

## Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub> for Negative Active Material of Lithium Secondary Cells

Xingjiang Liu, Hideo Yasuda, Masanori Yamachi, Yoshiji Matsuda,\* and Yoshihiro Imai\*  
Corporate R&D Center, Japan Storage Battery Co., Ltd.  
Nishinosho, Kisshoin, Minami-ku, Kyoto 601-8520,  
Japan

\*The Kansai Electric Power Co., Inc. 3-11-20, Nakoji,  
Amagasaki, Hyogo 661-0974, Japan

### Introduction

Recently, the electrochemical cells with high energy density and high power density have been strongly required for EV and electric power tool applications. Worldwide effort has been made to find alternative positive and negative materials for the rechargeable electrochemical cells to meet the applications. The 3d-transition-metal oxides such as CoO, NiO, CuO, and FeO were proposed as high-capacity negative active materials with a good rate-performance for lithium secondary cells.<sup>1</sup> We have successfully synthesized some Ni, Mn and / or Co oxide solid solutions, and attempted to apply them as negative active materials.<sup>2,3</sup>

In this work, an oxide solid solution of Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>x</sub> (1 < x < 1.5) with a unique charge-discharge behavior has been newly synthesized and investigated for a high-capacity negative active material of lithium secondary cells.

### Experimental

The Ni<sub>1-a</sub>Mn<sub>a</sub>OOH (0 < a < 1) solid solutions were synthesized through a soft chemical process firstly. These raw materials were then heat-treated at the temperature ranged from 150 to 1000°C in air for 16 h. The composition of the resulting compounds was analyzed by inductively coupled plasma technique (ICP).

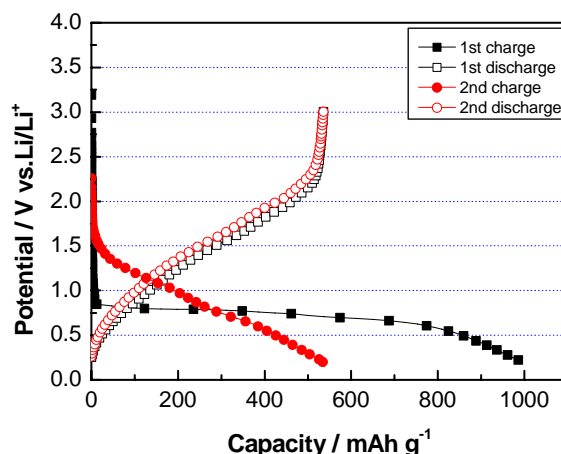
The Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>x</sub> and other solid solutions of nickel oxide and manganese oxide with various molar ratios of Ni / Mn, were electrochemically characterized as the negative active material by constant current charge / discharge measurement in three-electrode test cell. The working electrode was made of the active material, acetylene black electric conductor and PVdF binder with a mass ratio of 80 / 10 / 10, and the foamed Cu was applied as a current collector. The cell was charged to 0.20 V vs. Li/Li<sup>+</sup> and then discharged to 3.00 V vs. Li/Li<sup>+</sup> at a current density of 0.25 mA cm<sup>-2</sup>. All of the electrochemical measurements were carried out in Ar filled dry box (H<sub>2</sub>O: less than 1 ppm) at 25°C. Powder X-ray diffraction using Cu K radiation was employed to identify the crystalline phase of the materials.

### Results and Discussion

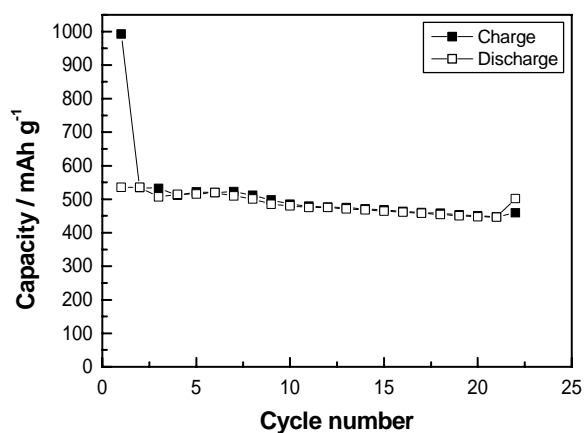
Firstly, the effects of Mn content in the Ni and Mn oxide solid solution on the property of resulted material were investigated. It was found that porous particles of nickel and manganese oxide solid solution were obtained by heating their raw material at higher temperature such as 1000°C, and the average discharge potential became negative with increasing Mn content in the compounds. However, large amount of Mn in the compounds caused the poor cycleability.

Next, the compound of Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub> prepared at 1000°C was evaluated. Figure 1 represents the initial charge-discharge characteristics for Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub> negative active material. A large discharge capacity over 500 mAh g<sup>-1</sup> with linearly potential changing from 0.50 V

to 2.25 V vs. Li/Li<sup>+</sup> was achieved for Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub> negative active material. However, it was also observed a larger irreversible capacity and potential hysteresis on the first charge-discharge process. The XRD analysis for Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub> showed that the diffraction peaks disappeared after the first charge. It indicates that an amorphous-like phase was formed during the 1st electrochemical reduction, and the large irreversible capacity is caused by the irreversible reduction of oxide together with electrolyte reduction. Figure 2 shows the capacity change for Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub> electrode during charge-discharge cycling. The oxide electrode showed a better cycleability and excellent charge-discharge efficiency except the first cycle. Therefore, the Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub> was found to be a promising candidate for high-capacity negative active material of lithium secondary cells.



**Figure 1.** Initial charge-discharge characteristics of Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub> prepared at 1000°C. The oxide electrode was charged to 0.20 V and discharged to 3.00 V vs. Li/Li<sup>+</sup> at 0.25 mA cm<sup>-2</sup>.



**Figure 2.** Cycle performance of Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.43</sub>. The oxide electrode was charged to 0.20 V and discharged to 3.00 V vs. Li/Li<sup>+</sup> at 0.50 mA cm<sup>-2</sup>.

### References

1. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, and J. M. Tarascon, *Nature*, **407**, 496 (2000).
2. X. Liu, H. Yasuda, and M. Yamachi, The 44th Battery Symposium in Japan, Sakai, 3A18 (2003).
3. X. Liu, H. Yasuda, and M. Yamachi, The 12th International Meeting on Lithium Battery, Nara, Japan, accepted (2004).