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Li_2TiO_3 pebbles reprocessing, recovery of ^6Li as Li_2CO_3

C. Alvani [a,*], S. Casadio [a], V. Contini [a], A. Di Bartolomeo [a], J.D. Lulewicz [b], N. Roux [b]

[a] *C.R. ENEA Casaccia, Via Anguillarese Km 3.01, 00060 Roma, Italy*
[b] *C.E.A.–C.E.N. Saclay, 91191-Gif-sur-Yvette cedex, France*

Abstract

A process for obtaining Li_2CO_3 from Li_2TiO_3 powder by wet chemistry was developed. This is considered useful in view of the recovery of the ^6Li isotope from lithium titanate breeder burned to its end of life in a fusion reactor. The process was optimized with respect to the chemical attack of titanate and the precipitation of carbonate from aqueous solutions to get a powder with chemical and morphological characteristics suitable for its reexploitation in the fabrication of Li_2TiO_3 pebbles. Reprocessing was also planned to adjust the ^6Li concentration to the desired value and to obtain a homogeneous distribution in the powder batch. Further development concerning reprocessing of sintered Li_2TiO_3 pebbles is in progress exploiting the results obtained with lithium titanate powders.

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1. Introduction

Lithium titanate is one of the most promising candidates for tritium breeding [1]. The temperature of tritium release from polycrystalline Li_2TiO_3 ceramic pellets and pebbles was found lower than that from other Li-ceramics [2,3]. This material shows also good chemical stability to the air environment and acceptable mechanical strength [4]. A review of the preparation, properties, irradiation performance and tritium release of lithium containing ceramics has been published [5,6]. Besides the chemical and physical characteristics of a Li-based ceramic breeder, its ^6Li enrichment must also be taken into account. Neutronics analyses indicate for Li_2TiO_3 pebbles with a mass density of 90% TD a ^6Li enrichment of 55–65 at.% and a maximum burn-up of 14.6 at.% for the HCPB Demo blanket [7].

The objectives of this activity were the investigation of the feasibility of reprocessing Li_2TiO_3 pebbles, at their 'end-of-life' and still containing 40–50 at.% of ^6Li, in order: (i) to recover the ^6Li isotope as Li_2CO_3 with the suitable chemical and morphological characteristics, requested for the reference fabrication route (extrusion) of Li_2TiO_3 pebbles [4] and reported in Table 1, and (ii) to increase the depleted ^6Li concentration to the value foreseen for this type of ceramic breeder assuring moreover a fully homogeneous distribution of ^6Li isotopes.

2. Experimental

Lithium titanate powder, obtained by solid state reaction between lithium carbonate and titania, was used for a preliminary set-up of the preparation procedure. This was planned in two principal steps:

(a) Attack of Li_2TiO_3 by wet chemistry, to separate completely Li from Ti and obtain a lithium containing solution.
(b) Recovery of Li as Li_2CO_3 including in this last step the above mentioned objective (ii) taking into account the chemical characteristics of the produced Li-solution from the first step.

2.1. Lithium separation from Li_2TiO_3 (a)

Two chemical methods were tested, the first (a-1) was based on our previous experience [8] on producing

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[*] Corresponding author. Fax: +39-6 3048 3327.
E-mail address: carlo.alvani@casaccia.enea.it (C. Alvani).

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Table 1
Some characteristics of the requested Li_2CO_3 powder

Apparent bed density	0.45 g/cm^3
Specific surface area	1–1.5 m^2/g
^{6}Li concentration	55–65 at.%
Main impurities	ppm
Al	20
Ca	35
Fe	9
K	30
S	10
Si	20
Zr	10

reprocessed litium titanate powders using hydrogen peroxide to dissolve Li_2TiO_3; within the second method (a-2), lithium was leached from titanate using nitric acid.

2.1.1. Li_2TiO_3 attack by H_2O_2 (a-1)

The dissolution of lithium titanate in hydrogen peroxide produced a clear yellow solution of a Li–Ti-peroxo-complex through the following reaction that can be schematically inferred:

$$2Li_2TiO_3(s) + 2H_2O_2(aq) + H_2O(l) \Rightarrow Li_4Ti_2O_5(OH)_6(aq). \quad (1)$$

The reaction was carried out under the following experimental conditions: 20 °C with a cooling system for 24 h, [Li] concentration = 0.91 mol/l, H_2O_2 concentration 12 wt%. $Li_4Ti_5O_{12}$ and traces of TiO_2, already present in the starting material, remained as insoluble phases and were identified by X-ray diffraction measurements (Fig. 1) performed on the filtered material just after reaction, Eq. (1). The yellow peroxo-complex solution was not stable and could be easily decomposed with oxygen evolution and pH increase into a Li-containing solution and a solid phase. This 'condensation', carried out at 80 °C for 2 h, produced different species depending on the final pH that was varied by adding different amounts of HNO_3. From XRD analysis on the dried and calcined solids the following reaction could be inferred:

(1) at pH > 12, without acid addition, only 50% of the total Li could be transferred into the solution:

$$3Li_4Ti_2O_5(OH)_6(aq) \Rightarrow Li_2TiO_3(s) + Li_4Ti_5O_{12}(s) + 6LiOH(aq) + 6H_2O(aq) + 3O_2(g), \quad (2)$$

(2) at pH < 2 with a ratio $[HNO_3/[Li] \approx 1.26$, lithium was quantitatively recovered into the acid solution:

$$Li_4Ti_2O_5(OH)_6(aq) + 4HNO_3(aq) \Rightarrow 2TiO_2(s) + 4LiNO_3(aq) + 5H_2O(aq) + O_2(g). \quad (3)$$

The XRD patterns of the solid products of the above reactions (2) and (3) are shown in Fig. 2 while a rough quantitative analysis at intermediate pH values is reported in Table 2.

2.1.2. Li_2TiO_3 attack by HNO_3 (a-2)

The experimental activity within the chemical attack by nitric acid, for the present abandoned, was resumed owing to the following considerations: (1) the use of HNO_3 was found unavoidable for a complete separation of lithium from titanate in the above described procedure (2) this type of ceramic breeder will probably contain, at its end of life, a certain amount of $Li_4Ti_5O_{12}$ insoluble in H_2O_2.

Experiments were performed in order to minimize the amount of HNO_3 necessary for a complete Li extraction according to the following foreseen reaction:

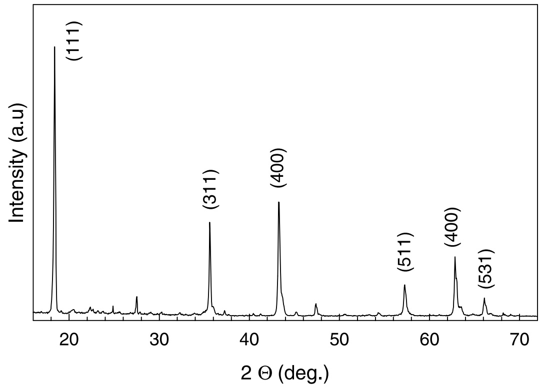


Fig. 1. X-ray diffraction pattern (Cu Kα) of the insoluble residue (≈4 wt% of the starting powder) obtained after 24 h dissolution of Li_2TiO_3 in H_2O_2 at low temperature. The principal phase is $Li_4Ti_5O_{12}$.

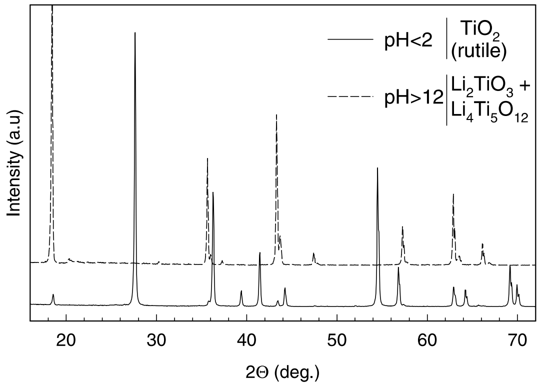


Fig. 2. X-ray diffraction patterns (Cu Kα) of the solid phases, dried and calcined at 800 °C, produced by the reactions (2) and (3).

Table 2
Quantitative evaluation of the solid phases produced by decomposition of the Li–Ti-peroxo-complex solution as a function of the final pH

pH	Li_2TiO_3	$Li_4Ti_5O_{12}$	TiO_2 (rutile + anatase)
>12	50%	50%	Traces
7	–	70%	30%
6	–	50%	50%
3	–	15%	85%
<2	–	Traces	≈100%

$$\begin{aligned} &Li_2TiO_3(s) + 2HNO_3(aq) \\ &\quad \Rightarrow 2LiNO_3(aq) + TiO_2(s) + H_2O(aq). \end{aligned} \tag{4}$$

Temperature and time were optimized in order to be compatible with a practical application of the process. The best results were obtained by leaching at the following conditions: boiling point under reflux for 6 h, Li concentration = 0.91 mol/l, HNO_3 concentration = 1.15 mol/l like in the reaction (3).

According to the procedure a-1, the resulting solid phase was dried and calcined at 800 °C. The X-ray diffraction pattern, reported in Fig. 3, showed the characteristic peaks of a TiO_2 rutile and anatase mixture without the presence of Li-containing phases. Therefore it was concluded that lithium was extracted also from $Li_4Ti_5O_{12}$ already contained in the starting material. This feature of the process will be in any case investigated by using pure $Li_4Ti_5O_{12}$ as raw material and will be the object of future activity.

2.2. Lithium recovery as Li_2CO_3 (b)

Lithium nitrate solutions were obtained from the above described procedures, moreover an excess of HNO_3 was necessary to assure a complete Li–Ti separation.

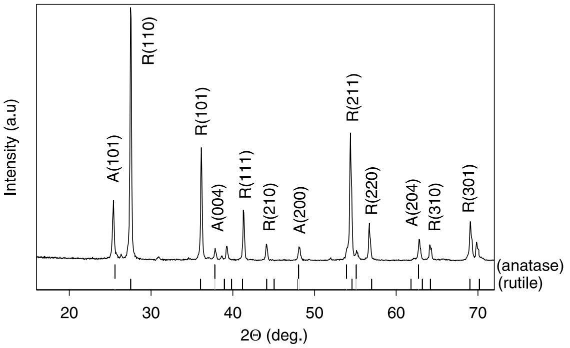


Fig. 3. X-ray diffraction pattern (Cu Kα) of the calcined solid obtained after leaching of Li_2TiO_3 in HNO_3. (A: TiO_2 anatase, R: TiO_2 rutile) No Li-containing phases were detectable.

Thermal decomposition of $LiNO_3$ from the dried solutions and subsequent reaction with CO_2 of the formed oxide were excluded due to problems arising in the control of the final morphology of the powder.

Therefore, owing to the quite low water solubility of Li_2CO_3, the final reprocessing step was addressed optimizing the precipitation of lithium by means of a carbonating agent in aqueous solutions as reported schematically:

$$2LiNO_3(aq) + CO_3^{2-}(aq) \Rightarrow Li_2CO_3(s) + 2NO_3^-(aq). \tag{5}$$

Since this reaction is possible only at high pH, addition of an excess of a strong base was necessary to neutralize the nitric acid and to rise the pH up to values >12. Good results were obtained by adding $LiOH \cdot H_2O$.

The addition of lithium hydroxide, to adjust the pH at this step of the procedure can be considered useful in a real reprocessing to increase the depleted ^6Li concentration assuring moreover a fully homogeneous distribution (objective (ii)) since the precipitation of carbonate occurs in a homogeneous solution with the already adjusted ^6Li concentration. Therefore, a lithium hydroxide containing the proper amount of ^6Li should be considered for a future application of this type of reprocessing. The amount added in this work corresponded to a ^6Li increase from 45 to 60 at.% provided $LiOH \cdot H_2O$ with 95 at.% of ^6Li/total Li was used.

Carbon dioxide, $(NH_4)_2CO_3$ and Na_2CO_3 were tested as carbonating agents; the concentrations and temperature were optimized to give an acceptable yield together with the requested morphological characteristics of the final product. The best results were reached by using Na_2CO_3 as the precipitating agent on solutions coming from both the a-1 and a-2 chemical attacks. The following experimental conditions were found to be the most suitable: 80 °C with stirring, $LiNO_3$ concentration = 1.82 mol/l, LiOH concentration = 0.78 mol/l, a molar ratio Na_2CO_3/total Li = 0.52.

In order to test the reproducibility of the procedures, several small batches of Li_2TiO_3 were reprocessed and characterized. Some characteristics of the obtained Li_2CO_3 powders are reported in Table 3, together with the total and recovered Li related yields.

Fig. 4 shows the X-ray diffraction pattern of the final powder which was identified as monoclinic Li_2CO_3 according to the standard ASTM JCPDS-831454.

3. Conclusions and future work

The set-up of the parameters suitable for recovery of lithium carbonate from titanate was performed following the schematic flow-sheet reported in Table 4. The activity was successfully addressed towards a

Table 3
Some characteristics of procedures and obtained Li_2CO_3 powders

Property	Requested	Type of chemical attack	
		a-1	a-2
Total yield (%)	–	70 ± 5	75 ± 5
Recovered Li (%)	–	62 ± 5	70 ± 5
BET surface area (m^2/g)	1–1.5	2.3 ± 0.1	2.8 ± 0.1
Apparent bed density (g/cm^3)	0.45	0.41 ± 0.02	0.39 ± 0.02
True density by He pycnometry (g/cm^3)	–	2.08 ± 0.01	2.09 ± 0.01

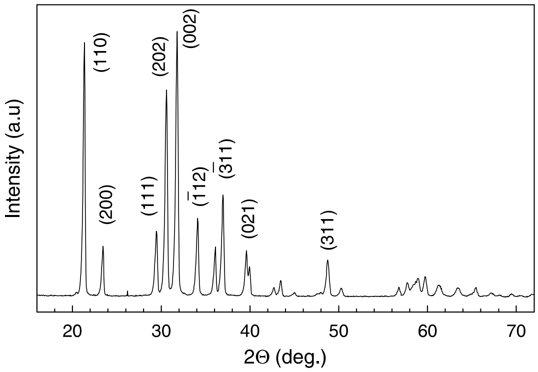
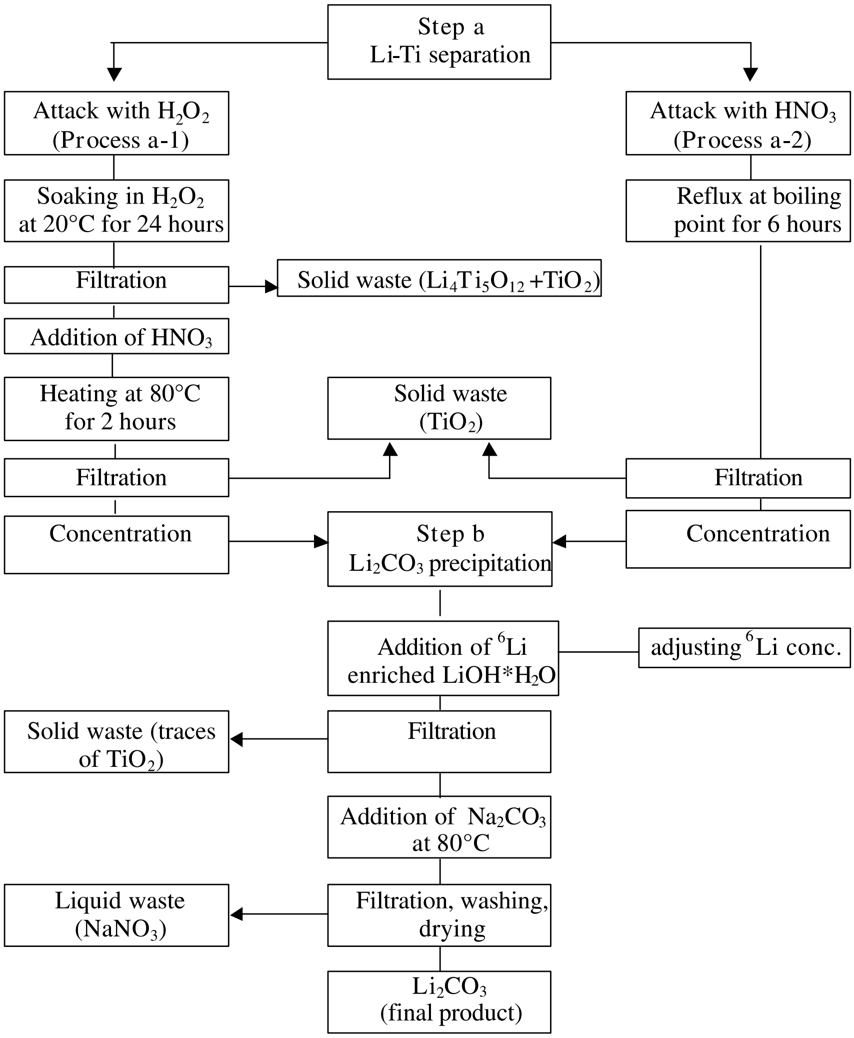


Fig. 4. X-ray diffraction pattern (Cu Kα) of monoclinic Li_2CO_3 obtained from reprocessing of Li_2TiO_3.

Table 4
Reprocessing flow sheet



quantitative separation of lithium from titanium oxide together with the recovery of a final product with the morphological characteristics very close to the requested ones. At this point of the reprocessing development the following considerations can be done:

- Differences on the yields obtained using a-1 and a-2 procedures can be attributed to the inability of H_2O_2 to dissolve the titanium rich phase $Li_4Ti_5O_{12}$ already contained in the raw material. In any case the evaluation of lithium extraction by the a-2 procedure from $Li_4Ti_5O_{12}$ will be the object of future activity.
- Efforts should be done in order to increase the efficiency of the precipitation step. Some problems probably arise from an increase of the Li_2CO_3 solubility due to a decrease of the activity coefficient in solutions at high ionic strength (the so called 'salting-in' effect).
- Following measurements of the impurity content (especially Na) in the final product, possibly a further purification step should be planned.
- In order to simulate a real reprocessing of the Li_2TiO_3 breeder material, the efficiency of the set-up procedures will have to be confirmed using small batches of sintered pebbles. Taking into account that the reactivity of such samples will be almost certainly lower with respect to the powders used up to now, some variations of the process parameters will be probably necessary and will be extensively investigated trying to avoid a preliminary troublesome pebble milling step. In addition within this activity a choice between the a-1 and a-2 processes will be done.
- The final experimental activity will be carried out with the production of a larger Li_2CO_3 batch suitable for the already mentioned reference fabrication route of Li_2TiO_3 pebbles.

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