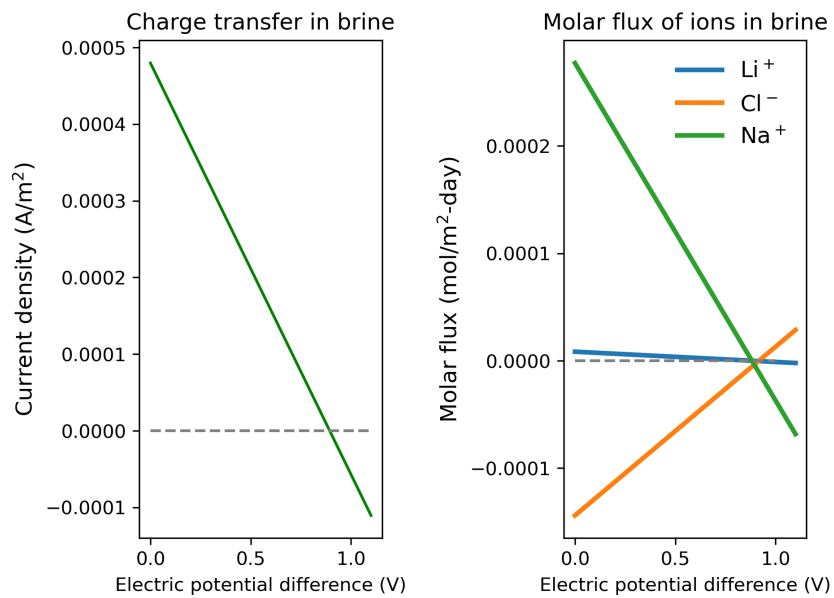Figure 3: Case 1: Only Li$^+$ and Cl$^-$ ions considered

Case 2, Li^+, Na^+

Figure 4: Li^+, Na^+, and Cl^- ions considered

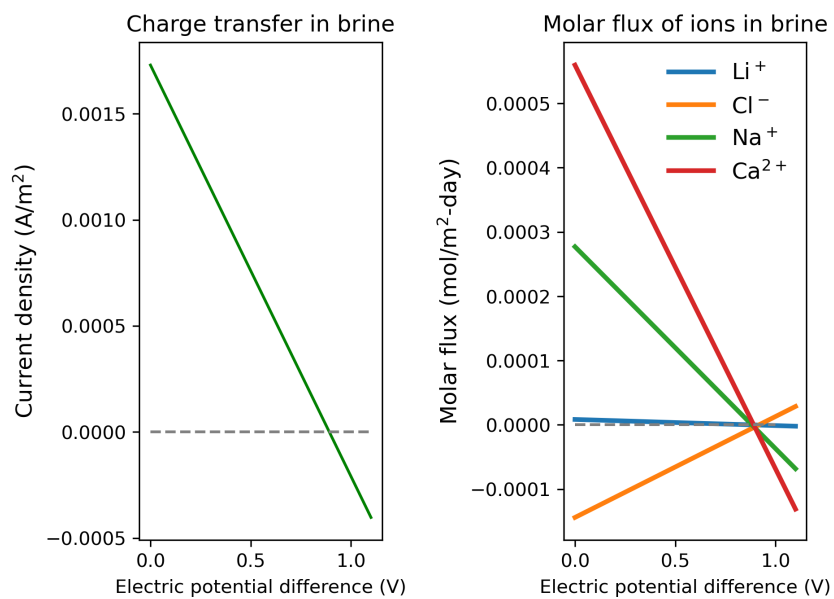**Case 3,** Li^+, Na^+, Ca^{2+}

Figure 5: Li^+, Na^+, Ca^{2+} and Cl^- ions considered

IV. Discussion

From my results, it appears that the presence of multiple species of cations in the brine negatively impacts the molar flux of lithium, as expected. We can quantify this drop in lithium production as equivalent to the decrease in mole fraction of lithium present in the solution. For example, between Case 1 and Case 2, the mole fraction of lithium decreased by a factor of 100, and the peak molar flux of lithium from Case 1 to Case 2 dropped from $8.42 * 10^{-4}$ to $8.24 * 10^{-6}$.

I have a few comments on the validity of my results:

- I did not change the electric potentials between each simulation, which is likely an incorrect assumption, since the presence of additional ions should affect the potential

- The mole fraction of lithium did not change between Case 2 and Case 3 (I added calcium and subtracted the mole fraction from the solvent to maintain the sum of the mole fractions = 1); which may have been an incorrect approach (it should have decreased)

- I assumed isothermal conditions and constant diffusion coefficients for each species; when in reality, temperature may evolve during operation, and diffusion coefficients are likely a function of temperature and concentration

All of those caveats aside, I have a few interesting things to point out:

- The voltage condition for zero current did not change between each case. I found this to be surprising, since I added more cations (but did not add anions), so I would expect the zero current voltage to change to favor production of chlorine anions (the only anion in the system) to balance out all of the cations.

- The max current density decreased from Case 1 to Case 2 (max of greater than 0.0010 A/sq m to less than 0.005 A/sq m), but then increased from Case 2 to Case 3 (max of over 0.0015 A/sq m). I am not sure what caused this; since I am only adding cations, I would expect to see a trend of increasing charge transfer from Case 1 to Case 3.

- Finally, the molar flux of lithium is very, very low. My calculations yield less than a milimole of lithium ions *per day*, which is certainly a very bad sign for electrochemical harvesting of lithium from brine ponds. I think that these results are so low because I specified a low (but accurate!) concentration of lithium in the electrolyte as 5mM, and my molar fraction of lithium was also very low. This should be revisted and compared with experimental results.

V. Conclusion

According to my study, efforts to remove Na^+ and Ca^{2+} ions from brine water before running an electrochemical lithium recovery cell would likely improve lithium quantity recovered per cycle by several orders of magnitude. This could either be done by using a chemical agent to precipitate out the other cations (which sounds like it could be an environmental hazard, or at least an added inconvenience), or to simply choose a cathode material that is selective for lithium cations, if possible. In fact, the latter is already being done - for example, the cathode material I selected (olivine $FePO_4$) undergoes a reversible transformation upon addition of lithium ions, where the lithium ions diffuse into the tetrahedral sites of iron phosphate. Sodium ions are too large to occupy these sites (or more precisely - the energy required to distort the host lattice to accommodate these larger ions is thermodynamically unfavorable). The incorporation of sodium into $FePO_4$ forms a new compound, maricite, which is an irreversible phase transformation. This irreversible and unwanted phase transformation is generally avoided by the fact that the diffusion energy of sodium is 119 meV higher than the diffusion energy of lithium ions [3], meaning that more lithium ends up diffusing into the cathode versus sodium.

Interesting next steps would include recalculating the diffusion coefficients used in this model to more accurately reflect the real diffusion behavior of each species, studying the impact porosity has on lithium recovery cells, and modeling the next three steps in the lithium recovery process. Particularly, I am interested to see if when all of the required energy is summed up (including the energy needed to swap out brine water for recovery solution, which I imagine requires some mechanical pumping input), how does the energetic cost vs lithium recovered ratio compare for electrochemical versus passive solar evaporation methods? This is ultimately the question that will drive whether passive methods continue, or electrochemical lithium recovery technologies develop.

Note on Python function

The python function that I built for this project, "LirecoveryFINALPROJECT.py", involves a set of coefficients that are called to calculate the molar flux but vary both in array dimension and values for the three different cases I modeled (different number of species are considered in each case). I ended up typing out the D_k, z_k, and X_k values for each of the three cases, and it was very cumbersome to comment out the 2 of the 3 unwanted blocks of code when I ran each simulation. I tried unsuccessfully to incorporate code similar to your "thermalflags" from the last homework assignment to only model the desired simulation without having to comment out the other two. Alas, no dice - but I am happy to report that I learned a lot about python coding in this class which was a goal of mine.

VI. References

1. A. Battistel, M.S. Palagonia et al., "Electrochemical Methods for Lithium Recovery: A Comprehensive and Critical Review," *Advanced Materials*, vol. 32, no. 23, 2020.

2. W. Liu, D.B. Agusdinata, S.W. Myint.,"Spatiotemporal patterns of lithium mining and environmental degradation in the Atacama Salt Flat, Chile," *International Journal of Applied Earth Observation and Geoinformation* vol. 80, pgs 145-156, Aug 2019.

3. JS Kim, YH Lee et al. "An Electrochemical Cell for Selective Lithium Capture from Seawater," *Environmental Science Technology* vol. 49, no. 16, 2015. DOI: 10.1021/acs.est.5b00032

4. M. Pasta, A. Battistel, F. La Mantia, "Batteries for lithium recovery from brines," *Energy Environ Sci* vol 5 pgs 9487–9491. 2012.

VII. Memes

Figure 6: Me coming to terms with the interconnectedness of electrochemistry

Figure 7: If you're reading this, I figured it out!

Figure 8: The struggles of determining sign convention of electric current in an electrochemical system