



# Electrochemical properties of all-solid-state batteries with ZrO<sub>2</sub>-coated LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> as cathode materials

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## ABSTRACT

All-solid-state lithium batteries were fabricated by use of LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> powders coated with ZrO<sub>2</sub> as positive electrode materials and amorphous Li<sub>3</sub>PS<sub>4</sub> as solid electrolytes. The ZrO<sub>2</sub>-coated powders were prepared by a sol-gel method associated with ultrasonic irradiation. The charge–discharge cycle performance of the all-solid-state cells was improved by use of the ZrO<sub>2</sub>-coated LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> powders. The ZrO<sub>2</sub> coating was effective in suppressing an increasing of the interfacial resistance between the LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> electrode material and the sulfide based solid electrolyte, a-Li<sub>3</sub>PS<sub>4</sub>, during charge–discharge cycling. The battery with the ZrO<sub>2</sub>-coated LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> showed an initial discharge capacity of 115 mAh g<sup>-1</sup> and good capacity retention even after 50 cycles at a current density of 0.1 mA cm<sup>-2</sup> at room temperature.

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## 1. Introduction

All-solid-state lithium batteries using lithium-ion conducting solid electrolytes have been attracted much attention as highly safe batteries against conventional lithium ion batteries using organic solvents as electrolyte solution. The advantage of all-solid-state batteries is ascribed to nonflammable properties of the inorganic solid electrolytes [1–4]. Although all-solid-state batteries have superior potential on the safety problems, there are some issues to be resolved for practical application. For instance, the operation under a high current density of more than several mA cm<sup>-2</sup> is difficult and cycle performance of the batteries is gradually decreased with an increase in charge–discharge cycle numbers, when the all-solid-state batteries are made by use of transition metal oxides such as LiCoO<sub>2</sub> which are widely used as positive electrode materials in the conventional lithium ion batteries with electrolyte solutions.

In the all-solid-state batteries, electrochemical reactions occur through the solid–solid interface between the electrode and solid electrolyte materials, and the interface governs the electrochemical properties. In order to improve the electrochemical properties, some studies have been conducted to form an effective electrode–electrolyte interface. Takada et al. have reported that interposed thin buffer layers such as LiNbO<sub>3</sub> [5,6], Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> [7] between LiCoO<sub>2</sub> cathode materials and the sulfide-based solid electrolytes are effective on the improvement of the electrochemical properties of LiCoO<sub>2</sub> in all-solid-state batteries. Sakuda et al. [8,9] have found that SiO<sub>2</sub>

coating on the LiCoO<sub>2</sub> positive electrode materials works as a buffer to suppress the formation of high-resistance layers between the positive electrode materials and solid electrolytes. To our knowledge, however, those previous reports have been concentrated on the LiCoO<sub>2</sub> cathode materials, and there are only a few reports on buffer-layer-coating effects on other cathode materials such as LiMn<sub>2</sub>O<sub>4</sub>, LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, etc. [10,11].

On the other hand, in the field of practical lithium ion battery with conventional electrolyte solutions, extensive studies have been carried out to improve the performance of the cathode active materials. Recently, manganese based layered compounds as positive electrode materials for lithium ion batteries are of great interest and are potential candidates to replace the commercial LiCoO<sub>2</sub>. Those include LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> [12], LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> [13–15], and its derivations such as LiNi<sub>x</sub>Mn<sub>x</sub>Co<sub>1–2x</sub>O<sub>2</sub> (0 < x < 1/3) [16,17]. Among them, LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> has been studied extensively as promising positive electrode materials, because it exhibits much higher electrochemical capacity more than 200 mAh g<sup>-1</sup> with enhanced safety. An alternate approach to improve electrochemical performance of the conventional lithium ion batteries is the surface modification of the positive electrode materials by coating their particles with some metal oxides [18–20]. Cho et al. [18] found that the thin-film coating ZrO<sub>2</sub> on the particle surface of LiCoO<sub>2</sub> had high fracture toughness which enabled to maintain structural stability of LiCoO<sub>2</sub> by suppressing its non-uniform lattice-constant changes during Li de-intercalation, thereby preventing capacity fading during electrochemical cycling for the cells with conventional electrolyte solution.

We have considered that ZrO<sub>2</sub> thin layer would work as a buffer layer between positive electrode materials and sulfide based solid electrolytes such as amorphous Li<sub>3</sub>PS<sub>4</sub> in all-solid-state batteries. In

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this study, we have formed different amounts of  $ZrO_2$  coating on  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  particles by use of sol–gel methods associated with sonication, and investigated the effects of  $ZrO_2$  coating on electrochemical performance of the  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  cathode material in all-solid-state batteries with amorphous  $Li_3PS_4$  solid electrolyte.

## 2. Experimental

The  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powder provided by Nippon Chemical Industrial Co., Ltd. was used as a starting material and a reference sample. Coating layers of  $ZrO_2$  on the  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powders were formed by use of a sol–gel method associated with ultrasonic irradiation. The  $ZrO_2$  coating sol was prepared from iso-propanol (99.5%, Wako), zirconium(IV) tetra propoxide ( $Zr(OC_3H_7)_4$ , Tokyo Kasei), ethyl acetoacetate (98%, Wako), and  $H_2O$  in a molar ratio 170:1:1.5:6. The  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powders were added into the coating sol and ultrasonically agitated at 40 °C for 30 min. The amounts of  $ZrO_2$  coating sol were calculated in order that the final product contains 0, 0.35, 0.7, 1.4, 3.5 mol%  $ZrO_2$ . The mixture was concentrated under reduced pressure, and the residual was obtained as a precursor. The precursor was heated at 750 °C for 2 h under  $O_2$  gas flow to decompose the organic components. The obtained samples were characterized by X-ray diffraction (XRD) with  $Cu-K\alpha$  radiation (RINT-2000, Rigaku). The morphologies of samples were examined by using a scanning electron microscope (JSM-6340F, JEOL).

An amorphous sulfide electrolyte,  $a-Li_3PS_4$ , was synthesized by a mechanical milling (MM) method [21,22] and was used for the electrochemical measurements. To investigate the electrochemical properties of the  $ZrO_2$ -coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ , we fabricated laboratory-scale solid-state cells with the  $a-Li_3PS_4$  as the solid electrolyte and  $Li_{4.4}Si$  alloy as the negative electrode. The  $Li_{4.4}Si$  alloy is a meta-stable phase which is prepared by the mechanical milling process and shows good charge–discharge reversibility [23–26]. The meta-stable alloy has a wide solid-solution range of  $Li_{3.8}Si$  to  $Li_{5.2}Si$ . Thus the meta-stable  $Li_{4.4}Si$  alloy is available for the negative electrode materials for the both types of all-solid-state batteries of which the charge–discharge cycles are started with the charge process (lithium insertion into the alloy) and/or with the discharge process (lithium extraction from the alloy). The  $Li_{4.4}Si$  is a convenient material for the electrochemical measurements. The positive electrode of the cells was a mixture of the obtained  $ZrO_2$ -coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  (59 mass%), the amorphous  $Li_3PS_4$  solid electrolyte (39 mass%), and acetylene black (2 mass%). The cell was prepared by successively pressing the positive electrode mixture, solid electrolyte powder, and the  $Li_{4.4}Si$  alloy powder at 380 MPa into a pellet of 10 mm in diameter. The loadings of the  $ZrO_2$ -coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  sample and  $Li_{4.4}Si$  alloy in the cell were 8.35 and 12.7  $mg\ cm^{-2}$ , respectively. Galvanostatic charge–discharge experiments for the cells were performed under a constant current density of 0.1  $mA\ cm^{-2}$  between 4.3 and 2.5 V at room temperature by use of a battery tester (HJR-110mSM6, Hokuto).

Electrochemical impedance spectroscopy measurements of the cells,  $Li_{4.4}Si | amorphous\ Li_3PS_4 | LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ , were performed by use of an impedance analyzer (1255B, Solatron Analytical) coupled with an potentiogalvanostate (1287, Solatron Analytical) after charging them to 4.3 V at 0.1  $mA\ cm^{-2}$ . The applied voltage was 50 mV and the applied frequency range was in the range of 10 MHz to 1 MHz.

## 3. Results and discussion

### 3.1. Structure and surface morphology of the $ZrO_2$ -coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ powder

The XRD patterns of the  $ZrO_2$ -coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powders are presented in Fig. 1. In the figure, the XRD pattern of the bare

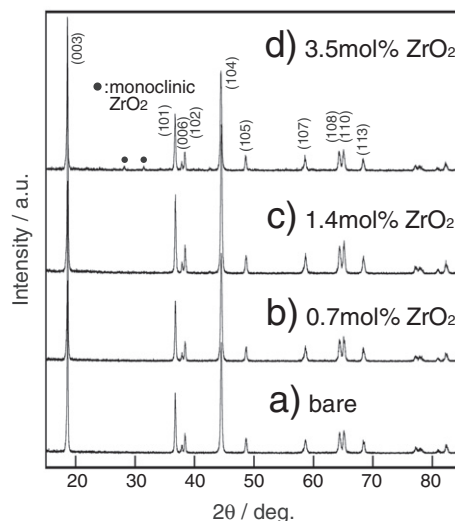


Fig. 1. XRD patterns of the original (bare) and the  $ZrO_2$ -coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powders: (a) the bare sample, (b) 0.7 mol%, (c) 1.4 mol%, and (d) 3.5 mol%  $ZrO_2$  coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  samples.

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powder is also shown for comparison. The main peaks can be indexed as a layered structure based on a hexagonal  $\alpha-NaFeO_2$  structure (space group R3m). There is no diffraction peaks of crystalline  $ZrO_2$  in the XRD of the  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powders coated with 0.7 and 1.4 mol%  $ZrO_2$ . On the other hand, the sample coated with 3.5 mol%  $ZrO_2$  shows two small peaks at around  $2\theta = 30^\circ$ . The two small peaks which are denoted by closed circles can be attributed to monoclinic  $ZrO_2$  phase. The samples coated with  $ZrO_2$  of not more than 1.4 mol% did not show any diffraction peaks attributed to  $ZrO_2$  in their XRD measurements. We supposed that the  $ZrO_2$  contents were too small to detect the diffraction line in the measurements.

FE-SEM observations and EDX measurements were carried out in order to observe morphology of the bare and the  $ZrO_2$ -coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powders. Fig. 2 shows FE-SEM images of the  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  particles coated with 0.7 and 3.5 mol%  $ZrO_2$ . The image of the bare  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powder is also shown in the figure for comparison. For the bare sample, as can be seen in Fig. 2(a), the primary particle size is about 0.5–2.0  $\mu m$  in diameter and these small particles aggregated each other to form spherical secondary particles about 5–7  $\mu m$  in diameter. In the 0.7 mol%  $ZrO_2$ -coated sample, there are no significant differences in the surface morphology and in the primary particle size. The size of secondary particles of the 0.7 mol%  $ZrO_2$ -coated sample, however, is somewhat larger than that of the bare sample. In the 3.5 mol%  $ZrO_2$ -coated sample, the spherical secondary particles further aggregated each other to form larger particles about 10–30  $\mu m$  in diameter. Furthermore, small white particles which are denoted by dotted circles in Fig. 2(c) are newly appeared. The newly appeared particles can be attributed to crystalline  $ZrO_2$ .

The EDX mappings of the 0.7 mol%  $ZrO_2$ -coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  are depicted in Fig. 3. Both Zr atoms of  $ZrO_2$  and Mn atoms of  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  are detected in the same area. This result indicates that the  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  particles are uniformly covered with  $ZrO_2$  coating. The thickness of the  $ZrO_2$  coating for the 0.7 mol%  $ZrO_2$ -coated  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  can be estimated to be about 10 nm from the specific surface area of the  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  powders and the chemical amounts of  $ZrO_2$ .

We also carried out EDX measurements in a low magnification mode ( $\times 250$ ) to estimate the average chemical contents of Ni, Co, Mn and Zr elements of the obtained samples. The results suggest that the chemical contents of the samples roughly agree with the nominal fractions of  $ZrO_2$  which is calculated from dose of Zr-

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