Electrochemical Properties of $Na_4Co_{3-x}M_x(PO_4)_2P_2O_7$ [M = Ni and Mn] for Sodium-ion Battery

Masafumi Nose, Hideki Nakayama, Kunihiro Nobuhara, Shinji Nakanishi and Hideki Iba

Battery Research Division, Toyota Motor Corporation
1200 Mishuku, Susono, Shizuoka, 410-1193 Japan
E-mail: nose@masafumi.tec.toyota.co.jp

Rechargeable batteries have been desired for high energy, high power, safety and sustainability to meet the requirements of large-scale applications such as hybrid vehicles (HVs), plug-in hybrid vehicles (PHVs) and electric vehicles (EVs). Therefore, much effort has been devoted to develop a variety of batteries. Very recently, sodium-ion batteries (SIBs) have gained considerable attention from the reasons as follows. The first is an abundant of sodium working as an ionic career instead of lithium and the other is the various (de-)intercalation structures which are not familiar with lithium equivalences. The diversity is characteristic of SIBs and it has recognized electrode material with new intercalation structure would still exist. Hence, extensive researches on novel electrode materials have been carried out in the world to overcome the disadvantage of low energy densities as compared with the current lithium-ion batteries.[1-2)]

In the course of our material research, we discovered the novel $Na_4Co_3(PO_4)_2P_2O_7$ electrode material, which has multiple sodium-ion pathways in the structure (Fig. 1), shows unique intercalation capabilities.[1, 3, 4)] As described in Figs. 2 and 3, $Na_4Co_3(PO_4)_2P_2O_7$ has the multi redox couples in the highest potential region between 4.1 V and 4.7 V among ever reported electrode materials for SIBs and the reversible capacity reached to ca. 95 $mAhg^{-1}$ with good cycle performance. The electrochemical properties strongly suggest the new intercalation structure of $Na_4Co_3(PO_4)_2P_2O_7$ should provide a new perspective for high-voltage type SIBs.

We are now investigating the novel solid-solution phases of $Na_4Co_{3-x}M_x(PO_4)_2P_2O_7$ [M=Ni and Mn], isostructural to $Na_4Co_3(PO_4)_2P_2O_7$. In this presentation, we will review our previous results of $Na_4Co_3(PO_4)_2P_2O_7$ and report the electrochemical characteristics of novel $Na_4Co_{3-x}M_x(PO_4)_2P_2O_7$ electrode materials.

References

1) M. Nose, H. Nakayama, K. Nobuhara, S. Nakanishi and H. Iba, *J. Power Sources*, **234** (2013) 175-179.
2) K. Chihara, A. Kitajou, D. Gocheva, S. Okada and J. Yamaki, *J. Power Sources*, **227** (2013) 80-85.
3) M. Nose, H. Nakayama, K. Nobuhara, S. Nakanishi and H. Iba, *ECS meet. abs.*, (2012) #1847.
4) M. Nose, H. Nakayama, K. Nobuhara, S. Nakanishi and H. Iba, THE 53RD BATTERY SYMPOSIUM IN JAPAN, 2E07 (2012) 308.
5) F. Sanz, C. Parada, U. Amador, M. A. Monge and C. Ruiz-Valero, J. Solid State Chem., 123 (1996) 129
6) F. Sanz, C. Parada, J. M. Rojo and C. Ruiz-Valero, Chemistry of Materials, 13 (2001) 1334

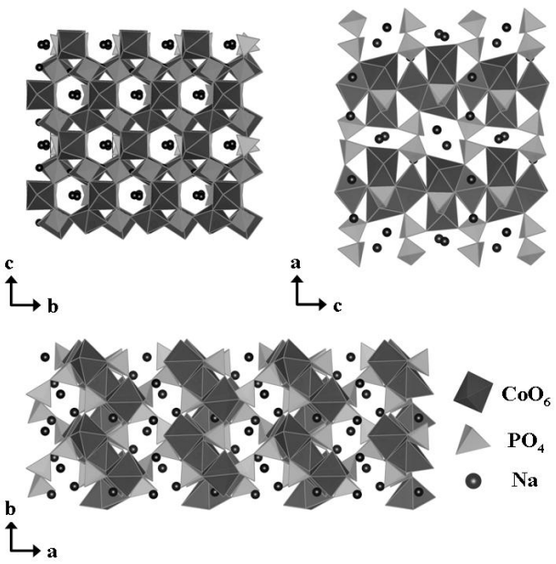

Fig. 1. Polyhedral view of $Na_4Co_3(PO_4)_2P_2O_7$. with $Pn2_1a$ space group along three different directions[5, 6)].

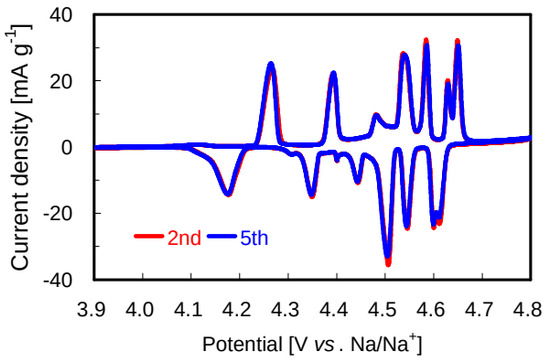

Fig. 2 Cyclic voltammograms at 2nd and 5th cycles of $Na_4Co_3(PO_4)_2P_2O_7$ at the scan rate of 0.01 mVs^{-1}.

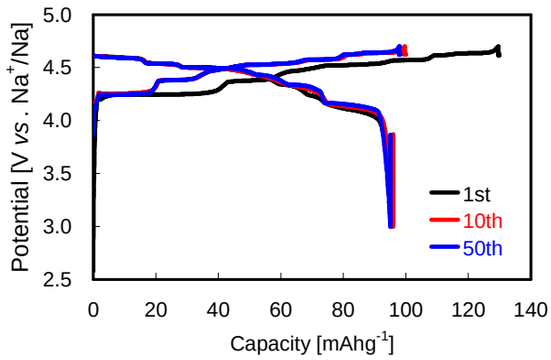

Fig. 3 Galvanostatic charge/discharge profiles at 1st , 10th and 50th cycles of $Na_4Co_3(PO_4)_2P_2O_7$ at the current density of 34 $mAhg^{-1}$.