

Densification of $\text{LiTi}_2(\text{PO}_4)_3$ -based solid electrolytes by spark-plasma-sintering

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Abstract

Spark-plasma-sintering (SPS) has been employed in an attempt to prepare dense $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) ceramics consisting of powders obtained hydrothermally. Pellet densities are relatively high, typically 81% of the theoretical X-ray density, compared with those (53%) of conventionally sintered ones. Conductivity of the SPS pellets was improved from ca. 10^{-8} to 10^{-6} S cm^{-1} at 50°C by SPS process, mainly due to the increase in the pellet density. Also the SPS technique was effective in producing a LTP/LiCoO₂ stacked pellet with clear interface, which may open the possibility of manufacturing all-solid-state lithium batteries. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium titanium phosphate; Spark-plasma-sintering; Ionic conductivity; Lithium cobalt oxide; All-solid-state lithium batteries

1. Introduction

Lithium titanium phosphate, $\text{LiTi}_2(\text{PO}_4)_3$ (LTP), is one of the promising Li^+ -conductive solid electrolytes and has been extensively studied because of its potential use in all-solid-state lithium batteries [1–11]. Although LTP shows relatively high chemical stability against ambient atmosphere, the ionic conductivity of polycrystalline pure LTP has been reported to be relatively low (10^{-7} S cm^{-1} at 25°C) for practical use [7,8]. Several researchers have reported the conductivity enhancement of LTP by partial replacement of the Ti^{4+} ion with trivalent ions (In^{3+} , Al^{3+} , Sc^{3+} , etc.) [1–8,10] or by the addition of lithium salts (Li_3PO_4 , LiNO_3 , etc.) [7,9,10]. Aono et al. [7–9] have concluded that the main reason for the conductivity enhancement in both cases seems to be attributable to the increase in the sintered pellet density. For further understanding of the enhancement mechanism, dense LTP pellets without impurity is required.

In addition to the preparation of highly conductive LTP pellets, forming a contact with cathode material, i.e., the preparation of a stacked pellet LTP/cathode is essential

for practical manufacturing of all-solid-state lithium ion batteries. Conventional sintering of attached pellet LTP/cathode in a muffle furnace does not seem to be effective because of plausible interfacial chemical reaction and/or difference of thermal expansion of both materials; rapid heating and quenching (i.e., short sintering period) may be suitable to avoid them.

Spark-plasma-sintering (SPS) is a process which makes use of microscopic electrical discharge between particles under pressure [12]. Although SPS is commonly used to produce dense metal and engineering ceramics, there are relatively few reports on the application of this technique to produce dense oxides materials for electrical ceramics. Also the SPS process is capable of making stacked pellets starting from different powders in much shorter sintering period, typically a few minutes [12], which would be applicable for making good contact of LTP with LiCoO_2 .

In the present work, we have employed SPS method to prepare dense LTP ceramics as an attempt to improve their conductivities without any additives. Hydrothermally-prepared LTP [10] has been used as a starting powder, which shows a single and narrow grain-size distribution (average grain size is ca. 2 μm). Also, we have attempted to prepare stacked pellet LTP/ LiCoO_2 by this technique and examined the interface for producing all-solid-state lithium batteries.

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2. Experimental

LTP was prepared by hydrothermal synthesis, as described before [10]. Aqueous solutions of stoichiometric $\text{LiOH} \cdot \text{H}_2\text{O}$, H_2TiO_3 and H_3PO_4 were mixed in a silver tube and allowed to stand in an autoclave filled with water at 380°C for 5 h. LiCoO_2 was also prepared by hydrothermal reaction [13]; CoOOH (obtained by bubbling the air through $\text{Co}(\text{OH})_2$) and $\text{LiOH} \cdot \text{H}_2\text{O}$ were mixed with distilled water in Teflon beaker and were treated hydrothermally in an autoclave at 220°C for 10 h. The resulting products were washed with distilled water, filtered and dried at 100°C . The powders obtained were subsequently sintered in the form of disks by SPS using SPS-515S (Sumitomo Coal Mining), as well as by conventional sintering in a muffle furnace for comparison.

Fig. 1 shows a schematic representation of the SPS system employed. LTP or LiCoO_2 powders were placed into a graphite die (1.5 cm in diameter) and an electric current of 800–1300 A was applied under a pressure of 39 MPa. During this procedure, the temperature, monitored at the surface of the graphite die by pyrometer, increased to 600, 800, 950, 1100, or 1200°C (depending on the applied current) at a rate of ca. $150^\circ\text{C min}^{-1}$. After it was kept at the desired temperature for 3–10 min, the electric current was stopped, pressure was released, and the sample was cooled to room temperature (it took about one min for cooling from 1200°C to 600°C). For making a stacked pellet LTP/ LiCoO_2 , both powders were placed in layered series into a graphite die and sintered by SPS at 600°C or 800°C for 3 min. Although the as-sintered pellets (1.5 cm in diameter and 0.2 cm in thickness) were black in appearance, the white appearance of the pellets was restored by polishing (for samples sintered less than 800°C) or by annealing in air at 800°C for 2 h (for samples sintered more than 950°C) (SPS-pellets). For the conventional sintering process, LTP was pressed into pellets under a pressure of 190 MPa and subsequently sintered in air at 1100°C for 3 h (CS-pellets).

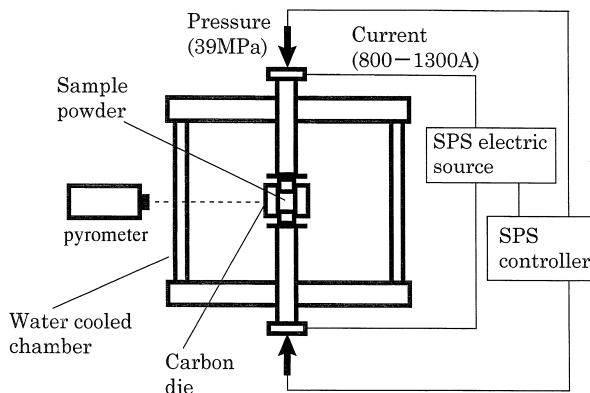


Fig. 1. Schematic representation of the SPS system (SPS-515S of Sumitomo Coal Mining) employed in this study.

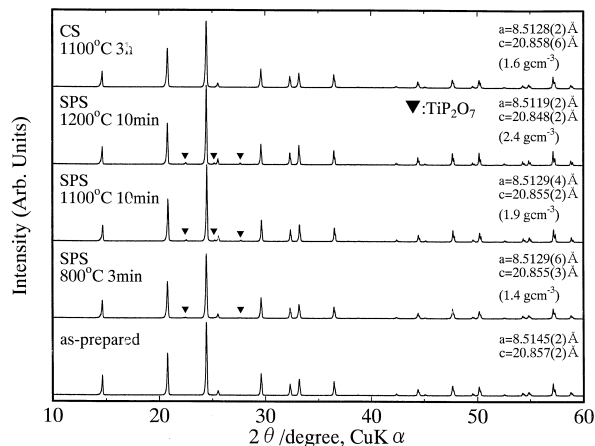


Fig. 2. X-ray diffraction patterns of the hydrothermally-prepared LTP and the SPS- and CS-pellets sintered at different temperatures.

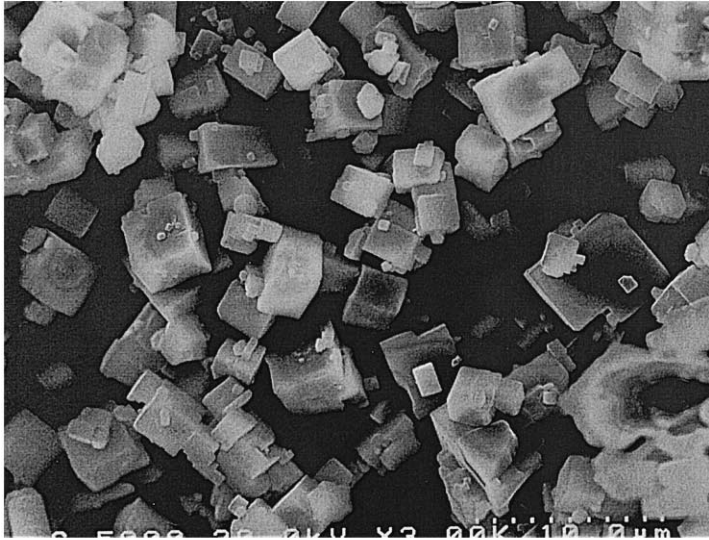
The pellets obtained were characterized by X-ray diffractometry (Rigaku RINT-1500 using $\text{CuK}\alpha$ radiation), field emission scanning electron microscopy (FE-SEM; Hitachi S-5000) with energy dispersion X-ray (EDX) microanalysis (Horiba EMAX-5770W), thermogravimetry/differential thermal analysis (TG/DTA; Rigaku TAS200), and infrared spectroscopy (IR; Horiba FT-200). AC impedance measurements for LTP pellets were carried out using Solartron 1260 instrumentation, covering the frequency range 10^{-1} to 10^6 Hz. Prior to electrical measurements, pellets were coated with Au paste electrodes (Engelhard A-3360) which were fired on at 700°C for 3 h. All samples were measured in a homemade cell over the temperature range 25 – 300°C after moisture inside the cell was purged by Ar flow at 300°C . Before recording data, the temperature was kept constant for 15 min to achieve thermal equilibrium. The AC conductance was determined by analyzing the complex impedance plots. No porosity correction on the electrical conductivity was made for any of the samples.

3. Results and discussion

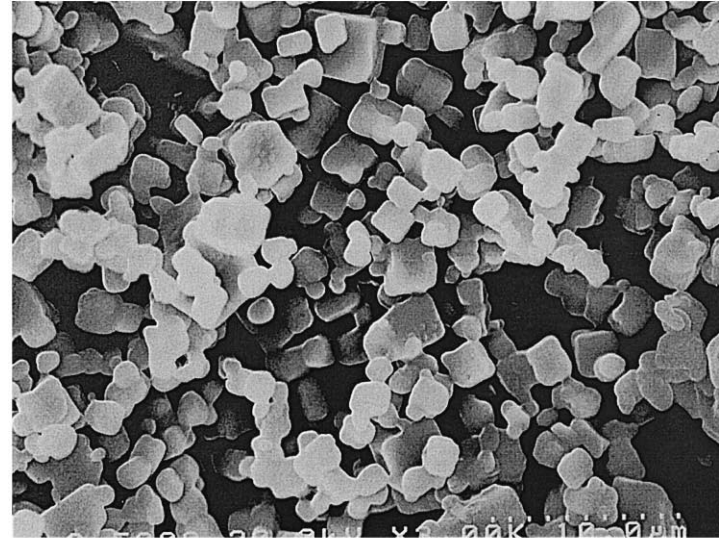
3.1. Preparation of LTP pellets

X-ray diffraction patterns of the starting LTP powder and the SPS-, CS-pellets sintered at different temperatures are shown in Fig. 2. All the profiles of the SPS pellets showed the presence of small amounts of TiP_2O_7 , whose peak intensities increase slightly with sintering temperature. Since CS pellets sintered at 1100°C showed no impurity phase, TiP_2O_7 would be formed by elimination of Li from LTP during the SPS process. Lattice parameters of LTP in the SPS pellets agree with those of the starting powder and with those reported previously [7]. Densities of the SPS pellets increased with sintering temperature up to 2.4 g cm^{-3} (81% of the theoretical X-ray density), larger than those of the CS pellets (1.6 g cm^{-3}).

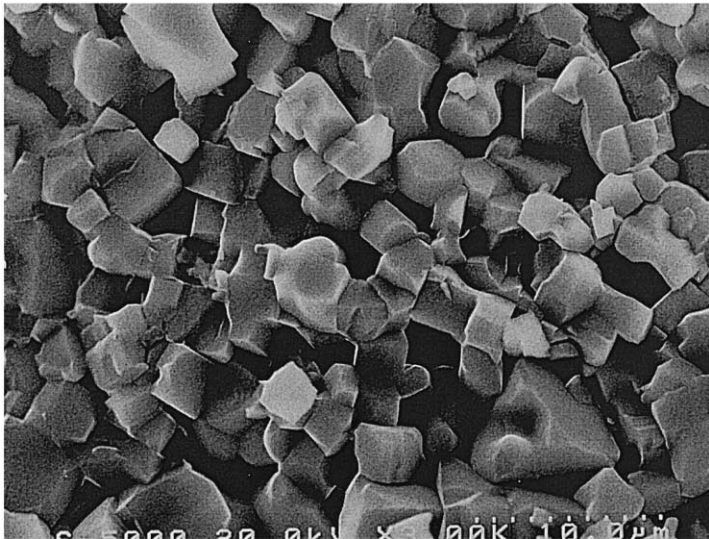
(a) as-prepared



(b) CS (1100°C 3h)



(c) SPS(1100°C 10min)



10μm

(d) SPS (1200°C 10min)

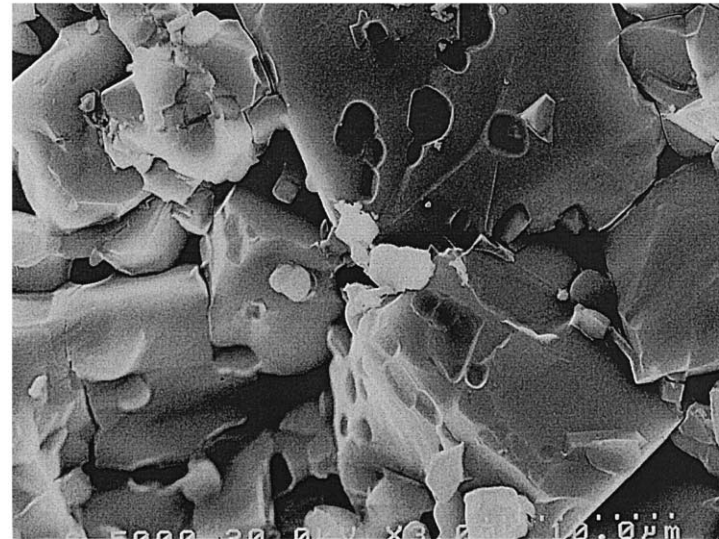


Fig. 3. SEM micrographs for (a) as-prepared LTP powder and fracture surfaces for (b) CS (sintered at 1100°C for 3 h), (c) SPS (1100°C 10 min), and (d) SPS (1200°C 10 min) LTP samples.

Results from the SEM micrographs of the fracture surfaces of the pellets, Fig. 3, showed that the CS pellet was rather porous with an average grain size of ca. 2 μm , similar to that of the starting powder. On the other hand, grains in the SPS pellets were in close contact with each other, and their sizes are relatively large (several to ten micrometers). These observations show that the SPS process is effective in improving the linkage between grains, leading to form dense pellets.

Electrical conductivity data are shown in the form of Arrhenius plots in Fig. 4. Conductivity of LTP is drastically improved by the SPS method; conductivity of CS pellets prepared from hydrothermally-prepared LTP was ca. 10^{-8} S cm^{-1} at 50°C , while that of the SPS (1200°C 10 min) pellets was about two orders of magnitude higher (ca. 10^{-6} S cm^{-1}). DC conductivity of SPS (1200°C 3 min) pellets was typically less than 10^{-9} S cm^{-1} at room temperature, which is less than ca. 0.1% of the AC conductivity value (6.9×10^{-7} S cm^{-1}), indicating that the contribution of electronic conduction in the SPS pellets was negligibly small. Also in IR spectrum, 3400 cm^{-1} band was not detectable clearly for the SPS pellets (1200°C 3 min), indicating negligible contribution of OH^- and/or H^+ conduction in the SPS pellets. The increase in conductivity is attributed due to pellet density and thermal treatment, Fig. 5. Thus, the SPS process is capable of preparing relatively high-conductive LTP pellets by densification.

For further investigation of the densification process, DTA measurements were performed on both the starting powder and the SPS pellets (1200°C 10 min). Endothermic and exothermic peaks at 803°C and 780°C were observed on heating and cooling, respectively, for the SPS pellets (both are lower than the melting point of LTP (1112°C [14])), whereas no peaks were detected for the starting powder. In TG measurements, the weight loss was less

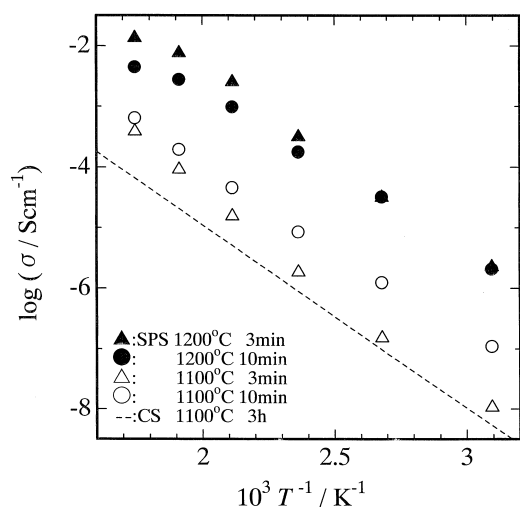


Fig. 4. Temperature dependence of conductivity for SPS- and CS-LTP pellets.

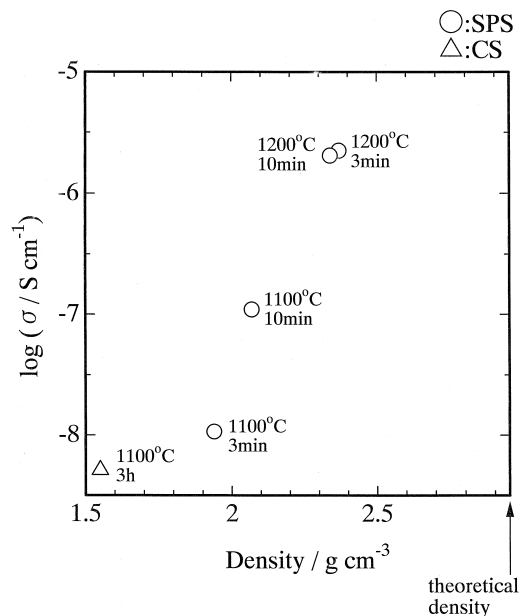


Fig. 5. Conductivity at 50°C as a function of pellet density for SPS- and CS-LTP pellets.

than 1% up to 1200°C for both samples. Therefore, it is reasonable to assign the endothermic peak (on heating) as partial melting and the exothermic peak (on cooling) as subsequent solidification for the SPS pellets. We have reported similar densification process for LTP + LiNO_3 composite electrolyte [11], in which $\text{Li}_4\text{P}_2\text{O}_7$, formed by a chemical reaction of LTP with LiNO_3 , acts effectively for the densification of LTP pellets. In the present SPS pellets, the presence of some phase, formed during the SPS process, would lead to partial melting/solidification of LTP around 800°C to form relatively dense pellets, resulting in the increase in ionic conductivity.

3.2. Preparation of stacked pellets LTP / LiCoO_2

Before trying to prepare stacked pellets LTP/ LiCoO_2 , we performed the SPS of LiCoO_2 to check the phase stability. The SPS pellets sintered at 1000°C showed the presence of CoO and Co_3O_4 , which would be formed by the decomposition and reduction of LiCoO_2 , Fig. 6. The density for SPS pellets sintered at 600°C and 800°C was typically 3.1 and 3.3 g cm^{-3} (61% and 65% of the theoretical X-ray density), respectively. Results from the lattice parameters of LiCoO_2 in the SPS pellets agree with those of the starting powder. A notable point is the development of c -axis orientation of LiCoO_2 by the SPS process at higher temperatures ($> 800^\circ\text{C}$) (see, e.g., (006) or (009) peaks), which is consistent with the SEM observations (development of hexagonal-platelet-like crystals; not shown). Then we performed the SPS of LTP/ LiCoO_2 at 600°C and 800°C .

The use of the SPS process was capable of enabling close contact of LTP with LiCoO_2 at 600 and 800°C ; the

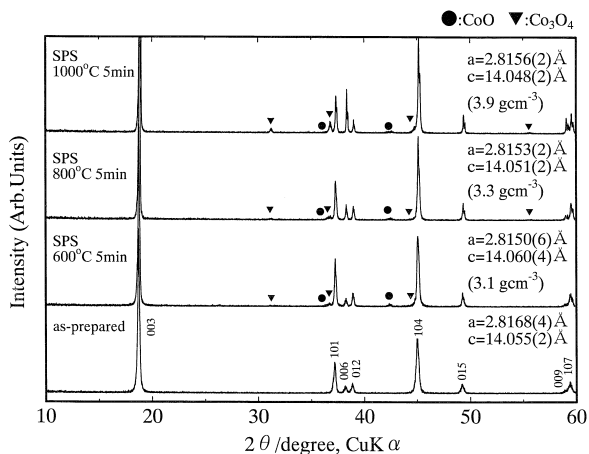


Fig. 6. X-ray diffraction patterns for hydrothermally-prepared LiCoO_2 and the SPS-pellets sintered at different temperatures.

interfaces of both pellets were clear in appearance. The stacked SPS (600°C) pellets were rather fragile during handling as compared with the 800°C -pellets. On the other hand, conventional sintering of a stacked powder LTP/ LiCoO_2 in a muffle furnace resulted in the breakdown of the pellets at the interface, probably due to the difference of thermal expansion of both materials. Fig. 7 shows typical SEM micrographs and elemental analysis by EDX at the line A–B for the fracture surface of SPS (800°C) pellets. LTP (left-hand side), LiCoO_2 (right-hand side), and the third phase (located in-between) were observed and their interfaces are rather clear. EDX results indicate that the third phase would be composed of at least Co, Ti, and O. For identifying the third phase, we performed the SPS at 800°C for 3 min for a mixed powder of equal weights of LTP and LiCoO_2 . The XRD profiles

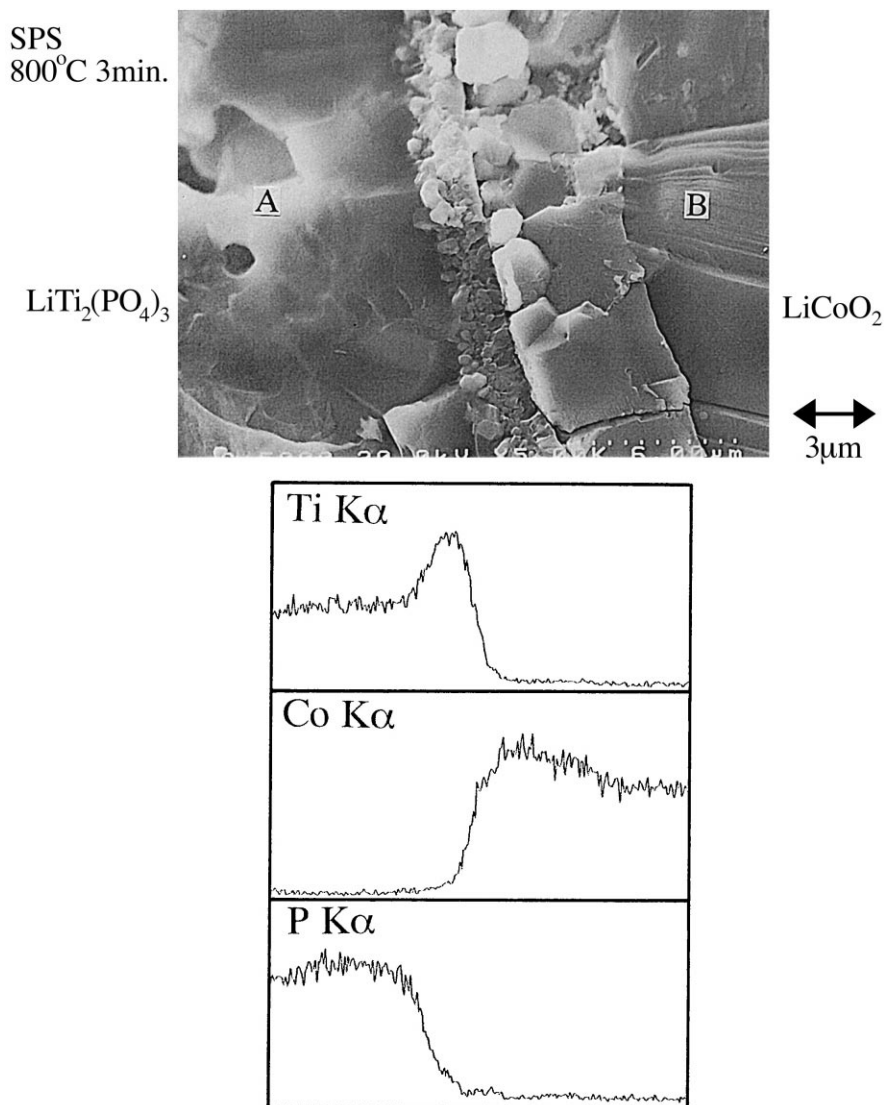


Fig. 7. SEM micrographs and EDX analysis for Ti, Co, and P contents in the line A–B for fracture surface of stacked pellet LTP/ LiCoO_2 prepared by SPS method (800°C , 3 min).

showed the presence of CoTiO_3 , Co_2TiO_4 , and LiCoPO_4 as well as other unidentified several peaks. The above EDX results suggest that the third phase is CoTiO_3 and/or Co_2TiO_4 . Although the SPS condition should be optimized further so as to form less amounts of impurity phases at the interface, the SPS method appears to be effective in enhancing contact of LTP with LiCoO_2 . Li metal is attached to the stacked pellets to form $\text{LiCoO}_2/\text{LTP}/\text{Li}$ and their charge/discharge measurements are now under study.

4. Conclusions

Relatively dense LTP pellets, typically 81% of the theoretical X-ray density, were prepared by the SPS method. The conductivity of the SPS pellets was typically $10^{-6} \text{ S cm}^{-1}$ at 50°C , two orders of magnitude higher than that of CS pellets (ca. $10^{-8} \text{ S cm}^{-1}$), mainly due to the densification by the SPS process. Stacked pellet LTP/ LiCoO_2 with clear interface was also prepared by the SPS process, which may open the possibility of manufacturing all-solid-state lithium batteries.

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