Advanced Cathode Materials for Na-ion Batteries with High Capacity and Excellent Structural Stability

Jing Xu, Dae Hoe Lee, Ying Shirley Meng*
Department of NanoEngineering, University of California San Diego, La Jolla, CA 92093-0448, USA
*shmeng@ucsd.edu

The research on Na-ion battery chemistries has become more intense in recent years, since sodium sources are far more abundant than lithium sources. A study by Lu et. al demonstrated that the P2 - layered oxide $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ could reversibly exchange Na-ions in sodium cells.[1] More recently, P2 – $Na_x[Fe_{1/2}Mn_{1/2}]O_2$ compound was studied by Yabuuchi et. al, and their Na-ion battery exhibited 190 mAh/g of specific capacity with acceptable cycling properties up to 50 cycles.[2] In addition, Li substituted $Na_{1.0}Li_{0.2}Ni_{0.25}Mn_{0.75}O_{2+\delta}$ was studied by Kim et. al and displayed good cycling and excellent rate capabilities, since Li endows the structural stability into the structure.[3] Since Na-ion is 70% larger in volume than Li-ion, unique and robust structures are required for long term stability and new intermediate phases due to Na-ion vacancy ordering may be expected during the cycling. Our previous work has re-investigated P2 - $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ and revealed that this material exhibits ~240 mAh/g of specific capacity in the voltage range from 1.0 V to 4.5 V at C/100 rate, and several intermediate phases due to Na-ion orderings. If the phase transformation region was excluded, excellent cycling and high rate performances up to 2C rate can be obtained.[4] We believe that P2 structured materials may be strong candidates as a cathode material for Na-ion batteries.

In this talk, we will report our work on layered phases of sodium transition metal (TM) oxides with Li doped, P2 - $Na_x[Li_yNi_zMn_{1-y-z}]O_2$ ($0<x, y, z<1$), working as cathode materials in Na ion batteries. In order to realize stable structure and high energy density at the same time, the composition was designed and optimized. Based on our result, both $Na_{0.80}[Li_{0.12}Ni_{0.22}Mn_{0.66}]O_2$, and $Na_{0.83}[Li_{0.07}Ni_{0.31}Mn_{0.62}]O_2$ demonstrated excellent structural stability and high specific capacity. Combination work of computational and experimental methods was conducted to investigate the working mechanism and improve the electrochemical properties. Compared with our previous work on P2 - $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$, the electrochemical profiles displayed significantly distinct features as shown in Fig 1, though all of these materials are shown P2 structure at pristine state. The synchrotron X-ray diffraction (XRD) illustrated that the two proposed materials have well maintained P2 structure even after charging to 4.2 V. The X-ray absorption spectroscopy was applied at different states of charge. The result suggested that the Ni-ions were oxidized from 2+ to 4+ as Na-ions were gradually extracted, and Mn-ions mainly stayed at tetravalent upon the entire cycle. In addition, our first principles calculation indicated that Li-ions preferred to stay at the TM layers and made significant contribution to stabilizing the P2 structure. A detailed mechanism will be proposed.

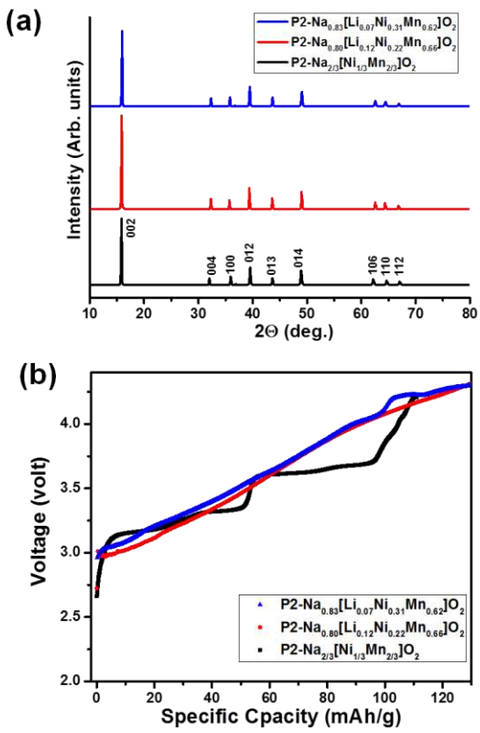

Fig. 1. (a) X-ray powder diffraction patterns of P2 - $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$, P2-$Na_{0.80}[Li_{0.12}Ni_{0.22}Mn_{0.66}]O_2$, and P2-$Na_{0.83}[Li_{0.07}Ni_{0.31}Mn_{0.62}]O_2$ as prepared. (b) The electrochemical profiles of three different materials.

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References

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