Title
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Journal
Joule, 4(7)

ISSN
2542-4785

Authors
He, Xin
Kaur, Sumanjeet
Kostecki, Robert

Publication Date
2020-07-01

DOI
10.1016/j.joule.2020.06.015

Peer reviewed

Joule

CellPress

Previews

Mining Lithium from Seawater

Xin He,[1] Sumanjeet Kaur,[1] and Robert Kostecki[1,*]

Unlike conventional land-based resources for lithium (Li), which are concentrated in a few geographic locations (e.g., closed-basin brines, pegmatites, lithium clays, and zeolites), seawater provides a massive and evenly distributed global Li reserve (230 billion tons), albeit at low (<1 parts per million) concentrations. As global Li consumption continues to rise over the next few decades, the development of cost-competitive technologies for Li extraction from seawater warrants intense research. In this issue of *Joule*, Steven Chu and colleagues introduce an electrochemical methodology to selectively remove Li from seawater. This selective removal is accomplished by exploiting the differences in electrochemical potentials for the Li^+ and sodium $(Na)^+$ insertion/extraction reactions, and their diffusion activation barriers in the $FePO_4$ framework of the ordered olivine $MeFePO_4$. This work demonstrates the possibility of energy-efficient Li extraction from seawater at relatively high rates with long-term stability by using the electrochemical ion insertion/extraction in battery electrode materials.

Lithium (Li) demand will continue to increase significantly over the next few decades, with estimates of 56 million annual electric vehicle sales and energy-storage deployment of over 1,095 GW globally by 2040.[1] Although one of the main concerns for the scale up of battery production is the availability of Li, the world's Li reserves together with recycling of spent Li-ion batteries are sufficient to meet this growing demand. The majority of Li today originates from natural land reserves, e.g., salar brines in South America and spodumene ores in Australia, with Li extraction and refinement currently involving multistep processes, including evaporation, selective adsorption/desorption, electrodialysis, and/or precipitation of various contaminants. These processes use large quantities of reagents, require significant waste management, and are energy inefficient, contributing to the overall cost and negative environmental impact of Li extraction.[2] Multidisciplinary research and development (R&D) efforts that integrate scientific research, engineering innovation, manufacturing, and process improvement can improve the economics and environmental footprint of processing from existing resources while enabling the use of new sources of Li that are not yet commercially viable (Figure 1).

Direct extraction of Li from seawater is a very desirable option because seawater contains approximately 230 billion tons of Li (in comparison with the 62 million tons in land-based reserves) and is not geographically limited.[3] However, it is very challenging to extract Li from seawater because the Li concentration is only 0.1–0.2 parts per million (ppm),[4] as opposed to the $\sim$10,800 ppm of sodium (Na). Hence, the selective removal of Li over Na is the key to efficient Li extraction. Recently, various research groups have explored methods to efficiently and selectively extract Li from seawater. Examples include the use of renewable and recyclable hydrogen manganese oxide (HMO)-modified cellulose film to absorb Li[5] and a solar-powered electrolysis technique using a NASICON solid-state electrolyte as the selective membrane for Li extraction.[6] In this issue of *Joule*, Steven Chu and colleagues[7] demonstrate selective Li extraction from seawater by using an electrochemical process based on Li-ion battery cathode olivine materials.

The authors propose a two-step electrochemical process, where delithiated Li_xFePO_4 (x = 0) and $NaFePO_4$ are used as active electrode materials for Li insertion and Na extraction, respectively.[7] During the first step, Li ions from seawater are inserted into the $FePO_4$ electrode under cathodic polarization while the same amount of Na ions are released from the counter $NaFePO_4$ electrode. This step is followed by a regeneration process, where the Li_xFePO_4 (x = 1) electrode is placed in fresh water under anodic polarization to release Li ions while water reduction occurs on the carbon counter electrode. The high selectivity of Li versus Na removal was achieved by exploiting the 0.17 V electrochemical redox potential difference for Na^+ and Li^+ insertion/extraction in the Me_xFePO_4 matrix and faster Li^+ insertion kinetics in the $FePO_4$ host and TiO_2 coating, which also improved the electrode wettability. In addition, the researchers explored the use of different galvanostatic current versus time profiles to further improve the selectivity and cyclability of Li. Short pulse-rest galvanostatic polarization resulted in a higher recovered Li/(Li+Na) molar ratio. The pulsed current polarization also helped maintain the structural stability of the $FePO_4$ host material for 10 cycles of Li extraction from seawater with molar selectivity as high as 1.8×10^4.

These initial results are promising and represent a leap forward for selective

[1]Energy Storage & Distributed Resources Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

*Correspondence: r_kostecki@lbl.gov

https://doi.org/10.1016/j.joule.2020.06.015

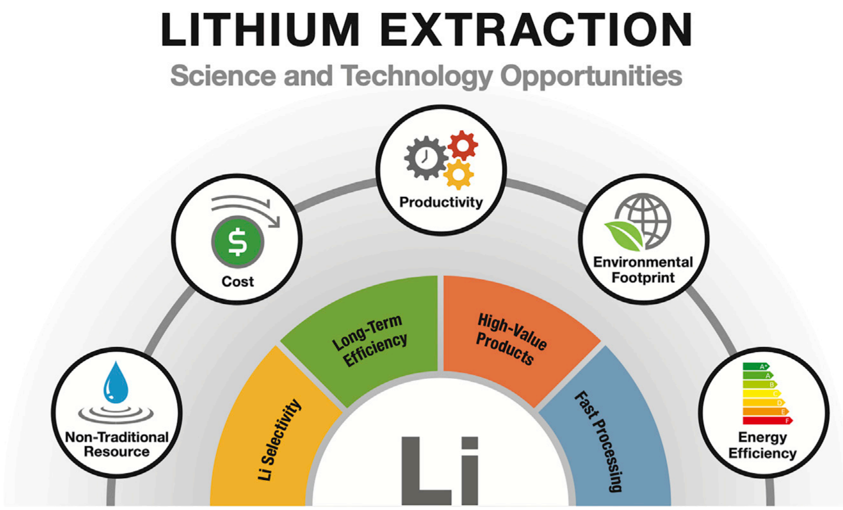

Figure 1. Lithium Extraction from Non-traditional Resources: Science and Technology Challenges and Opportunities

Li extraction from seawater by using Li- and Na-ion battery electrode materials. Seawater is a vast resource containing large amounts of minerals, including rare-earth elements, precious metals, Li, and uranium, all of which exist in relatively low concentrations and thus pose similar challenges for extraction. The Seawater Mining Report from the US Department of Energy emphasizes that even at low concentration, extracting minerals from seawater can be more environmentally friendly and economical if the energy source for extraction is locally generated and the operation cost is minimal.[8] One can envision renewable-energy-powered electrochemical processes as a viable route for seawater mining. The authors were able to demonstrate an effective methodology of direct extraction of Li from seawater, signifying that electrochemistry-based separation techniques can be translated into promising technologies for direct Li extraction from natural resources where the Li concentration is relatively high.

ACKNOWLEDGMENTS

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231f.

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