

Physical and Electrochemical Characterization of Layered Oxide Materials for High Power Application

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Introduction

Stabilized lithium nickel oxide (LiNiO_2) is receiving increased attention as a low-cost alternative to the LiCoO_2 cathode now used in rechargeable lithium batteries, especially for high-power applications. Recently, ANL (Argonne National Laboratory) has developed a new material, $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$, which employs titanium ion substitution at Ni sites of LiNiO_2 . In layered $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$, the titanium ions are tetravalent, which allows the accommodation of unstable ions (mostly divalent nickel) in the nickel layer, so that the existence of such as Ni^{2+} ions impurity in the lithium layer can be minimized.

Highly ordered, and pure-layered phase $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$ samples were prepared by solid-state reaction at 750°C under an oxygen stream. From initial investigation results, the electrodes prepared from these materials exhibited high specific capacity and excellent electrochemical reversibility. The structural integrity of the $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$ materials is preserved apparently because the Ti^{4+} ions prevent impurity Ni^{2+} migration into the lithium sites.

In order to apply $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$ materials for high-power application fundamental issues, such as the optimization of chemical composition and particle morphology to achieve excellent power performance, must be addressed. In this study, we show the electrochemical performance of a number of materials with different dopants in $\text{LiNi}_{1-x}\text{Ti}_x\text{M}_y\text{O}_2$, where M can be cobalt, manganese or aluminum. The resulting $\text{LiNi}_{1-x}\text{Ti}_x\text{M}_y\text{O}_2$ cathode materials show various kinds of electrochemical performances depend upon the their morphologies and the characteristics of substituting ions such as valence states and structural stability. The electrochemical properties are discussed in relation to chemistry and structural data. Advanced characterization methods, which include calendar and cycle life testing to measure electrochemical properties and electrode aging at high state of charge and high temperature were performed to investigate the stability of the positive electrode materials with the electrolyte. Differential scanning calorimetry was carried out to investigate the effect of dopants on the safety characteristics of the positive electrodes. High pulse power characteristic tests were conducted to confirm material performance for high power application.

Experimental

The $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ ($0 \leq x \leq 0.2$) oxides were synthesized by a solid-state reaction. The Stoichiometric amounts of raw material powders were ball-milled for 24 hours. The solid-state reaction proceeded at $700-850^\circ\text{C}$ under oxygen stream or in air.

The samples were characterized by powder X-ray diffraction and the lattice parameters were refined using the Rietveld method. The electrochemical properties of $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$ were carried out using slow cyclic voltammetry and galvanostatic cycling experiments. The coin-type cell of Li/LiPF_6 (1:1 EC: DEC)/oxides were prepared in dry room. The sample powders were mixed with 8% carbon and 8% PVDF binder in 1-methyl-2-

pyrrolidone as solvent. The resulting paste was cast on an aluminum foil. The working electrodes were punched out with 1.6 cm^2 and 15.5 cm^2 geometric area for coin cell and high power pulse characteristic testing, respectively.

Results and Discussion

Although the presence of titanium increased metal-metal intrasheet distance (a_{hex}), the average metal-metal interlayer distance ($c_{\text{hex}}/3$) also increased due to the relatively strong electrical repulsion between layers caused by Ti^{4+} substitution. The Ti^{4+} ions appear to have different local ionic ordering compared with Ni^{3+} ions and tend to form more ionic $(\text{Ni}_{1-x}\text{Ti}_x\text{O}_2)_n$ sheets, which yield high c/a values, although axis-a (intrasheet distance) enlarges simultaneously. The degree of trigonal distortion reflects typical c/a values of hexagonal-close-packed structures, 4.94-4.95. These c/a values differ somewhat compared with those from our previous report.¹⁰ Fig.1 shows spherical morphology of $\text{LiNi}_{0.95}\text{Ti}_{0.05}\text{O}_2$ sample.

Fig.2 shows high pulse power characteristic result of $\text{LiNi}_{0.95}\text{Ti}_{0.05}\text{O}_2$ with 8C rate. The material exhibit good power performance that exceeds the power requirement set by PNGV (the Partnership for a New Generation of Vehicles) program.

Acknowledgment

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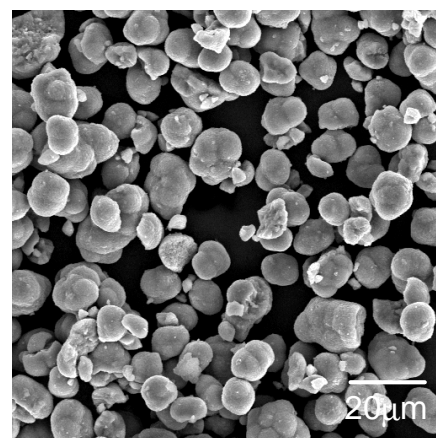


Fig. 1 SEM image of $\text{LiNi}_{0.95}\text{Ti}_{0.05}\text{O}_2$ sample.

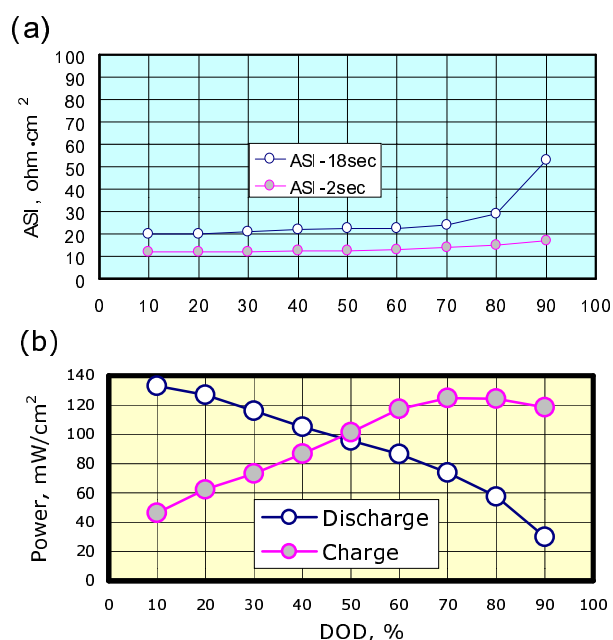


Fig. 2 (a) Pulse power area specific impedance and (b) pulse power capability results of cell with $\text{LiNi}_{0.95}\text{Ti}_{0.05}\text{O}_2$ material (8C rate).