Previews

Mining Lithium from Seawater

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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 FePO₄ framework of the ordered olivine MeFePO₄. 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.

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. However, it is very challenging to extract Li from seawater because the Li concentration is only 0.1–0.2 parts per million (ppm), as opposed to the ~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 and a solar-powered electrolysis technique using a NASICON solid-state electrolyte as the selective membrane for Li extraction. In this issue of Joule, Steven Chu and colleagues 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 LiₓFePO₄ (x = 0) and NaFePO₄ are used as active electrode materials for Li insertion and Na extraction, respectively. During the first step, Li ions from seawater are inserted into the FePO₄ electrode under cathodic polarization while the same amount of Na ions are released from the counter NaFePO₄ electrode. This step is followed by a regeneration process, where the LiₓFePO₄ (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 MeₓFePO₄ matrix and faster Li⁺ insertion kinetics in the FePO₄ host and TiO₂ 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 FePO₄ host material for 10 cycles of Li extraction from seawater with molar selectivity as high as 1.8 x 10⁴.

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

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