Lithium Adsorption from Surrogate Seawater using λ-MnO2/Activated Carbon Mixture Duc Tran, Aurelio Perez, Hongpeng Gao*, and Prof. Zheng Chen

Guided Engineering Apprenticeship in Research, University of California, San Diego, La Jolla, CA 92092

Objective

To study the lithium adsorption behavior of λ -MnO₂/Activated Carbon mixtures through lithium intercalation to produce LiMn₂O₄ from surrogate seawater using an continuous stirred tank set up. Thereby, determining the feasibility of seawater as an alternative lithium deposit.

Introduction

Lithium-ion batteries (LIBs) are the most popular choice for energy storage due to their high-power density and good cycling stability^[1]. Nonetheless, the massive projected demand of LIBs heavily outweighs the current production capacity of lithium^[2]. Therefore, finding alternative ways to produce usable lithium is important to maintain the growth of many industries.



Consumer Electronics Energy Storage Electric mobility Histogram showing battery demand per industry, by year in GWh.

Seawater is estimated to contain over 200 billion tons of lithium^{[3][4]}. Enough to ensure the foreseeable future of lithium dependent industries. As such, new lithium extraction methods such as selectrodialysis (SED), co-precipitation, and adsorption have been investigated for their lithium capturing capability.

Process	Steps	Results
Membrane ^[5] (electrodialysis)	Absorption/desorption of processed seawater with membrane wall	 (+) high selectivity (+) easily scalable (-) new
Co-precipitation ^[4]	Co-precipitate lithium in seawater to get a lithium concentrate	(-) costly(-) long time
Adsorption ^[3]	Use an absorbent to directly extract lithium from seawater	(+) high selectivity(+) high recovery rate

Of these, the adsorption-based process has been found to be extremely promising if a suitable adsorbent is available^[3].

Theory

Lithium adsorbents are made from precursors containing lithium but upon lithium removal using an acid, the vacancy sites are occupied and retained by hydrogen atoms. Through Li-H ion exchange, adsorption of Li⁺ from the solution is possible^[3]. Two common adsorbent types are manganese dioxide and titanium dioxide.



 λ -MnO2, a stable form of manganese dioxide (left). The product after adsorption is spinel lithium manganite (right).

Since Li⁺ have the smallest ionic radii among the monovalent metal ions in seawater, the vacancy sites on the adsorbents will only accept Li⁺ to be more stable, hence yields high selectivity for Li⁺ while not destroying the bulk crystal structure upon lithium insertion.

Activated carbon is non-reactive in aqueous solution and has small pores that can increase the surface area available for lithium adsorption. Mixing λ -MnO₂ with activated carbon is expected to increase the adsorption rate.



Methodology



Left image depicts extraction of liquid sample from reactor using syringe, right image depicts the insertion of liquid into glass vial through 200 nm filter.

1) Create surrogate seawater by mixing 800 mL of DI water with 10.00 ± 0.50 g of NaCl and 0.50 ± 0.10 g of LiCl until all salts dissolve 2) Create adsorbent material by mixing 0.50 ± 0.10 g

of carbon black (trial 1), Ketjenblack EC-600JD (trial2), and Super-P (trial 3) with 0.50 ± 0.10 g of λ -MnO₂

3) Stir reactor at 500 rpm, then use a syringe and filter to draw ~3 mL solution samples at the 0-, 30-, 120-, and 360- minute timestamps 4) Analyse samples via Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)









Graphs generated from ICP-MS data collected by Hongpeng* Mass of lithium remains in the solution after 0-, 30-, 120-, and 360- minutes timestamps (blue) are plotted with respect to reaction time. A decrease in mass of lithium correlates to the adsorption of lithium by the absorbent mixtures. The lithium recovery percentages are plotted on the right y-axis for comparison (red). The adjusted R² for all adsorbent mixtures are reported according to a decaying towards equilibrium model, with the exception of λ -MnO₂/Carbon Black reported as a linear regression model. All trials ran at ambient temperature.

Evaluation/Discussion			
Absorbent mixture	Average pore size (nm) ^[6]	Surface area (m ² g ⁻¹) ^[6]	
Carbon Black	11.4	56	
Ketjen Black	7.7	818	
Super-P	11.9	62	

Although Ketjenblack has the smallest average pore size compared to the other two carbon black types, the value is still much larger than the ionic radius of Na⁺ (116 pm), which exists in the solution at substantially higher concentration than Li⁺. As such, the selectivity of λ -MnO₂ should remain unaffected regardless of the type of carbon black used.

From the graphs, Ketjenblack and Super-P mass in solution eventually converges to a minimum, signifying that the reactions approach equilibrium. However, the trial with carbon black displays a constant rate of adsorption for 6 hours.

We speculate that the differences in adsorption behavior of carbon black to Ketjenblack and Super-P can be explained by the larger surface area offers by the latters. More surface area allows the available λ -MnO₂ to react more quickly with Li⁺ in the solution, and the reaction to go towards equilibrium at an earlier time. Therefore, we expect the same convergence to occurs with the carbon black trial if we were to run it for a longer time (t > 6 hours).

aspects.

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Conclusion

Using ICP-MS to measure the change in lithium concentration in surrogate seawater when exposed to λ -MnO₂/ carbon black, we were able to confirm the lithium adsorption capabilities of λ -MnO₂. Even though the rate of adsorption was relatively slow, selective adsorption still took place proving λ -MnO₂ is a capable adsorbent.

Now that we know the adsorption capabilities of λ -MnO₂ with carbon black, new research must be carried out in determining the adsorbents' viability in a semi-industrial or industrial scale. This includes the incorporation of real seawater and SED process beyond our surrogate solution into the experiment, the introduction of temperature as a variable, and a control group of pure adsorbent, among many other

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