

Layered $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z})\text{O}_{2-z}\text{F}_z$ cathode materials for Li-ion secondary batteries

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Abstract

Electrochemical properties of layered $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z})\text{O}_{2-z}\text{F}_z$ ($0 \leq z \leq 0.10$), which was synthesized by a sol–gel method, were investigated by galvanostatic cycling in the voltage range of 2.0–4.6 V at room temperature as well as at 55 °C. The initial discharge capacity slightly decreased with the increase in the content of fluorine dopant. However, cycling performance was greatly improved and cell impedance was significantly reduced by the fluorine doping. Capacity retention after 40 cycles at room temperature and the area specific impedance were 79% and $150 \Omega \text{ cm}^2$ for $z=0$, respectively, and 103% and $65 \Omega \text{ cm}^2$ for $z=0.05$, respectively. The $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.175}\text{Co}_{0.10}\text{Mn}_{0.525})\text{O}_{1.95}\text{F}_{0.05}$ material charged to 4.6 V also exhibited excellent thermal behavior due to the stability of the fully charged material.

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1. Introduction

Layered $\text{Li}(\text{Li}_{1/3-2x/3}\text{Ni}_x\text{Mn}_{2/3-x/3})\text{O}_2$ material possesses many interesting features such as a long irreversible plateau at ca. 4.5 V during the first charge and much larger capacity than theoretical one based on $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple [1–3]. Although the origin of the peculiar characteristics of the material is currently under debate among many research groups, we consider the material quite an attractive cathode for high-energy Li-ion batteries due to its high practical capacity ($>200 \text{ mAh g}^{-1}$), structural stability at high voltage ($>4.5 \text{ V}$), and good thermal behavior [1]. In previous papers, we reported synthesis and electrochemical properties of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ [3,4]. In this work, we synthesized co-substituted $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ materials on cation (Ni/Mn) and anion (O) sites. Cobalt and fluorine were chosen as substitutes on the cation and anion sites, respectively, based on our previous experience of their beneficial impact on the materials properties. This paper

reports the effect of co-substitution of Ni/Mn and oxygen with Co and F, respectively, on the impedance and cycling performance of the $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ high-energy material.

2. Experimental

Samples with nominal composition of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z}]\text{O}_{2-z}\text{F}_z$ ($0 \leq z \leq 0.1$) were prepared by a sol–gel method using glycolic and tartaric acid as chelating agents. In preparation of the compound, Ni- and Mn-content were adjusted so that the oxidation states of Ni, Co, and Mn were fixed as Ni^{2+} , Co^{3+} , and Mn^{4+} , respectively. Detail of the material preparation is described elsewhere [3]. The final $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z}]\text{O}_{2-z}\text{F}_z$ materials were obtained by calcinations at 900 °C for 12 h in air followed by furnace cooling. Crystallographic structure of the synthesized material was examined by powder X-ray diffractometer using $\text{CuK}\alpha$.

Galvanostatic charge/discharge cycling was conducted using coin cells. The positive electrode consisted of 80 wt.% oxide powder, 10 wt.% carbon, and 10 wt.% polyvinylidene

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difluoride (PVDF) binder on aluminum foil. The negative electrode was either metallic lithium or graphite on copper foil. The electrolyte was 1 M LiPF₆ in a 1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC). The coin cells were galvanostatically cycled between 2.0 and 4.6 V at room temperature and 55 °C.

3. Results and discussion

The XRD patterns of Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z are shown in Fig. 1. The diffraction patterns of the synthesized samples could be indexed based on the α-NaFeO₂-type structure (*R*3*m*) with small extra peaks at 20°–23°, which are generally attributed to ordering of Li and Mn in the transition-metal layers [1]. Chemical composition of cations, examined by the inductively coupled plasma (ICP) analysis, was close to nominal composition; qualitatively, the presence of fluorine in the synthesized materials was confirmed by ion chromatography.

Although not presented in this paper, Li[Li_{0.2}Ni_{0.2-0.5x}Co_xMn_{0.6-0.5x}]O₂ materials with various Co content (0 ≤ *x* ≤ 0.4) were also prepared and investigated, details of which will be reported elsewhere [5]. Among the samples investigated, Li[Li_{0.2}Ni_{0.15}Co_{0.10}Mn_{0.55}]O₂ exhibited the best performance; the area specific impedance (ASI) and the initial discharge capacity of Li[Li_{0.2}Ni_{0.15}Co_{0.10}Mn_{0.55}]O₂ were 67 Ω cm² and 240 mAh g⁻¹, respectively, whereas those of Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ were 290 Ω cm² and 158 mAh g⁻¹, respectively. However, the Co substitution was found to deteriorate the cycling performance. In this work, we investigated the effect of substitution of

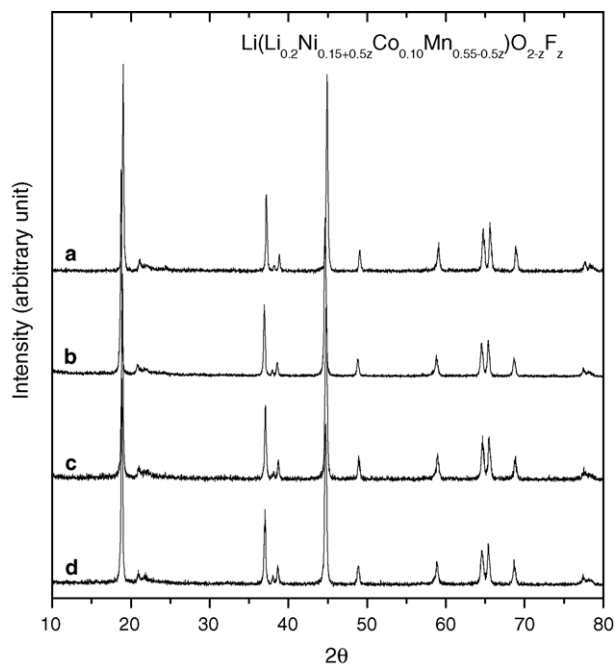


Fig. 1. XRD patterns of Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z. (a) *z* = 0; (b) *z* = 0.02; (c) *z* = 0.05; (d) *z* = 0.10.

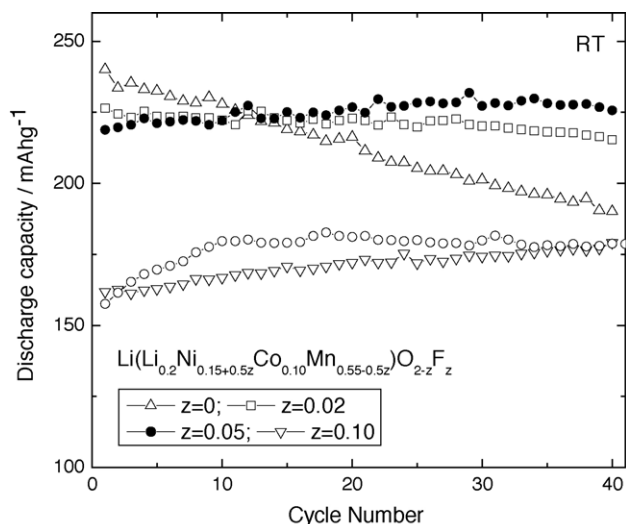


Fig. 2. Discharge capacity of Li/Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z cells cycled in the voltage range of 2.0–4.6 V at room temperature. Discharge capacity of Li/Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ (open circles [O]) is also shown for comparison.

oxygen with fluorine on the cycling performance. Fig. 2 compares the discharge capacity with cycle number of Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z materials with different content of fluorine dopant. The materials were cycled versus Li metal anode in the voltage range of 2.0–4.6 V at room temperature. Although the first discharge capacity was slightly reduced, the cycling performance was greatly improved with the increase in fluorine content. The capacity retention after 40 cycles of the undoped material was 79% whereas no capacity fade was observed from the F-doped materials. The positive effect of the fluorine dopant on the cycling performance is more clearly noticeable from 55 °C-cycling as shown in Fig. 3. While the undoped

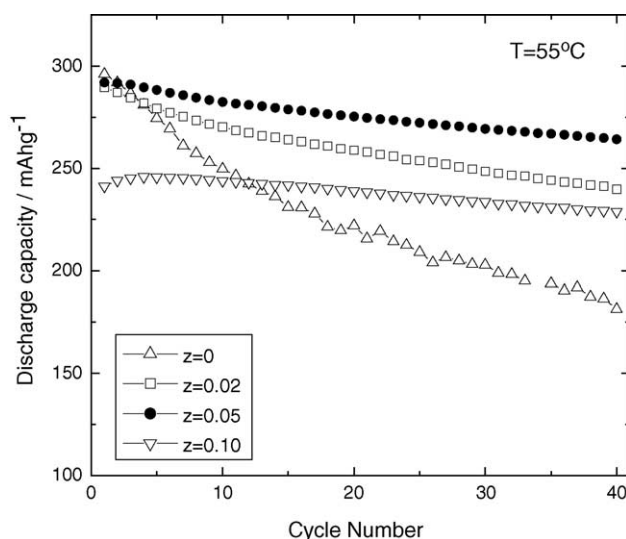


Fig. 3. Discharge capacity of Li/Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z cells in the voltage range of 2.0–4.6 V as a function of cycle number at 55 °C.

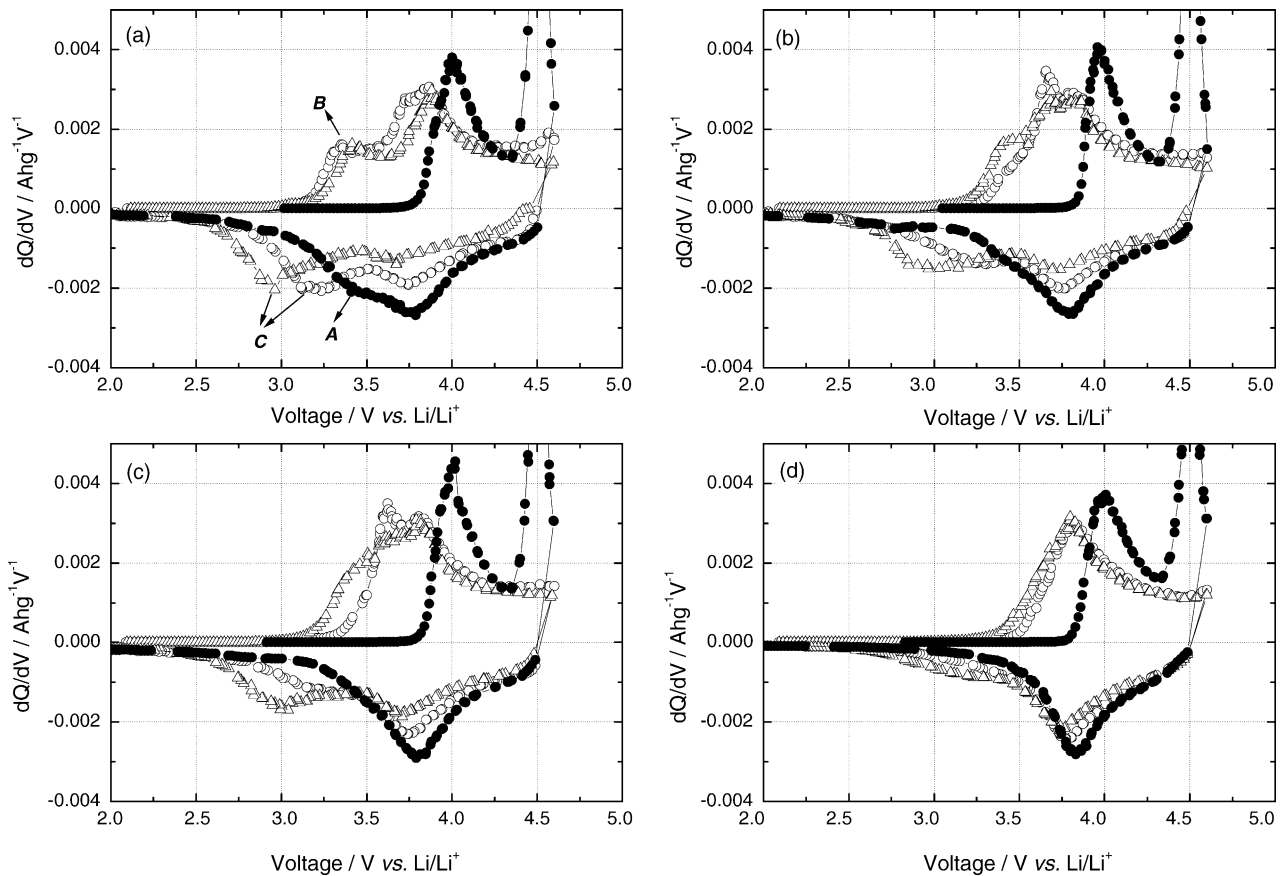


Fig. 4. Differential capacity vs. voltage of Li/Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z cells cycled at 2.0–4.6 V. (a) $z=0$; (b) $z=0.02$; (c) $z=0.05$; (d) $z=0.10$. (●) First cycle, (○) 10th cycle, and (△) 40th cycle.

material shows significant decline in the capacity with cycling, the fluorine-doped materials show excellent cycling characteristics at 55 °C. Fig. 4 shows the differential capacity versus voltage plots derived from the cycling curves at room temperature. Noticeable differences are observed in the differential capacity plots among the samples: (1) a shoulder near 3.4 V during the first discharge (marked as A), and (2) evolution of differential capacity peaks during successive charge and discharge (marked as B and C, respectively). As the fluorine content increased, the additional differential capacity peaks marked as A–C became less clear. The Li[Li_{0.2}Ni_{0.2}Co_{0.10}Mn_{0.5}]O_{1.9}F_{0.1} material, for instant, exhibits very simple and almost invariant differential capacity plots. This result is believed to be closely related with the excellent cycling stability of the material. Exploration of the origin of the extra differential capacity peaks and their correlation with cycling performance are under study.

The impact of the fluorine doping on the impedance of the materials was also examined. Fig. 5 shows the average ASI at 60–80% state of charge (SOC) of graphite/Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z cells. The ASI values were determined by $A \Delta V / I$, where A is the cross sectional area of the electrodes (1.6 cm²), ΔV the voltage change during

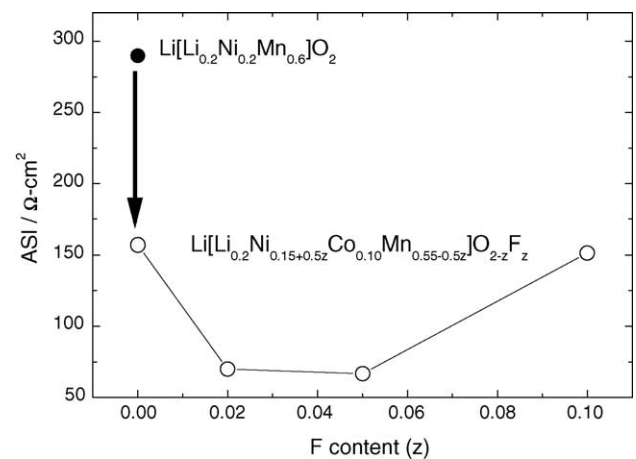


Fig. 5. Average area specific impedance (ASI) at 60–80% state of charge (SOC) measured with graphite/Li[Li_{0.2}Ni_{0.15+0.5z}Co_{0.10}Mn_{0.55-0.5z}]O_{2-z}F_z cells as a function of fluorine content. (●) The ASI measured with graphite/Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O₂ cell.

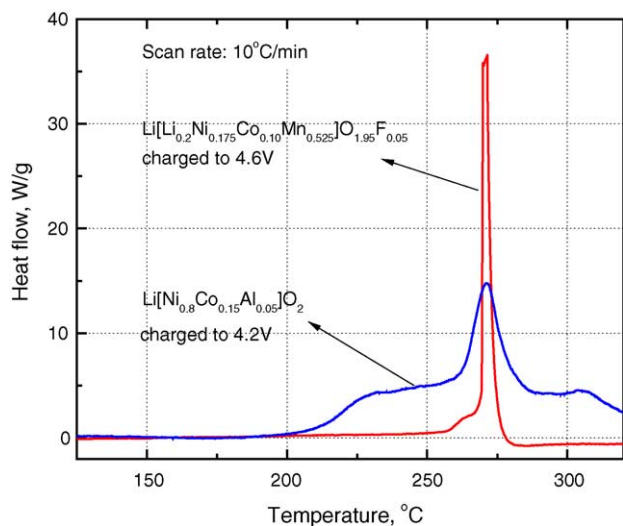


Fig. 6. Differential scanning calorimetry (DSC) profile ($10^{\circ}\text{C min}^{-1}$) of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z}]\text{O}_{2-z}\text{F}_z$ charged to 4.6 V. Those of $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.2}]\text{O}_2$ and $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}]\text{O}_2$ charged to 4.2 V (taken from ref. [6]) are also shown for comparison.

current interruption for 30 s at each SOC, and I is the current applied during the galvanostatic cycling. The ASI of graphite/ $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ cell is also shown in Fig. 5. When adding 10% Co to $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$, the ASI drops significantly from 290 to $150\ \Omega\ \text{cm}^2$. The fluorine doping further lowered the impedance of the material to as low as $65\ \Omega\ \text{cm}^2$ for $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.175}\text{Co}_{0.1}\text{Mn}_{0.525})\text{O}_{1.95}\text{F}_{0.05}$.

Fig. 6 compares the differential scanning calorimetry profile of the $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z}]\text{O}_{2-z}\text{F}_z$ ($z=0.05$) and the commercially available $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. In this case, $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z}]\text{O}_{2-z}\text{F}_z$ ($z=0.05$) was charged to 4.6 V while $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ was charged only to 4.2 V only. The $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z}]\text{O}_{2-z}\text{F}_z$ ($z=0.05$) material exhibits a small and narrow exothermic peak at 270°C with enthalpy of reaction of $850\ \text{J g}^{-1}$. However, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ charged only to 4.2 V, exhibit a broad exothermic peak with a much lower onset temperature of 195°C and much higher enthalpy of reaction of $1880\ \text{J g}^{-1}$. The superior thermal stability of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z}]\text{O}_{2-z}\text{F}_z$ compared with $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is attributed to the stability of the

fully charged $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.10}\text{Mn}_{0.55-0.5z}]\text{O}_{2-z}\text{F}_z$ material even at 4.6 V.

4. Summary and conclusions

Layered $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.15+0.5z}\text{Co}_{0.1}\text{Mn}_{0.55-0.5z})\text{O}_{2-z}\text{F}_z$ ($0 \leq z \leq 0.10$) materials were synthesized by a sol-gel method and the effect of the fluorine on the electrochemical properties of the cathode materials was investigated. Initial capacity of the material was slightly reduced by the fluorine dopant. However, cycling performance was greatly improved even during cycling at high temperature (55°C). The impedance was also significantly reduced by the fluorine dopant; the materials with $z=0.02$ and 0.05 showed about $65\ \Omega\ \text{cm}^2$ of ASI whereas undoped one's ASI was as high as $150\ \Omega\ \text{cm}^2$. Among the materials studied in this work, $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.175}\text{Co}_{0.1}\text{Mn}_{0.525})\text{O}_{1.95}\text{F}_{0.05}$ exhibited the best performance in terms of cycleability and impedance. Further optimization and characterization of the material is under way and will be reported later.

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