

N.Imanishi, Y.Inoue, T.Matsumura, A.Hirano, Y.Takeda  
Department of Chemistry, Mie University  
1515 Kamihamacho, Tsu, Mie 514-8507, Japan

## Introduction

In this paper, we study a different class of insertion compounds from those having layered or zeolitic structure that undergoes intercalation. Present practical electrode materials such as  $\text{LiCoO}_2$  and graphite, intercalate lithium ions during charge-discharge process. In this so called host-guest reaction, host and guest regions in the bulk can be separated in terms of both geometrical and electronic distributions. As guest species going in and out, the host basically maintains its original structure except for small volume change and/or slide of the layer.

Contrary, there are other types of oxide materials which can accommodate lithium ions reversibly, while the structure changes to amorphous state. In these materials the guest and host region can not be clearly defined, and lithium ions are recognized as a part of the lattice rather than a guest in the host matrix. They are described as solid lithium ion conductor functionalized with electronic conduction. The lithium usually makes a three dimensional networks and component transition metal bears electronic conduction. In this paper these cathode materials are studied as high capacity post-intercalation compounds.

One of such materials we have studied is  $\text{Li}_5\text{FeO}_4$ . It has the anti-fluorite type structure where two equivalent lithium vacancies ( $\text{Li}_{5-2}\text{FeO}_4$ ) are ordered among isolated  $\text{FeO}_4$  tetrahedra. The low temperature form is isostructural to  $\text{Li}_5\text{GaO}_4$  and the high temperature form, to  $\text{Li}_6\text{CoO}_4$ , respectively. Both the characteristics of high lithium ion mobility and easily changeable valence of the transition metal, Fe, facilitate Li de-intercalation and subsequent Li intercalation in these oxides. In this study,  $\text{Li}_5\text{FeO}_4$  and Co-substituted solid solutions were prepared and the performance as a cathode for lithium secondary batteries was studied.

Another examined sample is  $\text{Li}_2\text{CuO}_2$ , which has been known to have one-dimensional chain structure of edge shared  $\text{CuO}_4$  square planes. In the 3d transition metal series,  $\text{Ni}^{2+}$  also takes the isostructural coordination, but no electrochemical behavior of  $\text{Li}_2\text{NiO}_2$  for the cathode of lithium battery was reported. We first tried to prepare the solid solution of  $\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$  in order to find suitable synthetic conditions. The electrochemical behavior and accompanying structural change of the system,  $\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$ , is reported.

## Experimental

$\text{Li}_{6-x}\text{Fe}_x\text{Co}_{1-x}\text{O}_4$  was synthesized using traditional ceramic methods from  $\text{Li}_2\text{O}$  (Kojundo Chemicals Laboratory Co. Japan),  $\text{FeOOH}$ , and  $\text{Co}(\text{OH})_2$  (Nakarai tesque Co, Japan). A mixture of  $\text{Li}_2\text{O}$ ,  $\text{FeOOH}$  and  $\text{Co}(\text{OH})_2$  was pressed into tablets (8mm in diameter and 5.8mm in thickness) and then heated in an electrical furnace at various temperatures under  $\text{N}_2$  gas stream. The heated pellets were annealed to room temperature.

$\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$  was synthesized from  $\text{Li}_2\text{O}$ ,  $\text{CuO}$  and  $\text{NiO}$ . In the case of Ni rich side ( $x=0.9$  and  $1.0$ ), the active  $\text{NiO}_{1+\delta}$  prepared by decomposition of  $\text{Ni}(\text{OH})_2$  was used instead of  $\text{NiO}$ . The mixtures were pressed into tablets and then heated in an electrical furnace at  $800^\circ\text{C}$  for 24h under Ar gas stream. The samples for  $x=0.9$  and  $1.0$  were prepared by repeated heating at  $600^\circ\text{C}$  for 80h. Heating under low oxygen pressure was indispensable for the preparation of single phase in the Ni rich region.

X-ray diffraction (XRD) measurements were performed on a Rigaku RAD RC (12kW) using monochromated  $\text{CuK}\alpha$  radiation. To test the charge-discharge performance as a cathode, a conventional Li coin type cell was assembled. The oxide (50mg) was ground and mixed with acetylene black (10mg) as an electron conductor and Teflon (0.5mg) as a binder, and then the mixture was pressed into a tablet of 12mm in diameter under a pressure of 1MPa. The cell was assembled

using this tablet as the cathode, Li sheet as the anode and 1M  $\text{LiClO}_4/\text{ethylene carbonate}(\text{EC}) + \text{dimethylcarbonate}(\text{DMC})$  as the electrolyte.

## Result and Discussion

Figure 1 shows the cycling performance of  $\text{Li}/\text{Li}_{6-x}\text{Fe}_x\text{Co}_{1-x}\text{O}_4$  ( $x=0.6$ ) cell with a cut-off of 1.8/4.0V vs.  $\text{Li}/\text{Li}^+$  at a constant current density of  $0.3\text{mA}/\text{cm}^2$ . Charge process was also terminated when capacity reaches  $200\text{mAh}/\text{g}$ . The first charge curve shows plateau indicating two phase mixture. The XRD data tell that at  $y=0.5$  in  $\text{Li}_{5-y}\text{FeO}_4$ , the original phase begins to diminish and a new amorphous-like phase appears. Beyond  $y=1.5$ , only the new phase is observed. The reversible lithium insertion is possible if delithiation amount is kept at  $y<1.2$ . At the first discharge, 60% capacity loss is observed, but the discharge capacity increases with increasing cycle number. Within a couple of cycles the efficiency reaches to 100% at the  $200\text{mAh}/\text{g}$  of capacity. The degradation of the crystal structure proceeds at the same time.

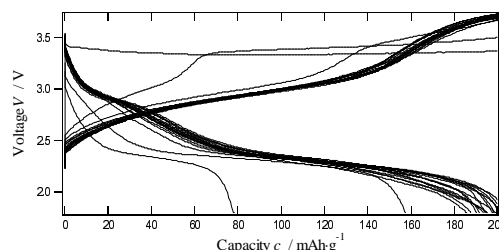


Fig.1 Charge-discharge curves for  $\text{Li}_{5.4}\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_4$  cycled in a cut-off voltage of 1.8/4.0V. Current density:  $0.3\text{mA}/\text{cm}^2$ .

In Fig. 2, the good cycling behavior under the capacity cut-off of  $250\text{mAh}/\text{g}$  for  $\text{LiCu}_{0.6}\text{Ni}_{0.4}\text{O}_2$  is shown. The characteristic feature for the first cycle is that the charge potential shows plateau region. The curves after the second cycle are different from the first one. During the first charge, the phase change occurs and the structure transforms to amorphous-like one. The behavior after the first cycle is due to the new phase. These features are very similar to  $\text{Li}_5\text{FeO}_4$  system, and can be understood as typical of this class of materials.

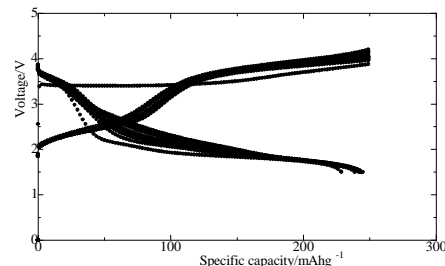


Fig.2 Cycle performance of  $\text{Li}/\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$  cell.

These materials that do not react topochemically, and instead show changes to amorphous state, are expected as a high-capacity electrode.