Synthesis and Electrochemical Properties of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ via Co-precipitation

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Introduction

Recently, the lithium transition-metal oxide $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ has received a great attention as a cathode material for rechargeable Li-ion secondary batteries [1-3]. As reported by Ohzuku et al, has been reported that $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ can deliver a capacity of about 150 $mAhg^{-1}$ in 3.5-4.2V or 200 $mAhg^{-1}$ in 3.5-5.0V[2]. Furthermore, $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ provides the advantage over $LiCoO_2$ system of being cost effective and thermal stability.

However $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ is known to have unstable cycling performance and their capacity fades especially when cycled to higher voltage (~ 4.5, 4.6V) and at high temperature (55 ^oC). The problem of capacity fading observed upon long-term cycling must be overcome, because such demerits may hinder this material to be used as a cathode material for battery applications.

Anion substitution appeared to be a good approach to modify the structural and electrochemical properties in spinel $LiMn_2O_4$ system, as reported by Sun et al. [4]. We have tried to improve the electrochemical properties of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ by doping the oxygen with Fluorine. Here, we would like to report the results of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$.

Experimental

$Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ was prepared by heating a reaction mixture of the dehydrated $[Ni_{1/3}Co_{1/3}Mn_{1/3}](OH)_z$ and $LiOH{\cdot}H_2O$ and LiF at 1000 ^oC for 10 hours. The prepared powders were examined by XRD, SEM, AAS, and ion chromatography. For electrochemical investigation, the prepared $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ was blended with Super S carbon black, and polyvinylidene fluoride (80:10:10) in *N*-methyl-2-pyrrolidone. The cell was assembled in an argon-filled dry box and tested at a current density of 20 mA g^{-1} at 30 ^oC. For differential scanning calorimetry experiments the coin cells were charged to 4.6 V at 20 mA g^{-1}. The samples were analyzed in the DSC using a temperature scan rate of 2 ^oC min^{-1}.

Results and discussion

Figure 1 shows X-ray diffraction (XRD) patterns of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ with x=0, 0.05, 0.1, 0.15, 0.2, and 0.5 which were synthesized at 1000 ^oC. All of the peaks can be indexed based on a hexagonal α-$NaFeO_2$ structure (space group: R-3m). The Li atoms occupy 3a sites, the Ni, Co, and Mn atoms are randomly placed on 3b sites, and oxygen atoms are on 6c sites. For $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ (x=0.2, 0.5), the diffraction intensity of the (003) peak was analogous to that of the (104) peak. And, the reflection of (018) and (110) for $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ are still distinguishable in the all compositions.

Figure 2 shows the voltage versus capacity of $Li/Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ cells with x=0, 0.05 between 2.8 and 4.6V. Initially, a higher capacity over 180 mAh/g are obtained for $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$. However, a rapid capacity fade is seen during cycling, from 184 mAh/g to 166 mAh/g. By F doping, it seems that though the initial capacity decreased some extend, the lithium de-/intercalation process is highly reversible with small polarization in Fig. 2. Details of the structure and electrochemistry of the current materials will be intensively discussed on the meeting.

Acknowledgements

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References

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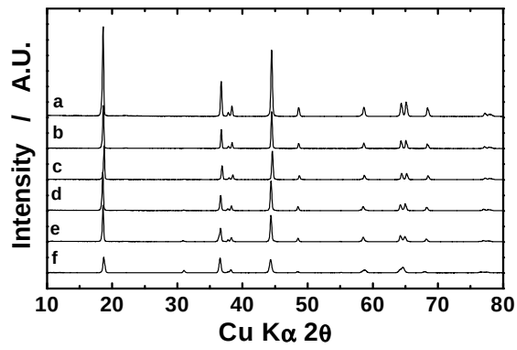

Figure 1. XRD patterns of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ (x=0, 0.05, 0.1, 0.15, 0.2, and 0.5) synthesized at 1000^oC.

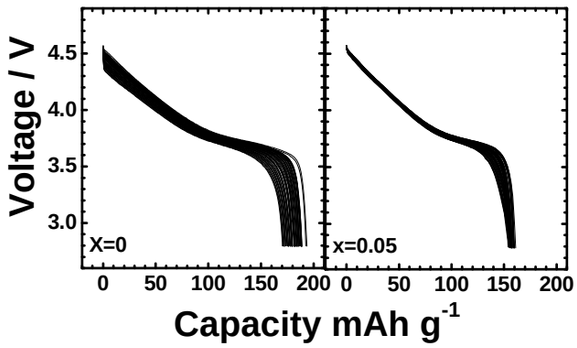

Figure 2. Continuous charge and discharge curves of $Li/Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2-x}F_x$ cells operated at 20mA g^{-1} cycled between 2.8 and 4.6V at 30^oC.