High-throughput Preparation and Characterization of Powder and Thin-film Library for Electrode Materials

Kenjiro Fujimoto, Kazuhiro Onoda and Shigeru Ito

Department of Pure and Applied Chemistry, Faculty of Science and Technology,
Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
fujimoto@rs.noda.tus.ac.jp

Abstract

Powder library of pseudo four components Li-Ni-Co-Ti compounds were prepared for exploring the composition region with the single phase of the layer-type structure by using combinatorial high-throuput preparation system "M-ist Combi" based on electrostatic spray deposition method. The new layer-type compounds were found wider composition region than the previous report. This process is promising way to find multi component functional materials.

Keywords : combinatorial chemistry, powder and thin-film preparation, electrostatic atomization, electrode materials

1. Introduction

Many researchers are exploring new cathode materials for replacing the high cost and toxic $LiCoO_2$ cathode material. Recently, the new-type electrode materials are exploring not only pseudo ternary compounds such as Li-Ni-Co oxides but also pseudo four component compounds which was added the other transition metals. However, most of previous paper was studing only preparation and characterization of a tie line in a pase diagram.

The exploration of new materials increasingly pursues multi-element structures. Therefore, investigation of the synthesis condition of the material under study increases considerably, and sample preparation by conventional methods is very time-consuming.

By using fully automated combinatorial high-throughput powder preparation robot system, we have hitherto found the single phase of pseudo-ternary Li-Cr-Ti ramsdellite-type compounds with wider composition region than the region of $Li_{2-x/3}Cr_xTi_{3-2x/3}O_7$ ($0 \leq x \leq 1.5$) by Kajiyama et al in a short time [1, 2]. This system has proven to be highly effective, but it must be applied separately when the shapes of the samples produced in a series of experiments take different forms, such as thin films and powders.

More recently, we have newly developed combinatorial robot system "M-ist Combi" based on electrostatic spray deposition method for overcoming this problem [3]. In electrostatic spray deposition method, materials to be deposited on a grounded substrate are atomized by applying a high voltage to the solution. The technique has recently been used to prepare thin films for lithium battery electrode materials [4] and solid oxide fuel cell (SOFC) materials [5]. Furthermore, control of the applied voltage may make it possible to prepare powders in addition to thin films, and the use of the system in various controlled atmospheres is also feasible.

In this paper, we prepared pseudo four components Li-Ni-Co-Ti library for finding the single phase of layer-type Li-Ni-Co-Ti compounds, which is promising as cathode materials with improved cycling performance andenhanced thermal stability [6, 7], by using the M-ist Combi system.

2. Experimental and Results

"M-ist Combi" consists of a high-voltage power suplly, a multiple-solution feed unit, a robot system for controlling the atomizing position, and a temperature control unit attached to the thermo-plate to dry the atomized solution. The composition of the mixed solution is controlled by the delivery speed of the multiple-solution feed unit. These solutions are mixed by the manifold, atomized from the tip of a stainless steel nozzle, exposed to high voltage, and dried onto the grounded and heated substrate holder. These modules are fully controlled by conventional PC hardware running a control program written in Visual Basic 6.0 (Microsoft Corp.).

Starting materials used were $LiNO_3$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and TiO_2 slurry. The concentaration of starting materials was adjusted by organic solvent. The atomizing distance from the tip of the stainless steel nozzle to the grounded substrate ($35 \times 35 \times 5$ mm^t each) was set at about 1 cm, and the applied voltage was set at 3500 V. The extrude speed from the syringe pump was adjusted at 5 ml/hour. Within only a few minutes, the atomization produced a small pile of powder within 3 mm in diameter. After preparation of one sample, the stainless steel nozzle changes the next position by triaxial robot system, and the new mixed solution was atomized onto the grounded and heated substrate holder. The powder library after heat-treating were identified by a combinatorial powder X-ray diffractometer designed for the rapid and high-throughput

characterization of products [2]. The diffractometer is equipped with a slidable X-Y stage and a position-sensitive proportional counter (PSPC). These components enable the device to obtain the diffraction pattern without a scanning detector, and within a brief period of only about 2 minutes per pattern. Once the reaction pallet is placed on the X-Y stage, the incident X-ray enters one of the samples, the data is collected, and the X-Y stage slides to measure the next sample.

Figure 1 shows the composition region of single phase with layer-type structure in the pseudo-four component Li-Ni-Co-Ti system reaction phase diagram of Li : (Ni, Co, Ti) = 70 : 30 and 60 : 40 heated at 973 K for 5hours. On the other hand, in the library of Li : (Ni, Co, Ti) = 50 : 50, the compounds of the single phase with layer-type structure was not detected. From the results of ICP emission spectroscopy measurement, it was found that the composition ratio of lithium reduced about 10 % after heated at 973 K for 5 hours. From these results, in this high-throughput preparation, it is necessary to study the condition of heat-treatment.

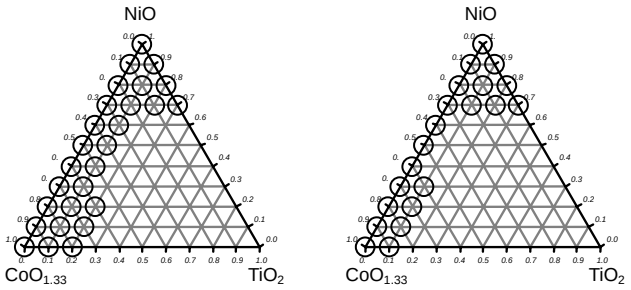

Fig. 1. Composition region of pseudo four components Li-Ni-Co-Ti single phase compounds with layer-type structure.

Liu [6] and Arai [7] et al., have hitherto reported the the single phase compounds with layer-type structure in the composition region of $LiNi_{0.8-y}Ti_yCo_{0.2}O_2$ ($0 \leq y \leq 0.1$). However, it was found that the single phase of layer-type structure in pseudo four component Li-Ni-Co-Ti compounds is obtained wider composition region.

In future, it is necessary to exploration for the composition region which can obtain single phase by using this M-ist Combi system in detail, and to evaluate electrode property. In order to evaluation of electrode property, the thin-film is needed with precise and without crack.

So, the M-ist Combi system is promising not only for the preparation of powder libraries, but also thin-film and liquid libraries. When applied for the preparation of a thin-film library, the system can obtain a homogeneous thin film covering an area of no more than about 10 cm^2 under the following atomization conditions: extrusion speed from the multiple solution feed unit, 0.5 - 2 $ml \cdot h^{-1}$; distance from the tip of the stainless steel nozzle to the grounded and heated substrate, 3 cm; applied voltage, 9000 V; substrate heating temperature, 300~400 ºC. After deposited on the substrate, the thin-film library can obtain by heat-treating at a high temperature.

Furthermore, Takada et al., have hitherto developed an electrode array in order to evaluate the combinatorial library that our combinatorial robot system outputs [8]. It enables us to evaluate 16 samples on the library within 3 hours. This combination of the M-ist Combi system and the electrode array is efficient for the exploration of electrode materials.

3. Summary

We prepared powder library and established reaction phas e diagrams of pseudo four components Li-Ni-Co-Ti compou nds by using combinatorial material exploration method. We found that the single phase of layer-type structure is obtain ed wider composition region than the already reported comp osition region of $LiNi_{0.8-y}Ti_yCo_{0.2}O_2$ ($0 \leq y \leq 0.1$).

4. References

1. A. Kajiyama, K. Takada, K. Arihara, T. Inada, T. Sasaki, S. Kondo and M. Watanabe, J. Electrochem. Soc. Vol.150(2), p.A157 (2003).
2. K. Fujimoto and M. Watanabe, Meas. Sci. Technol. Vol.16, p.41 (2005).
3. K. Fujimoto, H. Takahashi, S. Ito, S. Inoue and M.Watanabe, Appl. Surf. Sci. Vol.252, p.2446 (2006).
4. Y. Kobayashi, H. Miyashiro, T. Takeuchi, H. Shigemura, N. Balakrishnan, M. Tabuchi, H. Kageyama and T. Iwahori, Solid State Ionics Vol.152-153, p.137 (2002).
5. I. Taniguchi, R. C. van Landschoot and J. Schoonman, Solid State Ionics Vol.160, p.271 (2003).
6. H. Liu, J. Li, Z. Zhang, Z. Gong and Y. Yang, Electrochimica Acta Vol.49, p.1151 (2004).
7. H. Arai, M. Tsuda and Y. Sakurai, J. Power Sources Vol.90, p.76 (2000).
8. K. Takada, K. Fujimoto, T. sasaki and M. Watanabe, Appl. Surf. Sci. Vol.223, p.210 (2004).