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Journal of Nuclear Materials 347 (2005) 134–139

journal of nuclear materials

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Methodology for the recovery of lithium from lithium titanate

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Received 11 March 2003; accepted 9 August 2005

Abstract

A process is described offering efficiency and specificity to recover lithium carbonate from lithium titanate pebbles partially burnt by neutron irradiation. The chemical route considers the extraction of the lithium from the spent fuel ceramics and its recovery as lithium carbonate, by dissolution in water, followed by precipitation in ethanol. Lithium titanate prepared with the recovered lithium carbonate compares favourably with the product resulting from a commercial high purity lithium carbonate. An 83% overall efficiency is achieved for the recovery of lithium carbonate.

1. Introduction

For the development of nuclear fusion power, based on the deuterium–tritium reaction, tritium must be generated. To assure an adequate tritium supply, one of the current fusion reactor designs considers a lithium ceramic breeder blanket for tritium production, as per the reaction:

$$^{6}\mathrm{Li} + \mathrm{n} \rightarrow {}^{4}\mathrm{He} + {}^{3}\mathrm{T}$$

where the neutron (n) flux is generated by the fusion reaction itself, enhanced within a beryllium wall. Lithium-containing ceramics are recognized as attractive breeding materials for fusion reactor blankets because of their inherent thermal stability and chemical inertness.

Preparation, fabrication and recycling [1] of the spent fuel ceramics are important thematic areas in the development of ceramic breeder blanket materials. Lithium titanate is prepared by solid-state reaction of lithium carbonate and titanium dioxide. Fabrication involves pelletization and sintering of the powder. Because of the cost involved in the ^{6}Li enrichment, the recovery of this isotope from spent blanket has been a major concern. This is due to the low natural content of the lithium-6 isotope and its high cost of enrichment. The fraction of lithium-6 burned in the reactor is likely to be low; it is estimated to be 14.6% after 2.3 years of operation at full power [2]. Hence, ceramic breeder material removed from the reactor could still contain a substantial portion of its lithium-6 content which should be recovered for preparation of lithium carbonate powder. The approach taken here is to develop a humid route to extract the lithium-6 from the partially burned lithium titanate and recover it as lithium carbonate.

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doi:10.1016/j.jnucmat.2005.08.013

2. Development of processing methodology

Fig. 1 displays the conceptual methodology necessary to recover lithium from lithium titanate, identifying the major steps in the process, namely, the dissolution of lithium titanate in mineral acid followed by the recovery of lithium from the acid solution and its precipitation as lithium carbonate. The details of the different steps involved in the process are described below. The ultimate goal of this process is the preparation of high density lithium titanate pebbles by the solid-state reaction between the recovered lithium carbonate and titania.

As the starting point, we take two published reports: the first one addresses the dissolution of lithium titanate in different acids [3] and the second one reports a route for the recovery of lithium-6 [4] by dissolution and precipitation in aqueous solution. Dissolution alternatives were tested for the pebbles of Li_2TiO_3 with the purpose of extracting all the lithium remnant of the ceramic matrix. In the next step the lithium is precipitated as lithium carbonate, with characteristics appropriate for its utilization in the preparation of lithium titanate.

Finally the reactivity of the recovered carbonate was tested by the solid-state reaction with titania to produce lithium titanate. The characteristics of the resulting product were compared to the those of the same compound synthesized in our

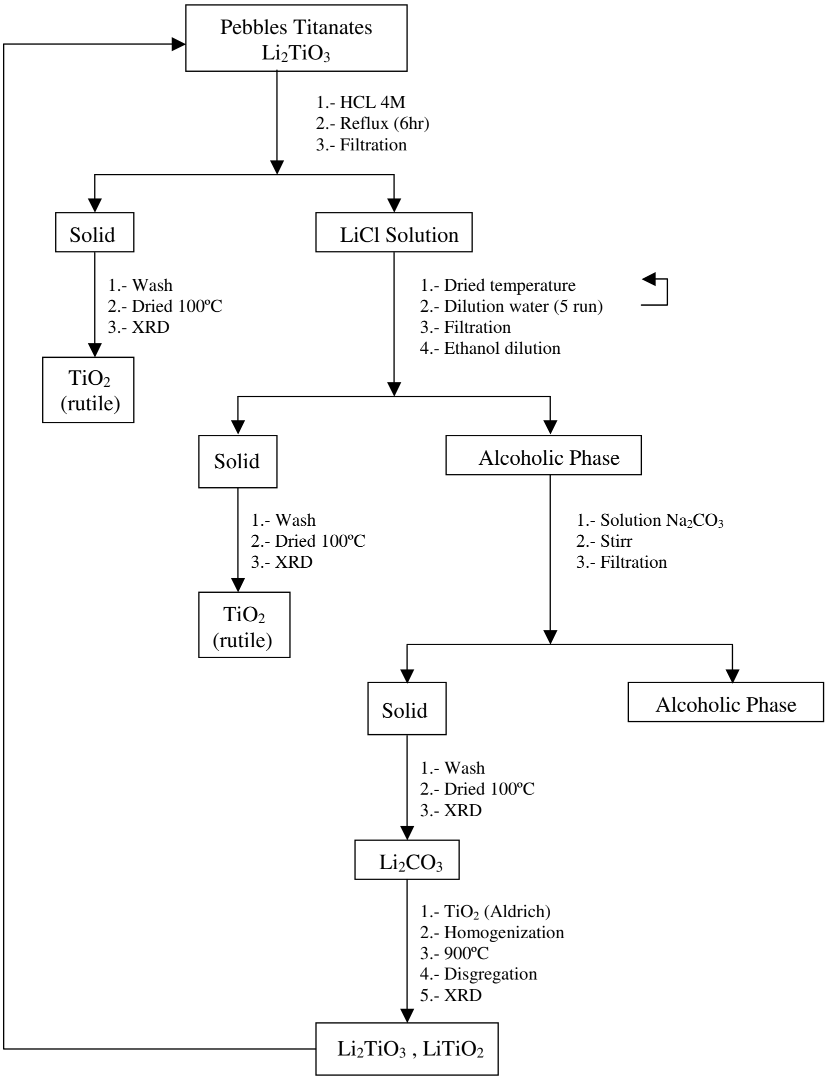

Fig. 1. Lithium reprocessing scheme.

laboratory starting out from commercial precursors (ALDRICH Li_2CO_3 and TiO_2).

2.1. Li_2TiO_3 pebbles dissolution

Leaching of several grams of Li_2TiO_3 pebbles was carried out under boiling reflux of 4 M hydrochloric acid for 6 h. The pebbles were readily destroyed by acid attack with formation of an insoluble white phase, which was separated from lithium chloride solution by vacuum filtration. The solid was washed, dried and characterized.

2.2. Lithium precipitation

The aqueous solution of lithium chloride was evaporated to dryness on a hot plate. The dried residue was dissolved in water. Successive evaporations were carried out followed by dissolution in water until reaching a pH value near 9. After the last evaporation, the dried solid was dissolved in ethanol. The alcoholic solution was filtered, washed, dried and characterized by X-ray diffraction, seeking to identify a small quantity of a white residue.

Various carbonating agents were tested for precipitation of lithium from the alcoholic solution. The best result was achieved by precipitating with an aqueous solution of sodium carbonate. The precipitated lithium was filtered, washed, dried and characterized. The reproducibility of the process was tested by application to several small batches of Li_2TiO_3 pebbles.

2.3. Li_2TiO_3 preparation

Lithium titanate powder was prepared by solid-state reaction of reprocessed lithium carbonate and titanium dioxide. A stoichiometric mixture was homogenized and then calcined in a furnace for 4 h at 900 °C. The resulting powder was characterized and compared to the lithium titanate obtained with the commercial precursors.

3. Results

Alternative dissolution approaches were tested for the Li_2TiO_3 pebbles with the purpose of extracting all the lithium from the ceramic matrix. Six hours of reflux of the pebbles of Li_2TiO_3 in hydrochloric acid were sufficient to separate the lithium from the ceramic matrix. The pebbles were completely destroyed with the formation of a white slurry. The peptized insoluble white phase was separated by filtration, washed and dried in air, the X-ray diffraction pattern of which corresponds to TiO_2 (Fig. 2).

The formation of titanium dioxide and lithium chloride occurs according to the following reaction:

$$Li_2TiO_3 + 2HCl \rightarrow 2LiCl + TiO_{2(s)} + H_2O$$

The percent of dry TiO_2 product is shown in Table 1 for three batches that were obtained after separating the lithium by means of acid reflux. The results confirm the full selective dissolution of

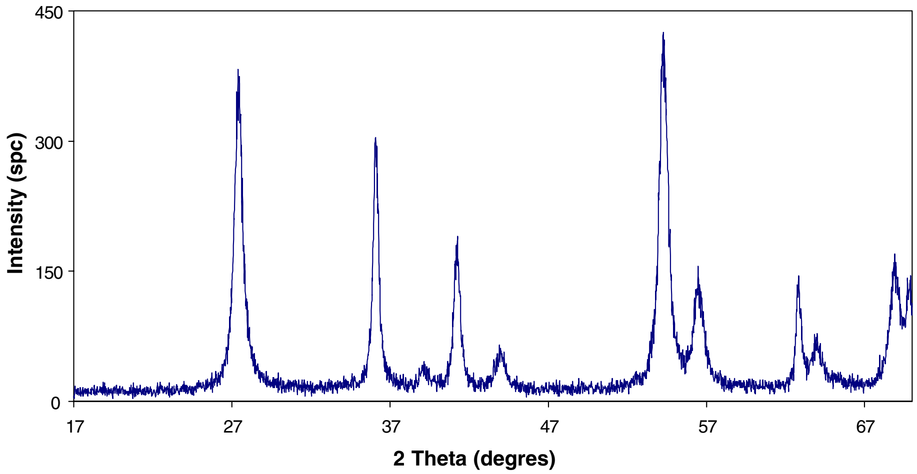

Fig. 2. X-ray diffraction pattern of the dry residue coming from Li_2TiO_3 reaction with 4 M HCl. Rutile is the present crystalline phase.

Table 1
Quantitative evaluation of the solids produced by acid dissolution precipitation of lithium carbonate

Experiment	XRD white residue	% Recuperation white residue	% Recuperation Li_2CO_3
Rep-1	TiO_2 (rutile)	98.33	83.0
Rep-2	TiO_2 (rutile)	98.85	82.0
Rep-3	TiO_2 (rutile)	99.54	82.0

lithium in the hydrochloric solution. As a comparison, Alvani et al. [4], reached 100% dissolution of lithium titanate in nitric acid.

3.1. Lithium precipitation

When the lithium titanate pebbles are placed in HCl, a very acidic LiCl solution is obtained with a pH less than 1. In acid solutions it is not possible to precipitate carbonates, so the pH was adjusted to a value above 9, to enable the formation of the lithium carbonate by repetitive evaporation—water dilution steps.

Water is a good medium for dissolution of lithium chloride and later precipitation of the carbonate, as demonstrated by Alvani et al. [4]; however, this solvent has a high tendency for solubilizing lithium carbonate, thereby decreasing the efficiency of the process. Also, water may contain significant amounts of CO_2 that displace the equilibrium towards the formation of soluble ions in competition with the insoluble carbonate. In our work, ethanol was used for dissolution following the pH increase (up to pH = 9), and as a precipitation medium, as described above (Section 2.2). The lower polarity of ethanol, as compared to water, is understood to allow for a higher precipitation efficiency following the addition of a carbonating agent.

Three carbonating (precipitating) agents were tested, ammonium carbonate, carbon dioxide and sodium carbonate. With the first one coprecipitation of ammonium chloride which is not eliminated by washing. The dioxide is not effective due to very slow reaction kinetics. Finally the precipitation with sodium carbonate resulted to be the most effective since the sodium chloride that also precipitates is eliminated by washing in water three times. Agitation and slow addition of sodium carbonate are necessary during the precipitation to assure a homogeneous product with the adequate morphology for the synthesis of Li_2TiO_3. The following reaction gives an account of the lithium precipitation.

$$2LiCl + Na_2CO_3 \rightarrow Li_2CO_{3(s)} + 2NaCl$$

The impurities found in the precipitate, namely NaCl and Na_2CO_3, were eliminated by washing the solid with hot water. The X-ray diffraction pattern of the dry product indicated only the presence of lithium carbonate, the position of lines and the relative intensities of the diffraction spectra of Fig. 3 confirm the presence of lithium carbonate and the crystallographic identity of the reprocessed product and the commercial reactive.

To determine the yield and the reproducibility of the procedure, several small batches of lithium titanate were reprocessed and characterized. As indicated in Table 1, an average yield of 83% results.

Alvani et al. [4] reached 70% and 75% yield for the processes called A-1 (attack with hydrogen peroxide) and A-2 (attack with nitric acid), respectively. The attack with nitric acid indicated that the process was very efficient. However, precipitation in water is not attractive because water has a high solubility coefficient for lithium carbonate, decreasing the efficiency of the process.

Important characteristics of the reprocessed powder are shown in Table 2, where comparisons to the commercial carbonate are included. The average particle size of the reprocessed product is somewhat greater. The temperature, velocity of addition of the precipitant agent and the concentrations can be studied experimentally in order to control the size of particles in the precipitation.

The reprocessed lithium carbonate was submitted to thermal analysis to verify the endothermic decomposition reaction, associated with an important weight loss, associated with the elimination of CO_2, in the differential thermogram. The thermograms in Fig. 4 show the decomposition peaks of both the reprocessed and the commercial products.

3.2. Li_2TiO_3 preparation

Finally, the suitability of the recovered $^6Li_2TiO_3$ for the preparation of ceramic pebbles by spheronization-sintering was tested. The Li_2TiO_3 powder was prepared by solid-state reaction of reprocessed Li_2CO_3 and TiO_2, and mixed in stoichiometric proportions according to the following reaction (Fig. 5):

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2$$

The powder obtained by reacting the constituents at 900 °C was characterized and compared to the

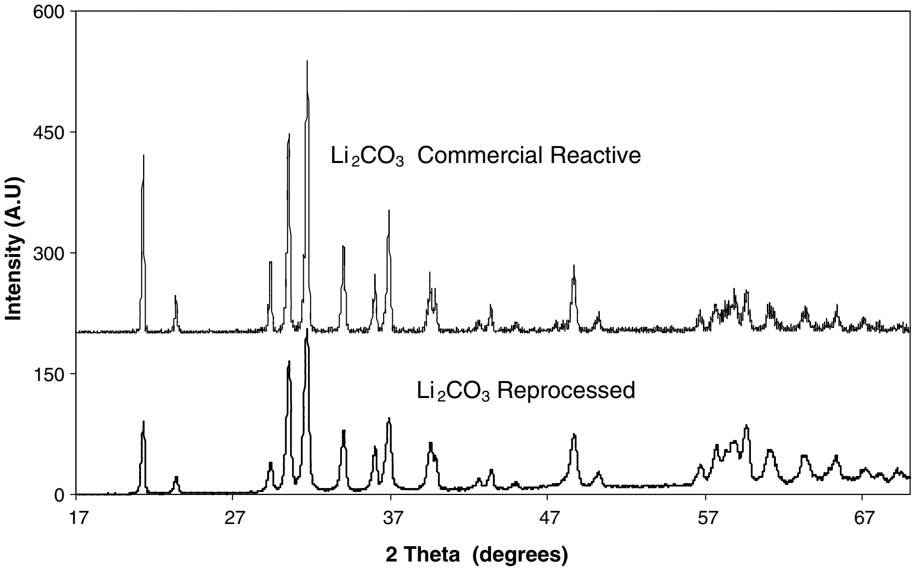

Fig. 3. X-ray diffraction pattern of the Li_2CO_3 powders obtained from Li_2TiO_3 and commercial reactive.

Table 2
Characteristics of Li_2CO_3 and Li_2TiO_3 powders reprocesses and commercial reactive

Analysis	Li_2CO_3 commercial reactive	Li_2CO_3 reprocessed	Li_2TiO_3 commercial precursors	Li_2TiO_3 reprocessed
Density (g/cc)	2.11	2.15	3.46	3.49
Average size particle (μm)	21.15	29.92	13.72	12.37
Superficial area (m^2/gr)	1.341 ± 0.06	3.917 ± 0.01	2.657 ± 0.02	2.548 ± 0.01
XRD	Li_2CO_3	Li_2CO_3	Li_2TiO_3, $LiTiO_2$	Li_2TiO_3, $LiTiO_2$

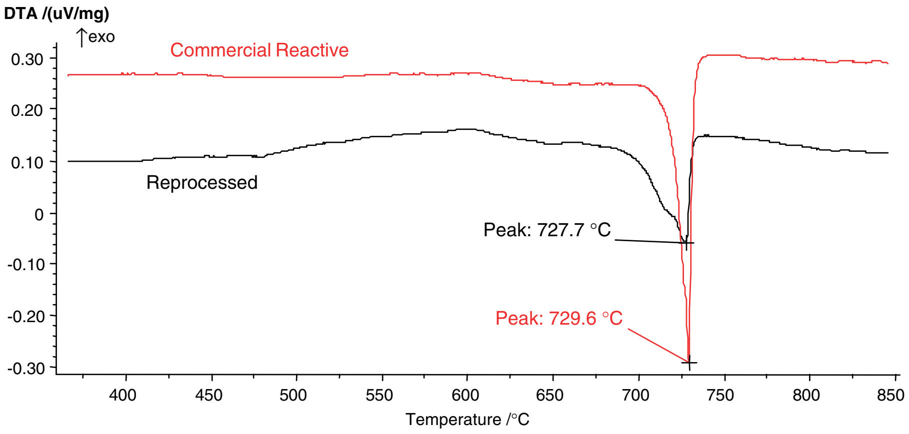

Fig. 4. Thermogram of the Li_2CO_3 powders obtained by reprocessing and the commercial reactive.

same product obtained with commercial precursors. The characteristics are shown in the Table 2. This evaluation of the powder is very important because of its bearing on the mechanical properties of the ceramic breeder bed.

4. Conclusions

When following the schematic flow sheet shown in Fig. 1 recovery of lithium, as lithium carbonate, and the conversion to lithium titanate, gave a yield

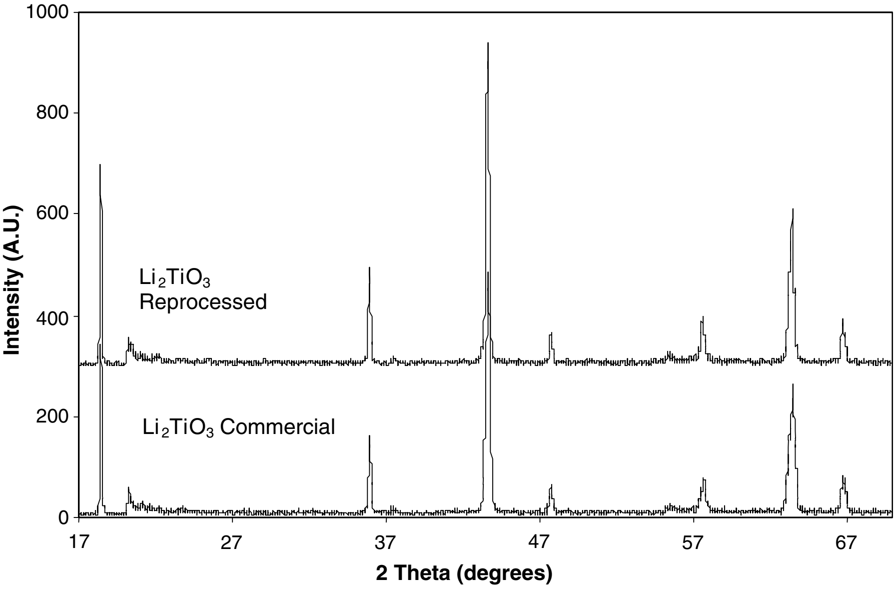

Fig. 5. XRD of Li_2TiO_3 powders commercial and reprocessed.

of 83% to lithium carbonate. Such high recovery is a promising and stimulating result. The route of preparation proposed for recovery of lithium fuel includes two important steps:

a. Attacking the ceramic for the selective dissolution of lithium.
b. Precipitation of the soluble lithium as lithium carbonate.

The first step readily separated lithium from the ceramic in a mineral acid with a recovery reaching 98.9%. However, the aggressive acid attack required for dilution of the original ceramic results in an ambient which keeps lithium from precipitation as carbonate. Repetitive dilution–evaporation steps to achieve a pH value near 9, followed by dilution in ethanol, were used for the final precipitation of lithium carbonate.

It is well known that the particular choice of solvent for precipitation may influence the particle size of the powder, and, thus, the efficiency of the process. In this regard, ethyl alcohol proved to be a good medium for the precipitation. There still remain some variables that need to be tested further, as higher efficiencies might be reached. Variables that affect the solubility and the size of the lithium carbonate particles may need attention. Process temperature, impurity concentration, and strength of the carbonating agent are some variables that, with further study could improve the efficiency of the proposed process.

An interesting future contribution would be to test this methodology on partially burned material. However, that would require other facilities that today are not available in our laboratories.

Acknowledgements

The authors would like to acknowledge the assistance of Dr Carl E. Johnson for his support. Dr. Ricardo Avila is gratefully acknowledged for his careful editing of the manuscript.

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