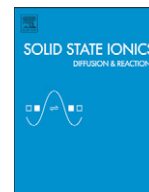




Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Effect of surface modification and oxygen deficiency on intercalation property of lithium nickel manganese oxide in an all-solid-state battery



Gwangseok Oh, Masaaki Hirayama*, Ohmin Kwon, Kota Suzuki, Ryoji Kanno

Tokyo Institute of Technology, G1-1, 4259, Nagatsuda, Midoriku, Yokohama 226-8502, Japan

ARTICLE INFO

Article history:

Received 17 July 2015

Received in revised form 9 November 2015

Accepted 1 January 2016

Available online 20 February 2016

Keywords:

LiNi_{0.5}Mn_{1.5}O₄

Sulfide electrolyte

Surface coating

Li₁₀GeP₂S₁₂

Lithium intercalation

ABSTRACT

LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄ powders were synthesized by a sol-gel method, and their intercalation property as a cathode material was investigated using all-solid-state batteries with Li₁₀GeP₂S₁₂ solid electrolyte and In–Li metal anode. The LiNbO₃ coating delivered reversible lithium intercalation of LiNi_{0.5}Mn_{1.5}O₄ through an electrochemical interface with the Li₁₀GeP₂S₁₂. Oxygen-deficient LiNi_{0.5}Mn_{1.5}O_{4–δ} with a higher electronic conductivity than LiNi_{0.5}Mn_{1.5}O₄ improved the intercalation activity. An all-solid-state battery consisting of 3 wt.-%-LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O_{4–δ}/Li₁₀GeP₂S₁₂/In–Li exhibited a discharge capacity of 80 mAh g^{–1} at the first cycle with an average discharge voltage of 4.1 V (vs. In–Li), which demonstrates the possibility of 5 V class all-solid-state batteries with a high voltage spinel cathode.

© 2016 Published by Elsevier B.V.

1. Introduction

Lithium ion batteries with high power and energy densities are being intensively investigated for use in new applications such as hybrid electric and electric vehicles. However, safety precautions are strictly required for such large-scale systems due to the flammable organic liquids that are used as the electrolyte. All-solid-state batteries with a nonflammable solid electrolyte have recently attracted growing interest due to their high stability. Another advantage of solid electrolytes is the wide electrochemical window over 5 V (vs. Li/Li⁺) compared to organic liquid electrolytes, which enables the use of high-voltage cathodes for high-energy-density batteries [1].

LiNi_{0.5}Mn_{1.5}O₄ and LiCoMnO₄ with a spinel-type structure are some of the most promising 5 V class cathode materials with energy densities of over 600 Wh kg^{–1} [2,3]. All-solid-state batteries with Cr-doped LiNi_{0.5}Mn_{1.5}O₄ and LiCoMnO₄ spinel cathodes and oxide-type solid electrolytes, such as Li_{3.2}PO_{3.8}N_{0.2} and Li₃PO₄, have been reported [3,4]. However, these all-solid-state batteries have been limited to thin-film battery systems because of the low ionic conductivity of the oxide electrolytes. Recently, sulfide-type solid electrolytes have been reported to exhibit high ionic conductivity of over 10^{–2} S cm^{–1} [1,5]. After material discovery, there have been several studies on all-solid-state batteries comprising 4 V class cathodes and solid sulfide electrolytes for large-scale systems [6,7].

Here, we report on the reversible lithium intercalation from a LiNi_{0.5}Mn_{1.5}O₄ cathode through a solid sulfide electrolyte Li₁₀GeP₂S₁₂.

The surface coating of amorphous LiNbO₃ on the LiNi_{0.5}Mn_{1.5}O₄ surface [8] and the formation of oxygen deficiency in LiNi_{0.5}Mn_{1.5}O₄ [9] were investigated to decrease interfacial resistance between the oxide cathode and sulfide electrolyte. The charge–discharge reaction of the LiNbO₃-coated LiNi_{0.5}Mn_{1.5}O₄ cathode was characterized using an all-solid-state battery with a Li₁₀GeP₂S₁₂ solid electrolyte and In–Li alloy anode.

2. Experimental

LiNi_{0.5}Mn_{1.5}O₄ powder (Toda Kogyo; average particle size of 9.5 μm and Brunauer–Emmett–Teller surface area of 0.53 m² g^{–1}) was annealed at 1023, 1073, and 1123 K for 10 h in air to form oxygen-deficient LiNi_{0.5}Mn_{1.5}O_{4–δ} with high electronic conductivity. LiNi_{0.5}Mn_{1.5}O_{4–δ} surfaces were coated with LiNbO₃ using the sol-gel method. Li metal was dissolved in ethanol under dry Ar, and the ethanol solution was mixed with Nb₂(OC₂H₅)₁₀. The LiNi_{0.5}Mn_{1.5}O_{4–δ} samples were immersed into the solution, which was agitated using a magnetic stirrer. The weight ratios of LiNbO₃ to LiNi_{0.5}Mn_{1.5}O_{4–δ} were 2, 3, and 4 wt%. The coated samples were dried under vacuum atmosphere and then heated at 623 K for 1 h in air to remove organic species.

The morphologies and crystal structures were characterized by scanning electron microscopy (SEM: JEOL, JSM-6610LV) and X-ray diffraction (XRD: Rigaku, SmartLab) using Cu Kα₁ radiation. The electronic conductivity was characterized by direct current (DC) conductivity measurement for the LiNi_{0.5}Mn_{1.5}O_{4–δ} pellets. Prior to the measurement, Au blocking electrode was coated on both sides of the pellets. A constant voltage of 50 mV was applied to the Au/LiNi_{0.5}Mn_{1.5}O_{4–δ}/Au pellets. The current was recorded after the current reached a constant value to eliminate the contribution of lithium ion diffusion to the electrical

* Corresponding author. Tel./fax: +81 45 924 5403.

E-mail address: hirayama@chem.titech.ac.jp (M. Hirayama).