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Electrochemical and Structural Characteristics of LiNi_{1-x}Co_xO₂ Positive Materials Synthesized Using α -Phase Composite Hydroxides

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INTRODUCTION

LiNiO $_2$ has been extensively studied as a positive electrode for lithium secondary batteries because of its lower cost and higher specific capacity than those of LiCoO $_2$. The LiNiO $_2$, however, exhibits a departure from stoichiometry (Li₁₋₂Ni₁₊₂O $_2$) because of the presence of extra-nickel ions within the lithium sites. The loss of reversibility at the first cycle is mainly related to the presence of the extra-nickel ions, which makes lithium re-intercalation difficult. A convenient way to overcome this drawbacks may be to partially replace the nickel by other elements such as cobalt³¹, aluminium⁴¹ because the presence of other elements stabilizes the structure in a strictly two-dimensional fashion, thus favouring good reversibility of the intercalation and deintercalation reactions. In the present work, α -phase composite hydroxides (α -Ni_{1-x}Co_x(OH) $_2$) were used to partially substitute nickel with cobalt in lithium nickel oxide system. α -phase composite hydroxide has homogeneous mixing of nickel and other elements and larger spacing between the NiO $_2$ slabs than that of β -phase hydroxide, which is expect to help the lithium diffusion during the calcination reaction.

EXPERIMENTAL

LiNi_{1-x}Co_xO₂($0 \le x \le 0.3$) was prepared using α -phase of Ni_{1-x}Co_x(OH)₂ and LiNO₃ as starting materials. α -phase of Ni_{1-x}Co_x(OH)₂ (x>0) was synthesized by dropwise addition of nitrate solutions of nickel and cobalt into NaOH solution. α -phase of Ni(OH)₂ was prepared by pouring the ammonia solution into the nickel nitrate solution. The limited substitution of nickel with cobalt was necessary to stabilize the α -phase of hydroxide. The obtained materials were then well mixed with LiNO₃ and pressed into pellets. The pellets were calcined at the temperature between 550°C and 850°C in oxygen stream. Prepared α -phase of Ni_{1-x}Co_x(OH)₂ and LiNi_{1-x}Co_xO₂ were characterized by x-ray diffraction and neutron diffraction and the composition of materials was determined by ICP-AES. A cathode mix, which consisted of 88w/o LiNi_{1-x}Co_xO₂, 6w/o denka black, and 6w/o PVDF was used. The electrolyte used was 1M LiClO₄ in propylene carbonate (PC) solution. Lithium metal was used as anode and reference electrode.

RESULTS AND DISCUSSIONS

The X-ray diffraction patterns of α -type nickel hydroxides exhibit low angle 001 lines and two hk dissymetrical bands. The location of 001 lines indicates that α -Ni(OH)₂ has larger interslab distance compared with β -Ni(OH)₂. In the case of LiNiO₂ from the α -Ni(OH)₂, the pattern shows a large integrated intensity ratio I(003)/I(104)=1.45 and clear split of the (006) and (102) as well as (108) and (110) peaks which are correspond to electroactive materials. More detailed discussion will be made about the relationship between electrochemical and structural characteristics in the meeting.

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