

# Crystal structure Analysis and Electrochemical for Chemically Delithiated $\text{Li}_x\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_{2-\delta}$ of Mg Rechargeable Battery Cathode Materials

Naoya Ishida<sup>a</sup>, Ryuta Nishigami<sup>a</sup>, Naoto Kitamura<sup>a</sup>, Yasushi Idemoto<sup>a</sup>

<sup>a</sup>Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba, JAPAN

E-mail: naoya-ishida@rs.tus.ac.jp

The Mg secondary battery has been studied for the purpose of the development of the rechargeable battery beyond the Li-ion battery. We have focused on the  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ , which is a positive electrode material of the high capacity and can be applied as the cathode material capable of inserting Mg ions<sup>1)</sup>. However, there is no knowledge about redox potential without overpotential derived from anode. The purpose of this study was to evaluate the electrode property of delithiated  $\text{Li}_x\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_{2-\delta}$  in Mg battery with reference electrode, to analyze the crystal structure and valence state changes before and after Mg insertion and furthermore to examine the charge/discharge mechanism.

$\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  was synthesized and delithiated by using  $\text{NO}_2\text{BF}_4$ <sup>1)</sup>. The products were characterized by XRD and ICP-AES. The electrochemical measurements in the Mg cell with Ag reference were subjected to a charge-discharge cycle test. The XAFS and synchrotron XRD measurements were performed on the  $\text{Li}_x\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_{2-\delta}$  and the  $\text{Mg}_y\text{Li}_x\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_{2-\delta}$  electrode after Mg insertion.

Chemically delithiated  $\text{Li}_{0.13}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_{2-\delta}$  was successfully synthesized. The result of the Rietveld analysis revealed the partially phase conversion from the monoclinic ( $C2/m$ ) to the trigonal ( $R\bar{3}m$ ). From discharging test of this sample with the Mg alloy anode and the Ag reference, the discharge capacity was over 400 mAh  $\text{g}^{-1}$  (Fig. 1) which corresponded to Mg = 0.59 apfu insertion and to approximately half of chemically eliminated Li. The synchrotron XRD measurements were performed and analyzed by Rietveld method to refine the lattice parameters (Table 1). The expansion in the lattice volume after Mg insertion indicated the increase of ionic radius of Mn, Ni and Co due to the reduction accompanied by Mg insertion. It was also revealed by XAFS to show about 1 pfu valence as the reduction amount and to match the Mg = 0.59 insertion. Therefore, the discharge mechanism was explained by the reduction of transition metals and the intercalation of Mg into the interlayer.

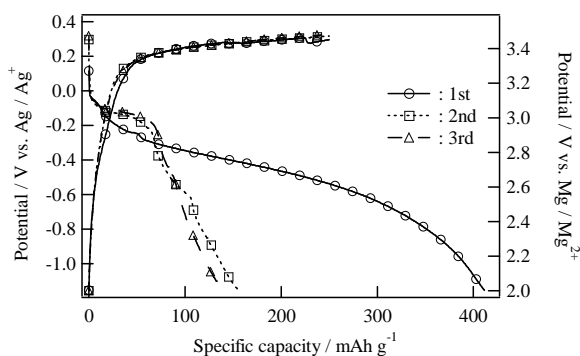


Fig. 1 Discharge and charge curves of  $\text{Li}_{0.13}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_{2-\delta}$  cathode using a three-electrode cell.

Table 1 Refined lattice parameters for synchrotron XRD patterns.

	Pristine	After Delithiation	After 1st discharge
Phase 1 ( $C2/m$ )			
$a$ /nm	0.49408(2)	0.4914(1)	0.4966(2)
$b$ /nm	0.85538(2)	0.85538(8)	0.8674(2)
$c$ /nm	0.50250(1)	0.5094(1)	0.5111(3)
$\beta$ /°	109.237(3)	108.81(2)	109.39(5)
$10^{-3} \times V$ /nm <sup>3</sup>	200.51(1)	202.73(7)	207.6(2)
Phase 2 ( $R\bar{3}m$ )			
$a$ /nm	—	0.28455(3)	0.28629(7)
$c$ /nm	—	1.4050(3)	1.4267(5)
$10^{-3} \times V$ /nm <sup>3</sup>	—	98.53(2)	101.27(5)

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## Reference:

[1] N. Ishida, R. Nishigami, N. Kitamura, Y. Idemoto, *Chem. Lett.*, **46** (2017) 1508–1511.