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Low temperature synthesis of ion sieve for lithium recovery from brines

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PURPOSE OF THE ABSTRACT

Mainly used in Li-Ion batteries (65% of the market), lithium is a coveted raw material, more available in brines in dissolved form than in the continental crust. Generally, lithium in brine is recovered by a simple evaporation process over several months. An alternative method, using ion sieves, has been tested with the objective of faster lithium recovery (1).

The ion sieve, with its high ionic selectivity and its important regenerative power, is a key material for the exploitation of lithium brines. The Li2TiO3 (LTO) phase is particularly investigated due to its high Li/Ti=2 ratio and reversible Li+-H+ exchange allowing Li+ capture and release (2). In addition, this material offers real industrial interest considering its chemical stability and low production cost.

Among processes to produce LTO particles, hydrothermal synthesis, allowing a possible morphological modification of particles and size tuning at the nanoscale, is for choice as compared to the solid-state method (3,4).
The hydrothermal synthesis is usually composed of two steps. The first one is the formation of a metastable cubic alpha-Li2TiO3 (space group Fm-3m), starting from anatase particles dispersed in concentrated lithium hydroxide solution in autoclave with temperatures ranging from 120°C to 200°C. The resulting powder is then heated at high temperature (ranging from 300°C to 700°C) to obtain a monoclinic Beta-Li2TiO3 (space group C/2c) recognizable in XRD, and considered as the relevant crystallographic phase for Li+ exchange according to literature. Literature shows that hydrothermally synthesized particle are performant for Li recovery, nevertheless hydrothermal processes are expensive to implement at an industrial scale due to the considered pressure. As a consequence, the first step must be reconsidered.

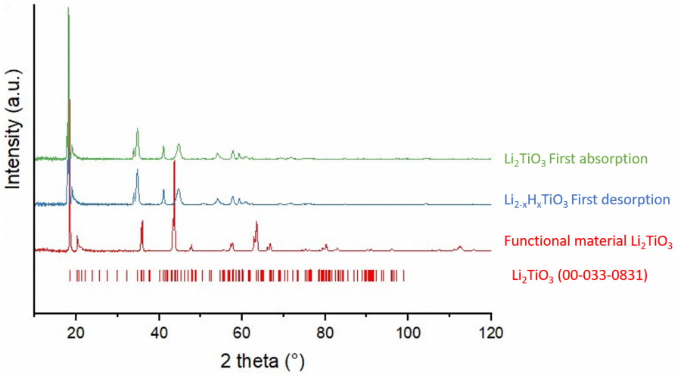
The aim of this study was to synthesize LTO using softer conditions and especially under atmospheric pressure, which is the key to an industrially acceptable process. This material must have better or equal capture performance as the products resulting from hydrothermal syntheses listed in the literature.

In our study, instead of using autoclave under autogenous pressure, the synthesis was performed at lower temperatures (approximately 100°C) than usual to allow the use of an atmospheric pressure reactors. Energy and chemical costs were minimized by changing the titanium precursor (homemade precipitate vs commercial titania), reducing the ratio Li/Ti necessary to get the right phase, lowering the synthesis time and the temperature under the reflux temperature. After a heating of the resulting powders at 700°C, the products from this parametric study were characterized in XRD, SEM, TEM and BET to characterize the structural and textural changes.

Once the ion sieve has been synthesized after these two steps, the lithium has to be removed by H+ ion-exchange to get an activated product able to capture Li+. This ion-exchange takes place upon treatment with a certain concentration of chlorhydric acid to form Li2-xHxTiO3, with x depending on desorption rate of the material with Li_2TiO_3 and H_2TiO_3 as end-members. This activated titanate $Li_{2-x}H_xTiO_3$ can reversibly exchange H^+ by Li^+ from brine.

The best product resulting from this new synthesis exhibited the same capture performance as the materials reported in the literature. The concentration of desorbed and absorbed lithium was monitored by atomic absorption spectroscopy and the synthesized material had a lithium exchange capacity of 33 $mg.g^{-1}$ (mg of Li per g of material), which represents 26% of the maximum (theoretical) lithium exchange capacity. By continuously monitoring the exchanges, kinetics could be described in order to find the optimal cycle time to maximize the average quantity of lithium recovered per time unit. Based on all these results, a scale-up synthesis (34L) could be initiated, which paves the way to a continuous industrial process for lithium recovery from brines.

FIGURES



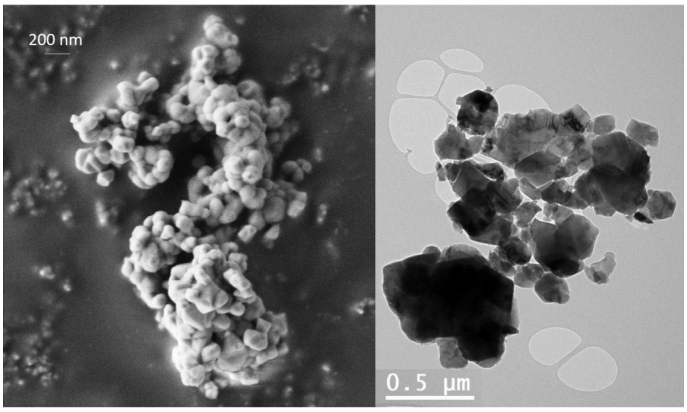


FIGURE 1

XRD product after synthesis, first desorption and first absorption

In red the functional materiai after synthesis and its indexation (00-033-0831) (reference 5)

In blue, the functional material Li(2-x)TiO3 after the first desorption.

In green, the functional material Li2TiO3 after the first absorption

FIGURE 2

Scanning and transmission electron micrograph of the functional material Li2TiO3

Left to the picture: Scanning electron micrograph of the functional material Li2TiO3

Right to the picture: Transmission electron micrograph of the functional material Li2TiO3

KEYWORDS

Water lithium resources | Lithium ion-sieve technology | Lithium adsorption/desorption mechanisms | Lithium titanate oxide

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BIBLIOGRAPHY

(1) Weng, D.; Duan, H.; Hou, Y.; Huo, J.; Chen, L.; Zhang, F.; Wang, J. Prog. Nat. Sci. Mater. Int. 2020, 30 (2), 139–152.
(2) Laumann, A.; Fehr, K. T.; Wachsmann, M.; Holzapfel, M.; Iversen, B. B. Solid State Ion. 2010, 181 (33–34), 1525–1529.
(3) Ramaraghavulu, R.; Buddhudu, S.; Bhaskar Kumar, G. Ceram. Int. 2011, 37 (4), 1245–1249.
(4) Chitrakar, R.; Makita, Y.; Ooi, K.; Sonoda, A. Dalton Trans 2014, 43 (23), 8933–8939.
(5) ICDD 00-033-0831