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Extracting Lithium Using the Steric Bulk of an Aminimide Functional Group

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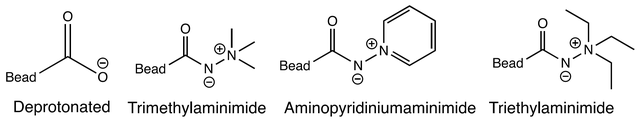
Abstract

An aminimide is a zwitterionic group containing a cationic nitrogen bonded to an anionic nitrogen. The goal of this project was to use the steric bulk and electronic properties of the aminimide to block other species in a brine solution such as potassium, and selectively pick up lithium. To test this, polymethacrylate beads which contain carboxyl groups were modified to the desired aminimide. Three different aminimide groups were tested, a trimethylaminimide, aminopyridiniumaminimide, and a triethylaminimide. The modified beads would be introduced to a solution containing lithium and the lithium concentration was measured before and after exposure to the beads using atomic absorption spectroscopy. Our realistic brine solution contained 10,000 ppm K, 200 ppm Li. Only the aminopyridiniumaminimide and the triethylaminimide exhibited selectivity. The aminopyridiniumaminimide took up 43.9 ppm Li, while the triethylaminimide took up 59.35 ppm Li.

Types of Aminimides

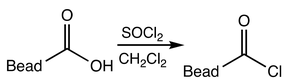


Background

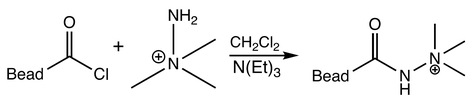
The demand for lithium continues to grow as new uses for it become increasingly prevalent. Our current method of purifying lithium involves an evaporative brine process, which involves pumping water into a lithium rich area and bringing the brine to the surface. Solar evaporation is used to concentrate the solution. Further chemical processes such as filtration and solvent extraction are used to get the pure lithium from the brine[1]. This process typically only yields 50% of the starting lithium and can take 12-18 months to arrive at the final product. Other direct extraction methods have been tried such as crown ethers, but they are expensive[2]. Our project proposes a new direct method to selectively take lithium from a brine solution quicker and cheaper than our current methods allow.

Methods

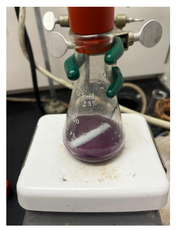
1. **Synthesizing Beads**
   A. Polymethacrylate beads were treated with thionyl chloride to make an acyl chloride



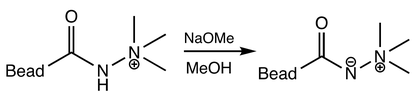
   B. The acyl chloride would react with a hydrazinium



This image shows the reaction between aminopyridiniumaminimide and the acyl chloride.

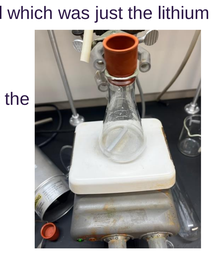


   C. The new hydrazinium would be treated with sodium methoxide to make an aminimide



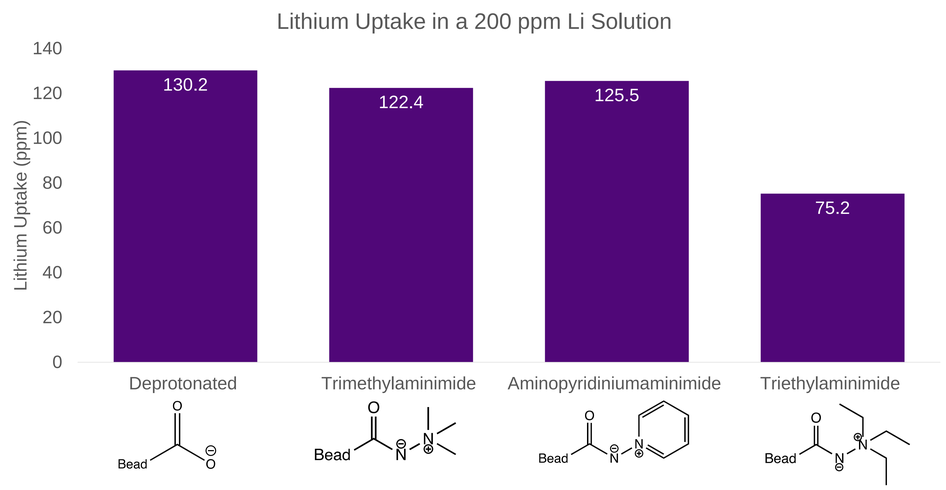
The image to the right shows the trimethylaminimide beads (left) and the aminopyridiniumaminimide beads (right).

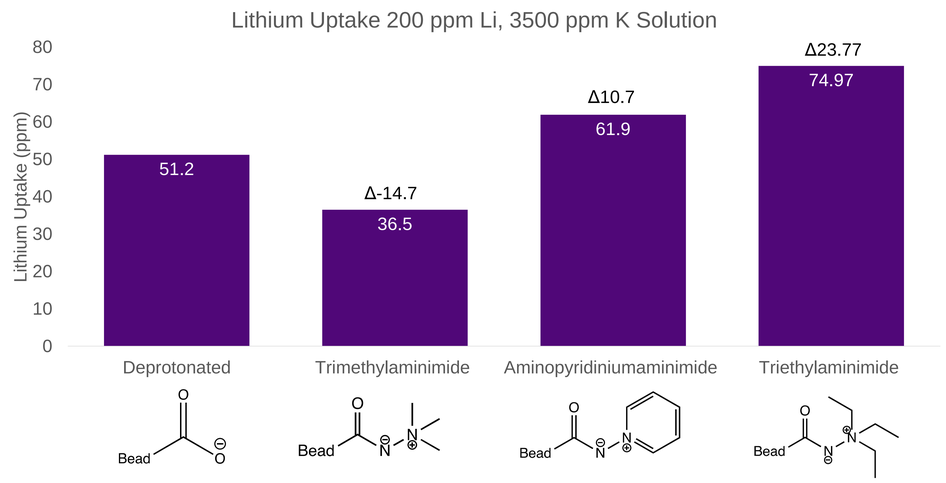
2. **Testing the Beads**
   a. The beads were stirred in a lithium containing solution This can be seen in the image below
      i. The controls used for this experiment included a control which was just the lithium solution and deprotonated beads.
   b. The solution would then be separated from the beads and tested by atomic absorption spectroscopy (AA) to measure the lithium concentrations.

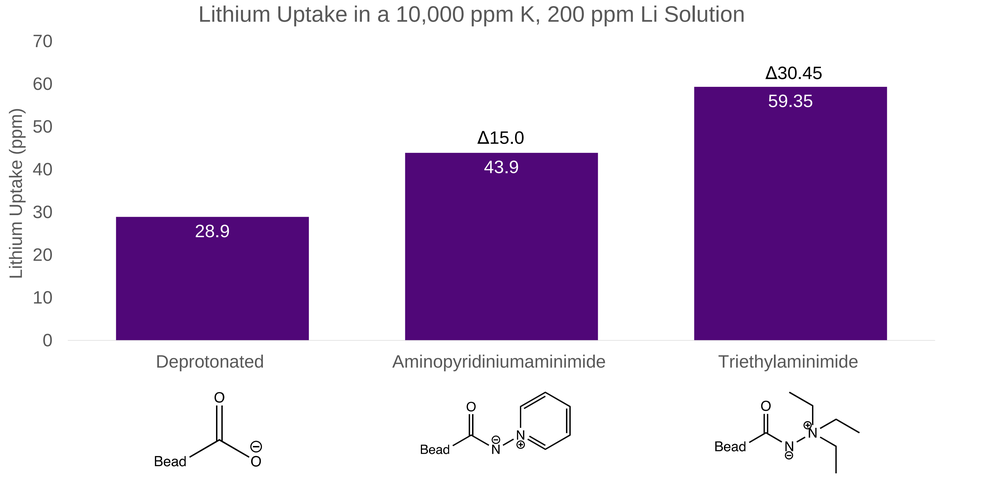


Results

15 mg of beads, or (Binding Sites) were used in each trial with 10 g of solution.

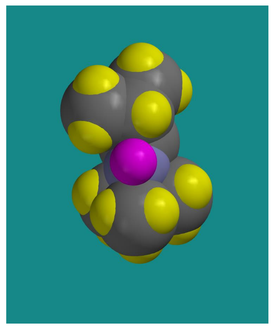


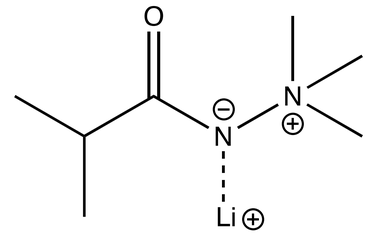




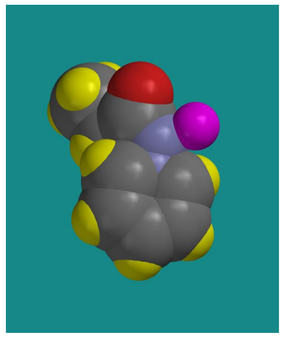
Model

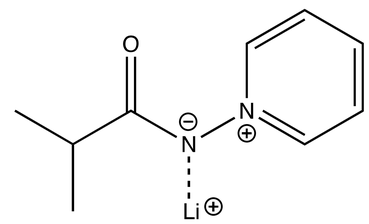
The steric hinderance of each molecule was modeled using the computer software Spartan. This helped us visualize how crowded each lithium binding site was. The pink atom in all the pictures represents the lithium atom.



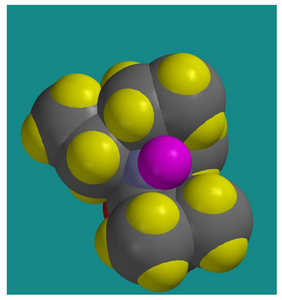


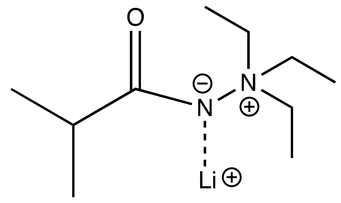
Trimethylaminimide





Aminopyridiniumaminimide





Triethylaminimide

Conclusions

All the aminimides that were tested displayed an ability to uptake lithium in a 200 ppm Li solution. Only the aminopyridiniumaminimide and the triethylaminimide beads were able to selectively uptake lithium in a 200 ppm Li, 3500 ppm K solution. The aminopyridiniumaminimide was able to pick up 61.9 ppm of lithium in the test while the triethylaminimide was able to pick up 74.97 ppm of lithium. In a realistic brine solution, the aminopyridiniumaminimide was able to pick up 43.9 ppm while the triethylaminimide picked up 59.35 ppm. This data proves that the aminimide is capable of selectively taking up lithium, but the rates at which the aminimide picks up lithium is worse than our current methods of obtaining lithium.

Citations

1. Warren, Ian. 2021. *Techno-Economic Analysis of Lithium Extraction from Geothermal Brines.* Golden, CO: National Renewable Energy Laboratory. NREL/TP-5700-79178. https://www.nrel.gov/docs/fy21osti/799178.pdf.

2. Warnock , S., & Susanani, R. (2021, September 7). *Engineering Li/Na selectivity in 12-crown-4–functionalized polymer ...*Engineering Li/Na selectivity in 12-Crown-4–functionalized polymer membranes. Retrieved July 17, 2022, from https://www.pnas.org/doi/10.1073/pnas.2022197118

Acknowledgements

1. Dr. Steve Heilman, for financial support
2. Dr. Martin Chin
3. Linda Wilson, for technical support
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