

Preparation of lithium titanate by sol-gel method

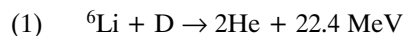
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Abstract Medium sized spherical particles of Li_2TiO_3 (with diameters below 100 μm) can be prepared from peroxy lithium titanate solution (stabilized with citric acid) by a modified INCT variant of the sol-gel process. The process consists of the following main steps: (I) formation of aqueous phase emulsion in 2-ethylhexanol-1 containing the surfactants 1v/o SPAN-80 and 1v/o Ethomen S-15 (EH); (II) gelation of emulsion drops by extraction of water with partially dehydrated EH; (III) filtration and washing with carbon tetrachloride or acetone; (IV) non-destructive thermal treatment. The tritium release from sol-gel process preparation of Li_2TiO_3 micro-spheres was found very close to that observed for other traditional material however, the new process is more efficient than other processes because of the morphology of the sintered specimens.

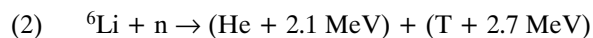
Key words fusion reactor • lithium titanate • sol-gel

Introduction

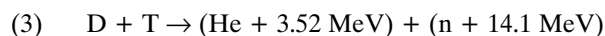
Future Fusion Reactor (FR) power plants are based on the following nuclear fusion reaction:



The role of the lithium-6 fuel is generation of tritium by the following ${}^6\text{Li}(n,\alpha)\text{T}$ nuclear reaction:



inside the blanket of the thermonuclear reactor by exploiting the fast neutrons (n) coming from the D-T fusion as vectors carrying out of the plasma most of the produced energy in this stage:



Since the fission products [tritons (T) and α particles (He)] of Equation 2 will release 4.8 MeV total energy inside the blanket, the engineering must provide removal and recovery of both the tritium needed for Equation 3 and heat, an amount which is an important fraction (21.4%) of the overall process in Equation 1.

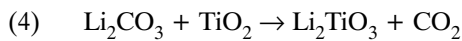
One of the research directions to make this process Equation 2 feasible for the FR is based on blanket engineering concepts using Li-ceramics in a way similar to that developed for fission reactor power plants using U-Pu oxide ceramics as fissile fuels. The work performed in the last two decades in this field has been reviewed by C.E. Johnson [9] who pointed out the lack of data concerning Li_2TiO_3 as a most promising candidate for FR.

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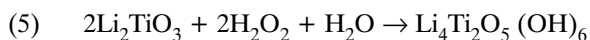
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Within the frame work of the Fusion European Programme, the evolution of Li-ceramics based blanket design led to concentrate research efforts on the “Helium Cooled Pebble Bed” (HCPB) blanket, for which the envisaged Li-ceramics are Li_4SiO_4 [4] or Li_2TiO_3 (under development at CEA with ENEA involved in its re-processing [1]), in the form of dense spheres (pebbles) with diameters of about 1 mm. These Li-titanate pebbles of size about 1.2 mm in diameter are fabricated by the “extrusion-spherulization-sintering” [1] of the powder obtained by the following solid state reaction:



Lithium density in the blanket is an important parameter for the economy of FR. An increase in this value leads to a reduction of the lithium-6 enrichment needed to ensure “self-breeding” of the stage in Equation 2. The smear density of the pebble bed cannot exceed the theoretical value of 62% of TD (theoretical density, based on the Li_2TiO_3 single crystal density of 3.43 g/cm^3) for a packed bed of spheres with nearly the same radius. Lithium density is in fact an important parameter in the economy of FR. A significant increase of the pebble bed density to 88% of TD may be obtained by a bimodal distribution of the pebbles size that is optimized by introducing pebbles with diameters decreased by a factor of ten in respect to the original diameter ($\sim 1 \text{ mm}$).

In former work [6, 7] fabrication of dense Li_2TiO_3 spheres with a diameter ranging within 1–100 μm , using the INCT variant of sol-gel process [5, 8], was described. As a starting material industrial TiCl_4 was used. However, the ENEA reprocessing of depleted Li_2TiO_3 [2] consists of its dissolution in hydrogen peroxide according to the following reaction:



Consequently, we decided to apply the INCT sol-gel process for fabrication of spherical powders with diameters $< 100 \mu\text{m}$ using this solution instead of classical hydroxylsols. There are no published literature data concerning preparation of medium sized solid particles by any variant of the sol-gel process.

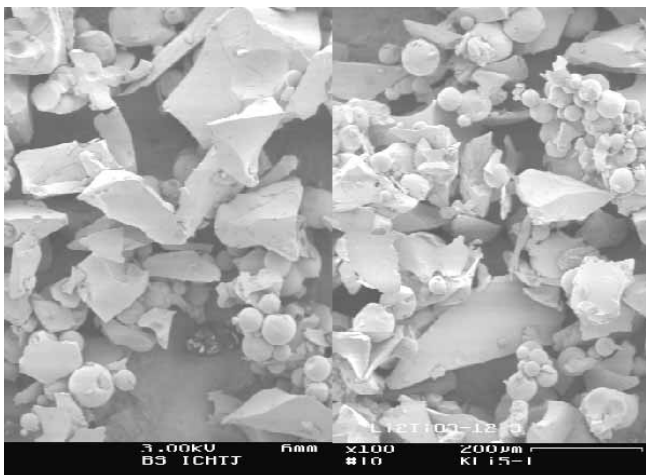


Fig. 1. SEM micrographs of the sample obtained with applied routine EH:aq. phase volume ratio = 100:1 after drying at 100°C .

Methods

In the INCT process, the formation of microspheres from aqueous phase consists of the following steps:

- formation of aqueous phase emulsion in 2-ethylhexanol-1 containing the surfactants 1v/o SPAN-80 and 1v/o Ethomen S-15 (EH);
- gelation of emulsion drops by extraction of water with partially dehydrated EH;
- filtration and washing with carbon tetrachloride or acetone;
- non-destructive thermal treatment.

Conditions kept during these steps should be adequate for control of the physicochemical parameters of the aqueous phase (concentration, viscosity) and desired size, composition, crystallisation grade and density of the final product.

Gels and products produced by this thermal treatment process (in a programed Carbolite furnace type CSF 1200) were characterized by the following methods:

- thermal analysis (TG, DTA) using a Hungarian MOM Derivatograph (sample weight – 200 mg; heating rate – $10^\circ\text{C}/\text{min}$; atmosphere – air, static; reference material – Al_2O_3 ; sensitivity: TG-200, DTG-1/5, DTA-1/5);
- X-ray diffraction (XRD), Cu K_α (Philips Diffraction System);
- SEM observations using DSM 942 (Zeiss).

The Li-ceramics tritium release testing was performed by TPD methods described elsewhere [3].

Results and discussion

According to routine principles of the INCT process, the aqueous phase should have a high concentration of solids ($> 100 \text{ g/l}$) and viscosity of at least several cSt. Consequently, the parent solution was prepared according to Equation 5 following the recipe given elsewhere [1, 2], however, without any addition of citric acid stabilizer, the solution was concentrated 2–3 times to $\sim 200 \text{ g/l}$ (dried

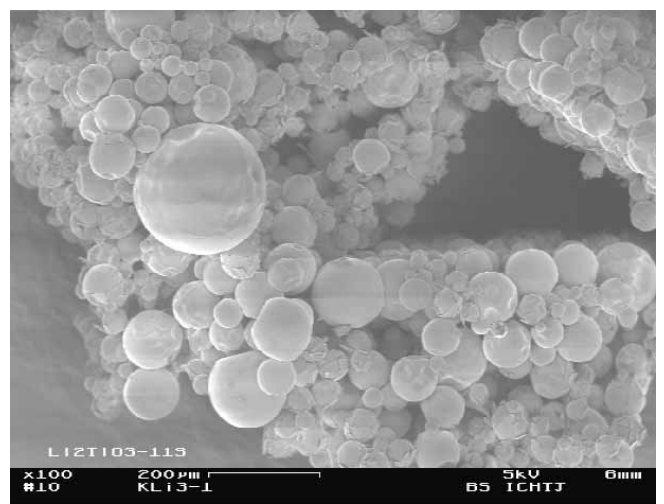


Fig. 2. SEM micrographs of the $\text{Li}_4\text{Ti}_2\text{O}_5(\text{OH})_6 \cdot x\text{H}_2\text{O}$ gels microspheres dried at RT.

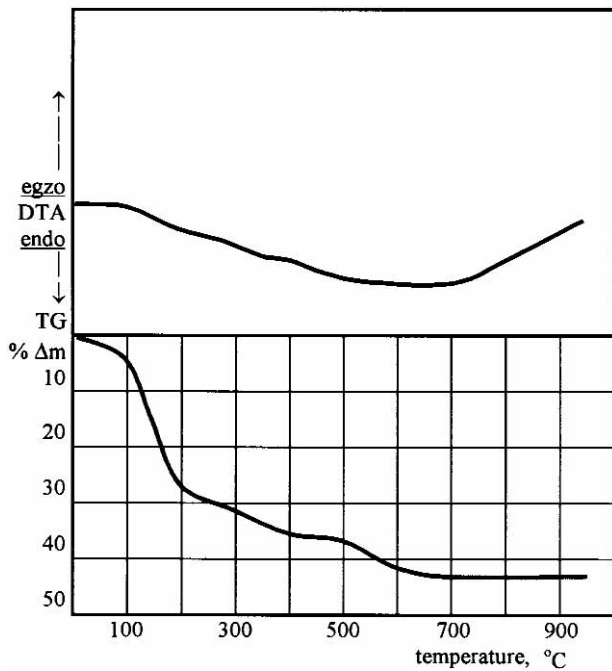


Fig. 3. Thermal analysis of $\text{Li}_4\text{Ti}_2\text{O}_5(\text{OH})_6 \cdot x\text{H}_2\text{O}$ gels microspheres dried at RT.

assay heated for 2 h at 900°C) and viscosity ~ 100 cSt. As is shown in Fig. 1, only partial gelation to microspheres was observed using the routine EH:aq. phase volume ratio equal to 100:1.

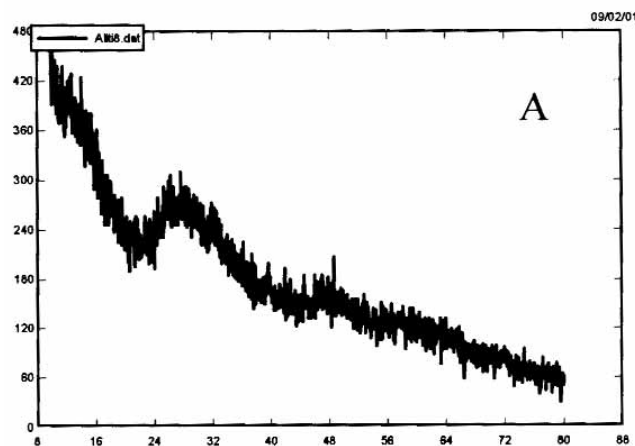
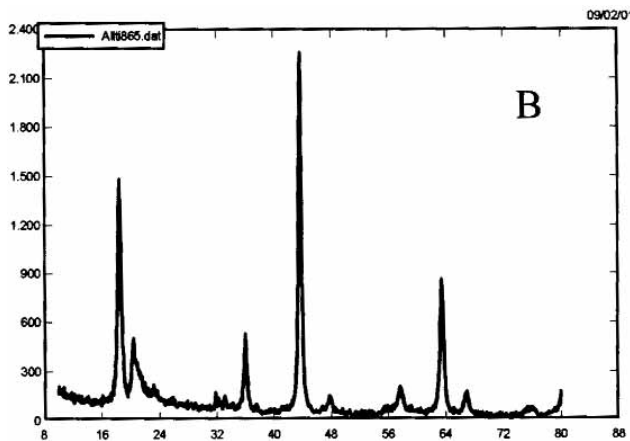


Fig. 4. XRD patterns of $\text{Li}_4\text{Ti}_2\text{O}_5(\text{OH})_6 \cdot x\text{H}_2\text{O}$ gels after drying at 110°C (A) and Li_2TiO_3 prepared from them by sintering for 2 h at 650°C (B).

Table 1. Solubility of water and hydrogen peroxide in EH.

Aqueous phase	Solubility* ml/1 EH at various temperatures	
	20°C	60°C
Hydrogen peroxide	21	50
Water	56	

* solubility tests were performed in a liquid separator, measuring the volume of non-soluble aqueous phase. Estimated error $\pm 3\%$.

Evidently the non-gelled part of the aqueous phase formed irregularly shaped particles, this part caused sticking of freshly formed microspheres to large aggregates. This suggests that the process of extraction of $(\text{H}_2\text{O}_2 + \text{H}_2\text{O})$ is less effective than that of water. Solubility tests of both substances are presented in Table 1 and confirms this suggestion.

Results shown in Table 1 suggested that for effective gelation of the titanium complex, a solution 2–3 times more concentrated should be used in comparison with the routine INCT process, i.e., 200–300 volumes of EH to 1 volume of the aqueous phase. Gel grains obtained under this condition are perfectly spherical (Fig. 2).

Washing of gels with acetone or carbon tetrachloride did not change the gel shape. Moreover, analytical data show

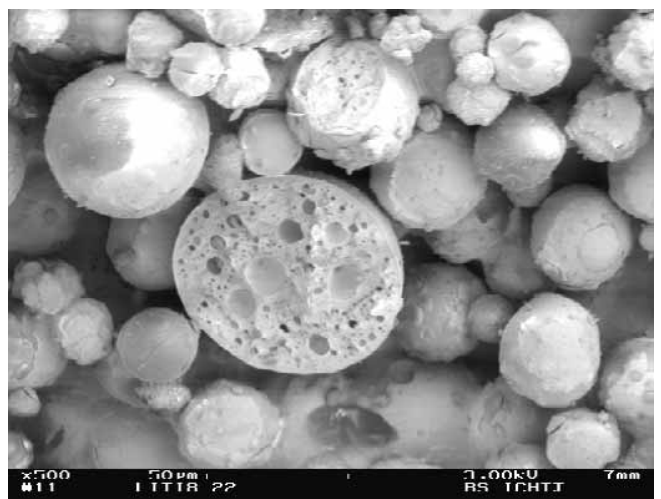
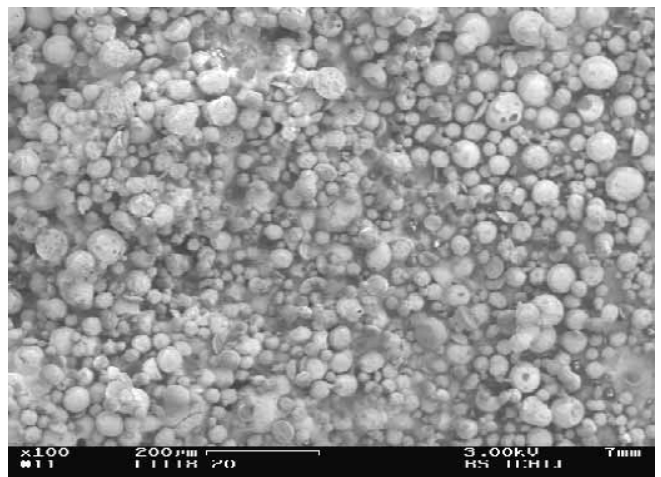


Fig. 5. SEM micrographs of the Li_2TiO_3 microspheres prepared from the $\text{Li}_4\text{Ti}_2\text{O}_5(\text{OH})_6 \cdot x\text{H}_2\text{O}$ at 650°C , 2 h.

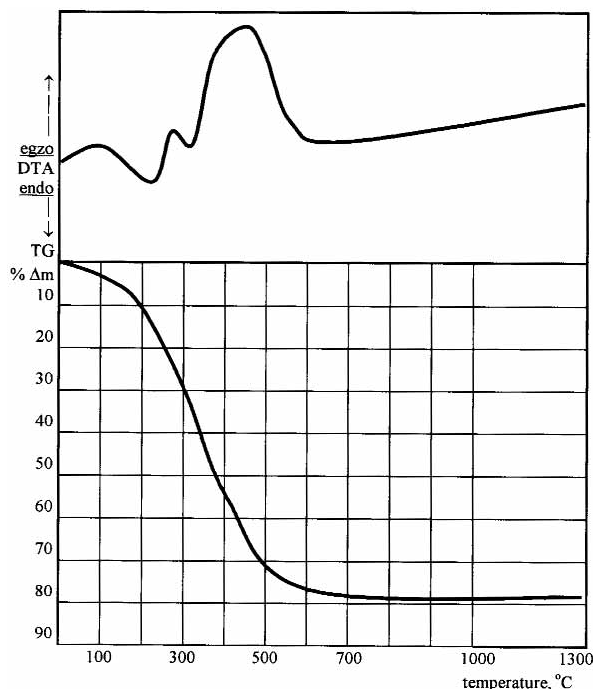


Fig. 6. Thermal analysis of citrate-peroxide Ti gel microspheres dried at 80°C for 2 h.

that the Li:Ti molar ratio remains practically unchanged (1.97–2.05) in contrast to the microspheres obtained by gelation of highly acidic ($\text{pH} < 0$) nitrate Li-Ti sols [6, 7] and decreasing Li:Ti ratios to 0.3. This is evidently connected with the high alkalinity ($\text{pH} \sim 9$) of the peroxide complex used. Thermal analysis of the gel (Fig. 3) shows that the decomposition is complete at 630°C. XRD patterns indicate that the initially amorphous gels (Fig. 4A) formed nearly perfect Li_2TiO_3 crystalline structures (Fig. 4B) with spherical shapes (Fig. 5) at 650°C.

The most serious disadvantages of this process are that during the concentration process a white suspension is formed and the final solution is very unstable (<1 h). Using data presented elsewhere [1, 2], we added citric acid (100 g/l). It was observed that higher concentrations (~ 200 g/l) and viscosities (> 100 cSt) of the solutions can be achieved, which gave improved results for the gelation step. The gelation step was not altered and the final gel microspheres were

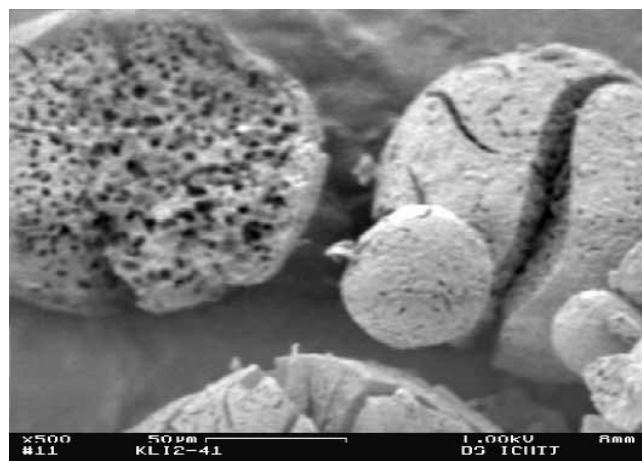
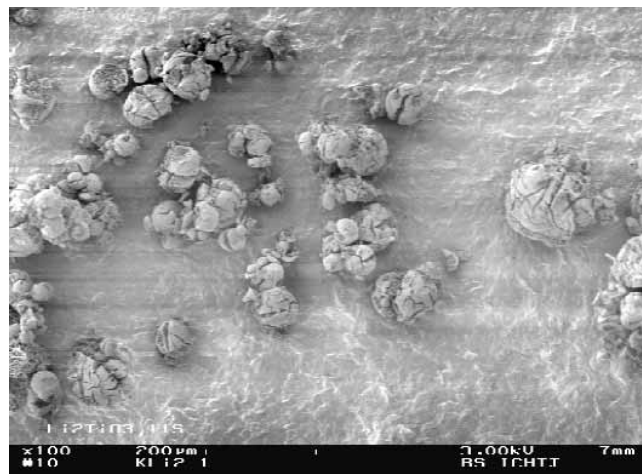


Fig. 7. SEM micrographs of the sample of citrate-peroxide Ti gel microspheres calcined at a heating rate of 10°C/min at 900°C, 1 h.

similar as in Fig. 1. Thermal decomposition of this citrate-peroxide Ti gel microspheres (Fig. 6) was more complex.

A strong exothermic effect (with onset at 550°C) indicated that thermal treatment should be carried out with special precautions. A sample calcined with a heating rate of 10°C/min was completely destroyed (Fig. 7). By decreasing the heating rate 10 times with the 2 h ramp at 450°C allowed us to obtain spherical particles as is shown in Fig. 8.

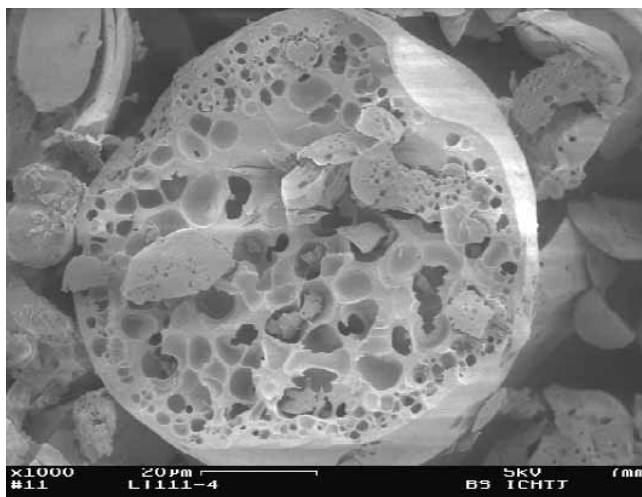
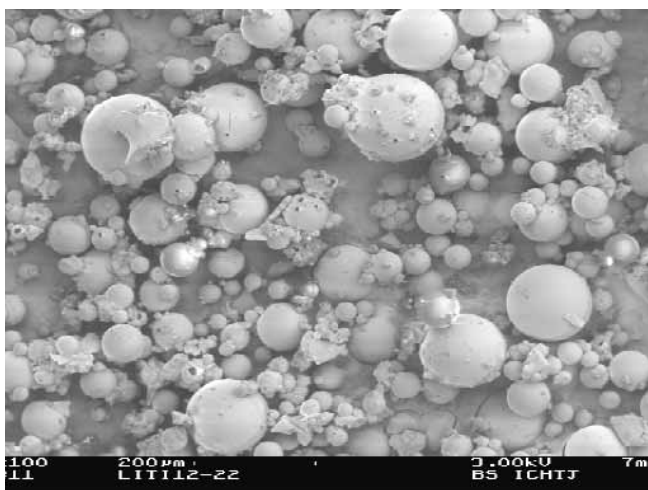


Fig. 8. SEM micrographs of the sample of citrate-peroxide Ti gel microspheres calcined at a heating rate of 0.1°C/min at 650°C, 2h.

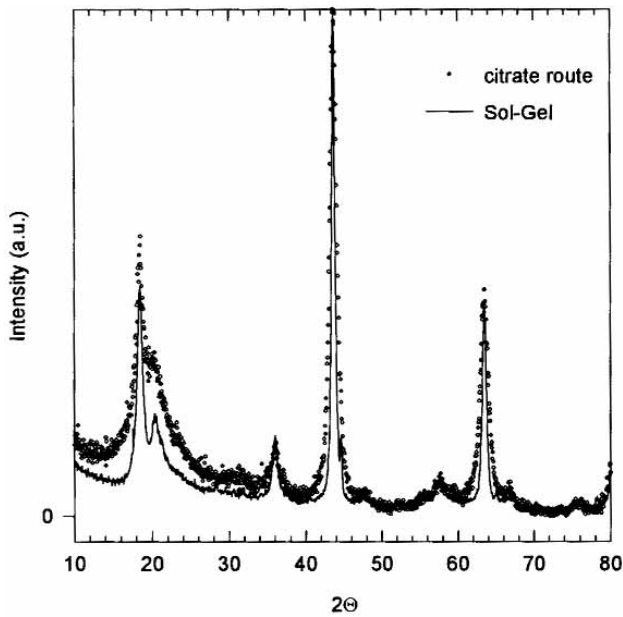


Fig. 9. XRD patterns of inorganic and citrate Li-Ti gels.

It can be seen that the microspheres formed under these conditions have small pores inside that are advantageous for tritium release. XRD patterns did not show any essential differences between inorganic and citrate gels (Fig. 9).

In order to evaluate tritium release properties, the specimens sintered at 1100°C were irradiated in a TRIGA reactor of the Casaccia Center. Then, the generated tritium implanted in the pebbles was removed by annealing them by an heating ramp (heating rate = 5K/min) from 200 up to 800°C, while helium containing H₂ (0.1%) gas purge was flowing at 200 cc/min. The tritium removal rate from the pebbles is reported in Fig. 10 as “normalized” to the maximum (peak) value. It seems that the sol-gel sample releases tritium earlier than the other. This samples can be connected with the morphology of specimens. Polished cross sections shown in Fig. 11 indicate a lower grain size and more interconnected pores in the sol-gel sample than in other reported samples prepared by agglomeration of powders.

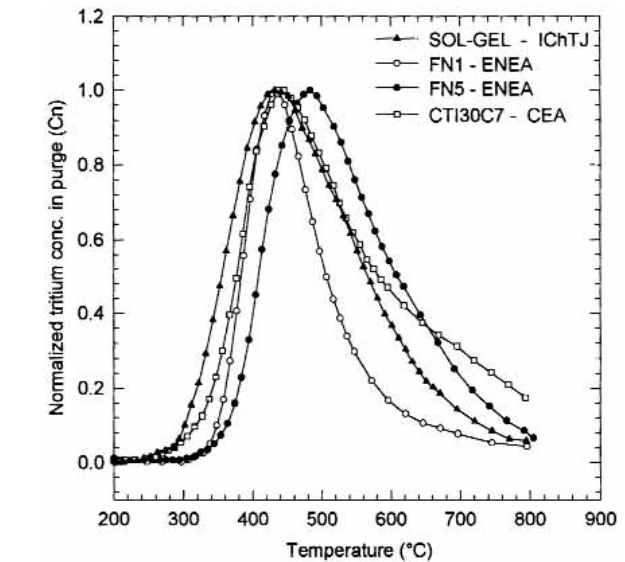
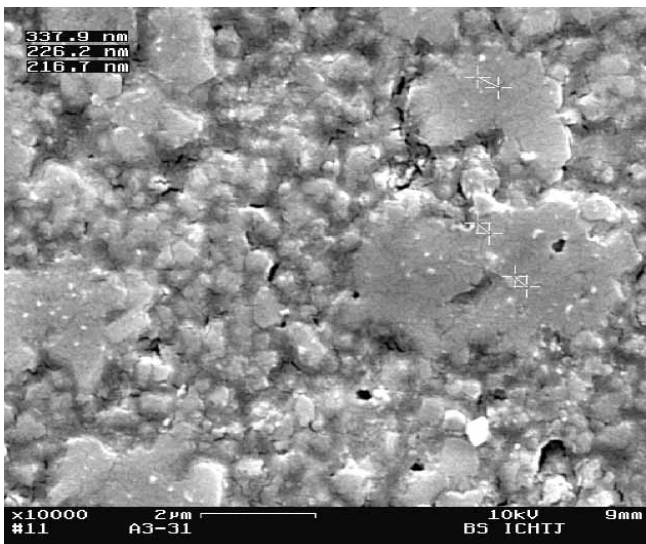


Fig. 10. Concentration of released tritium “normalized” to the peak values (Cn) vs. temperature for TPD runs in R-gas purge. Heating rate $\beta = 5^\circ\text{C}/\text{min}$.

Conclusions

1. The INCT variant of the sol-gel process by water extraction from drops of the emulsion of peroxy lithium titanate complex in ethylhexanol was successfully applied for the preparation of gel microspheres.
2. Increasing of EH volumetric ratio in the aqueous phase was necessary.
3. The final thermal treatment should be carried out with a definitely lower heating rate for citrate stabilized sols in comparison with used for the inorganic ones.
4. The feasibility of a sol-gel route to produce Li₂TiO₃ micro-spheres with a diameter ten times lower than the actual size of the “extruded-spheronized-sintered” pebbles, allowing in principle an increase in the smear density of the bed hence in the lithium density in the FR blanket, without any apparent modification in the tritium release properties of the pebble bed.
5. Tritium release process starts slightly earlier for the samples prepared by sol-gel which could be connected with the morphology of specimens.

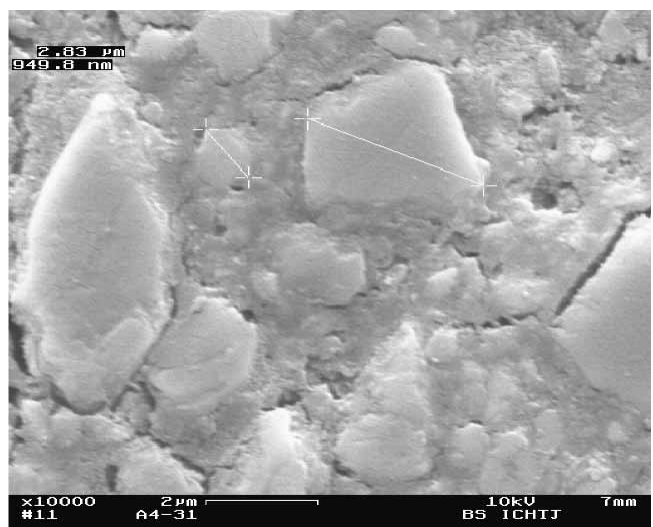


Fig. 11. SEM photomicrographs of polished cross section of inorganic sol-gel and ENEA samples Li₂TiO₃ (see Fig. 9) used for tritium release rate measurements from different Li₂TiO₃ samples.

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