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Sustainable Methods for Lithium Recovery from Water and Unconventional Resources

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Abstract

Lithium and sustainability are probably two of the most used words in today's economy, governance and research world, often combined with the terms *green process* and *renewable energies*. Lithium is indeed widely used in light of its many interesting properties in a variety of sectors, among which batteries are at the forefront. Although the market for this element constantly increases as does its use in hybrid vehicles, smart grids, portable and precision electronics, sadly its availability does not. Therefore, new unconventional resources have been researched and studied considering the fact that the processes currently employed to commercially extract it by evaporation from salt lake brines are both water and time consuming and ores are gradually degrading. More environmentally friendly alternatives to these processes have also been investigated in an attempt to reduce the footprints of this industry. Furthermore, as one of the critical raw materials recognized by the United Nations, a responsible and sustainable supply of lithium becomes part of the 12th Sustainable Development Goal (chapter 1).

Several attempts at recovering lithium from aqueous solutions have been conducted in the past years, focusing either on concentrated brines, geothermal water, and even seawater. After an introduction on the role of lithium availability, the state of the art of these different technologies is presented in chapter 2. Those processes can be divided into two main families, namely adsorption and electrochemical processes. However, although the many endeavors, only a few pilot plants can be now found commercially extracting lithium from aqueous resources.

In this work, two different sustainable approaches to recover lithium are proposed after a brief excursus on the experimental methods (chapter 3). The first one belongs to the passive adsorption family and comprises a functionalized graphene oxide membrane working in a pressure-assisted filtration setup (chapter 4). The selectivity of crown ethers was here used in combination with the properties of the highly stacked graphene oxide membrane prepared under vacuum. This system proved to work well with fairly diluted streams and achieved an impressive recovery of 70% of lithium from a 1 mM solution.

The second system was instead used in an electrochemical setup and was composed of anodically grown TiO_2 nanotubes hydrothermally converted into $LiTiO_x$ (chapter 5). After optimizing the synthesis and hydrothermal treatment, the electrodes showed impressive stability and reversibility in morphology and composition when intercalating lithium into the structure. Indeed, up to 17 at.% lithium was stored into the nanotubes in two different compounds. Furthermore, a static acidic de-lithiation treatment was also investigated, after which the samples were able to recover their storage ability. Preliminary tests for their use in aqueous environments were also conducted, with promising results in terms of selectivity.