



# Preparation of Water-Resistant Surface Coated High-Voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode and Its Cathode Performance to Apply a Water-Based Hybrid Polymer Binder to Li-Ion Batteries

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## ABSTRACT

Water-resistant  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$  spinel cathode was prepared by surface coating with carbon,  $\text{Al}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  to use a water-based hybrid polymer (TRD202A, JSR, Japan) as a binder and to form the cathode film on an Al current collector. The surface composition and degree of the surface coverage of carbon,  $\text{Al}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  were characterized with field-emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$  particles not only exhibited water-resistant property but also showed no decrease in discharge capacity and only a small degradation of discharge rate performance. In addition, the coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$  particles, that were exposed to water-based binder solution for one week, exhibited the same charge/discharge cycle performance as observed for the cathode of the pristine  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particles, suggesting that the coated particles are promising as cathode materials with a water-resistant property and therefore water can be used as solvent for preparing the cathode slurry solution in the place of *e.g.*, carcinogenic N-methyl-2-pyrrolidone which is used actually.

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## 1. Introduction

Recently, water-soluble and aqueous polymers (water-based polymers) have attracted much attention as binders for lithium ion batteries (LIBs) because of the need for low-cost materials and environmentally compatible electrode fabrication processes [1–13]. N-methyl-2-pyrrolidone (NMP), which is listed as a carcinogenic chemical with reproductive toxicity [1,14,15], is often used as a solvent to prepare a binder slurry. The slurry is composed of cathode material particle, conducting carbon additive, conventional polyvinylidene difluoride (PVdF) binder and NMP solvent, and is casted on an aluminum current collector and finally is dried to evaporate the NMP. The NMP solvent should be recycled without releasing it to the atmospheric environment. A reduction in costs of

the LIBs is severely constrained because of facility investments for the process used currently. Therefore, shift of a nonaqueous solution-based fabrication process of LIBs to an aqueous solution-based one is widely investigated. For graphite anodes, styrene-butadiene rubber has already been employed as a water-based polymer binder in fabricating some commercially available Li-ion batteries [16,17]. Applying water-based polymer binders to the cathode is a next target to develop the low-cost and environmentally friendly fabrication process for LIBs. Some companies have produced prototype models using water-based polymer binders, and their battery test results have been reported to be comparable with those obtained with the conventional PVdF polymer binders [18,19]. We also have applied a water-based hybrid polymer binder composed of acrylic polymer and fluoropolymer, TRD202A (JSR, Japan) to high-voltage Li-rich solid-solution cathode, in which the water-based polymer binder slurry was used immediately after its preparation to prepare the cathode films [20]. Uniform cathode films were prepared with a Li-rich solid-solution ( $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ ) cathode material and water-based hybrid

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polymer binder (TDR202A), carboxymethyl cellulose (CMC), and conducting carbon additive. The films exhibited stable charge/discharge cycle performances (average discharge capacity:  $260 \text{ mAh g}^{-1}$ ) when cycled between 4.8 and 2.0 V for 80 cycles. The cathode film prepared with the water-based hybrid polymer binder showed longer-term reliability as well as higher electrochemical resistance when compared with that prepared using the conventional PVdF binder. Through our researches so far carried out concerning cathode/water-based hybrid polymer binders, we have understood that the water-based polymers binders cannot be applied to some cathode materials because of solubility of the cathode material surfaces in water (not shown in this paper). Many papers on the cathode materials/water-based polymers binders have been published [18–20], but in these cases, the water-based polymer binder slurries were used immediately after their preparation. In a practical production level, however, the cathode materials are put in water-based binder slurry solution at least for one week and therefore they are required to keep a “water-resistant” property for one week (“water-resistant” means slowing the penetration of water (but is not water-proof)).

In this study, we tried to modify the cathode surfaces with carbon material and water-stable metal oxides to isolate them from the aqueous solutions of the water-based slurry and to obtain stable charge/discharge cycle and rate performance even after the prepared cathode materials are exposed to the aqueous solutions of the cathode slurry for one week. The surface coating of the cathode material surfaces with carbon [21,22] and metal oxides [23,24] has been reported and the improvement of the charge/discharge cycle durability [24–26] and the rate performance [27,28] have been achieved with the aid of the surface coatings. The surface coating should not prevent the intercalation/deintercalation of  $\text{Li}^+$  ions to/from the cathode material layers although it is required to isolate the cathode material surface from the water-based polymer binder slurry during the cathode fabrication process. The surface coatings with a unique property, *i.e.*, they do pass  $\text{Li}^+$  ion, but not  $\text{H}_2\text{O}$  molecule, were investigated using carbon, aluminum oxide and niobium oxide. A  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$  spinel cathode material was selected for the present surface coating. The  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has attracted a lot of attention from many research groups in the field of energy storage, owing to its high specific energy of  $658 \text{ Wh kg}^{-1}$  [29–31], which is much higher than commercially available cathode materials such as  $\text{LiCoO}_2$  ( $518 \text{ Wh kg}^{-1}$ ),  $\text{LiMn}_2\text{O}_4$  ( $400 \text{ Wh kg}^{-1}$ ),  $\text{LiFePO}_4$  ( $495 \text{ Wh kg}^{-1}$ ), and  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  ( $576 \text{ Wh kg}^{-1}$ ). In addition, the upper potential applicable for the charge/discharge reaction of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is around 4.7 V (*vs.*  $\text{Li}/\text{Li}^+$ ) and thus it is suitable to test the electrochemical oxidation resistance of the water-based polymer binders which are required to possess a high resistance to electrochemical oxidation. Furthermore, metal oxide cathodes containing a high percentage of  $\text{Ni}^{2+}$  ions such as  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  tend to suffer from chemical damage which is caused by the contact with water, *i.e.*,  $\text{Ni}^{3+}$  ion on the cathode material surface is reduced with  $\text{H}_2\text{O}$  to form  $\text{Ni}^{2+}$  ion. As a result of this reduction, lithium carbonate and lithium hydroxide are formed on the cathode material surface and dissolved into aqueous solutions. This leads to the corrosion of aluminum current collectors, especially in the case of water-based binders. Pieczonka et al. [32] reported self-Mn and Ni dissolution behaviors. The self-discharge reaction of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  causes a decomposition of electrolyte, and the resulting HF can accelerate Mn and Ni dissolution from  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , and consequently various reaction products, such as  $\text{LiF}$ ,  $\text{MnF}_2$ ,  $\text{NiF}_2$ , and polymerized organic species, are found on the surface of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrode. So, the cathode surface coating is important for inhibiting the degradation of cathode performance.

Therefore, the present study on the coating process to inhibit the chemical dissolution of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  containing a high percentage of Ni and Mn ions is considered to be suitable for realizing the degree of target achievement about the water-resistant property of cathode materials which could use a so-called water-based slurry binder solution in the practical fabrication process of LIBs.

## 2. Experimental

### 2.1. Preparation of carbon and metal oxide-coated cathode materials

A  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle sample was purchased from Hohsen Corp. (Japan). The particle was used as a cathode material without any purification. Surface coatings with carbon,  $\text{AlO}_x$  and  $\text{NbO}_x$  were conducted as mentioned below.

**Carbon coating:** Sucrose (Wako Pure Chemicals Co. Ltd. (Wako), Japan) as a source of carbon layer for coating was weighted with a proper amount to prepare 0.5, 1 and 10 wt% carbon-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle samples (0.5 wt% carbon-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  means that the sample was composed of 0.5 wt% of carbon and 99.5 wt% of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ). The sucrose and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle weighted were mixed at first using agate mortar. Afterward, the mixed powder was further mixed using a wet planetary ball-milling machine with a Teflon jar (672 mL) containing Teflon balls (diameter 1.5 cm, 88 balls) and acetone (80 mL) at ambient temperature at a speed of 300 rpm for 1 h. After ball-milling, the mixture was dried up at  $120^\circ\text{C}$  for 3 h. The dried mixture was then sintered at  $600^\circ\text{C}$  for 3 h under argon atmosphere to form the carbon coating on the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle surface.

**$\text{AlO}_x$  coating:** 0.03 g of aluminum nitrate ( $\text{Al}(\text{NO}_3)_3$ , 98%, Wako) was dissolved in 20 mL of water. The precursor of  $\text{AlO}_x$  was precipitated by controlling the solution pH with ammonium aqueous solution. In this case, the solution pH was monitored with pH meter throughout the precipitation process. The precipitate was filtrated and dried. Afterward, the dried precursor of  $\text{AlO}_x$  was weighted to fix the coating weight percentage of  $\text{AlO}_x$  and was mixed with weighted  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle. After ball-milling at the same condition as the case of the carbon coating, the mixture was dried at  $120^\circ\text{C}$  for 3 h. The dried mixture was then annealed at  $450^\circ\text{C}$  for 6 h under air-atmosphere to form  $\text{AlO}_x$  coating on the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle surface. 0.5, 1 and 2 wt%  $\text{AlO}_x$ -coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  samples were prepared by controlling the mixing ratio of  $\text{AlO}_x$  precursor and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle before annealing.

**$\text{NbO}_x$  coating:** 0.15 g of niobium (V) chloride ( $\text{NbCl}_5$ , Sigma-Aldrich, 99.9%) was dissolved in 20 ml of water. After that, in a similar manner as the formation of  $\text{AlO}_x$  coating on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle surface, 0.5, 1 and 2 wt%  $\text{NbO}_x$ -coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  samples were prepared.

The weight percentage of carbon on the carbon-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle was estimated with thermogravimetry (Thermo plus EVO TG8120, Rigaku) by calculating the difference of weight before and after annealing of the carbon-coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  sample under air-atmosphere. The weight percentages of  $\text{AlO}_x$  and  $\text{NbO}_x$  in the coated  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle samples were determined by ICP-MS using an Agilent, 7700x spectrometer after chemically dissolved in concentrated acids and diluted with water and by evaluating the concentrations of Al and Nb ions.

### 2.2. Characterization of synthesized cathode materials

The average sizes and shapes of the cathode particles were evaluated with a field-emission scanning electron microscope (FE-

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