

Short communication

Synthesis and electrochemical properties of $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x = 0, 0.02$) via co-precipitation method

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Abstract

$\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x = 0, 0.02$) was synthesized via co-precipitation method. Partial Zr doping on the host structure of $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ was carried out to improve the electrochemical properties. The Zr-doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$ was evaluated in terms of specific discharge capacity, cycling performance and thermal stability. The Zr-doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_{0.02}]\text{O}_2$ shows the improved cycling performance and stable thermal stability. The major exothermic reaction was delayed from 252.1 °C to 289.4 °C.

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1. Introduction

Recently, a lot of attention has been paid to $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ layered material as alternative cathode material to commercialized LiCoO_2 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ materials for lithium ion battery system [1]. $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ is considered as an attractive cathode material due to its stable electrochemical performance resulting from the existence of stable tetravalent Mn^{4+} in the structure. The $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ delivered a reversible capacity of 150 mAh g^{-1} in the voltage range 3.0–4.3 V with no indication of transformation to the spinel phase during electrochemical cycling. $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ could be cheaper cathode material with longer cycle life and good thermal stability. However, the $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ shows relatively poor rate capability at higher C-rates due to its lower electronic conductivity compared to LiCoO_2 and $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. In order to use $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ in high power batteries, further improvement is necessary. So, Co-doping in $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ was studied to get a good rate capability and a higher capacity [2]. Various kinds of metal doping were also investigated to improve electrochemical properties [3].

In this study, we report the synthesis of $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x = 0, 0.02$) via co-precipitation and electrochemical properties.

2. Experimental

The $[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x](\text{OH})_2$ ($x = 0, 0.02$) compounds were synthesized by co-precipitation. An aqueous solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ were used as the starting materials and NaOH solution and desired amount of NH_4OH solution (aq) as a chelating agent were also used. The obtained $[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x](\text{OH})_2$ ($x = 0$ and 0.02) powders were dried in 110 °C for 12 h to remove adsorbed water. Finally, powders were simply mixed with Li_2CO_3 using ball-miller for 4 h, and then the mixed powders were calcined at 950 °C in a box furnace.

Powder X-ray diffraction (Rigaku, Rint-2000) using $\text{Cu K}\alpha$ radiation was used to identify crystalline phase of the prepared powders. The morphology of the powders was recorded using a scanning electron microscope (SEM, JSM 6400, JEOL, Japan).

Chemical compositions of the prepared powder were analyzed with an atomic absorption spectroscopy (Vario 6, Analyticjena).

Electrochemical performance of the prepared powder was evaluated with coin type cell (CR2032). The positive electrode and the lithium metal negative electrode were separated by the porous polypropylene (PP) film. The positive electrode was fabricated with the mixture of the prepared powder and conducting binder (mixture of teflonized acetylene black (TAB) and graphite). The mixture was carefully ground and pressed on a 2.0 cm^2 stainless screen by hydraulic pressing. The electrolyte

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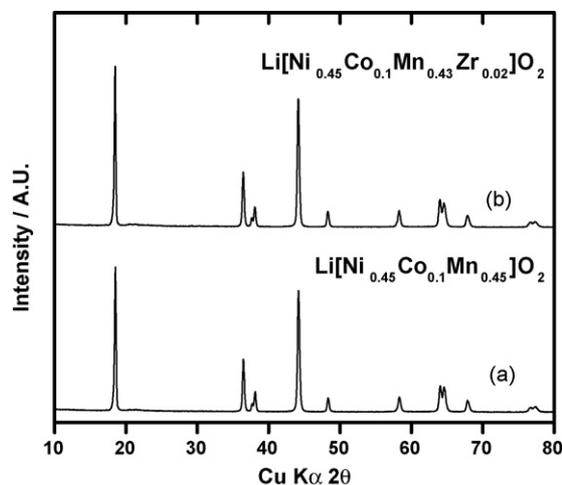


Fig. 1. XRD patterns of the prepared (a) $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ and (b) Zr-doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$.

was a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1 M LiPF_6 by volume. The cells were charged and discharged in the voltage range of 3.0–4.6 V at a constant current density of 0.4 mA cm^{-2} (0.20 C).

Differential scanning calorimetry (DSC) experiment was carried out for positive electrode material by fully charging the coin cell to 4.6 V followed by constant voltage charge. The fully charged cell was opened in an Ar-filled dry room. Measurements were carried out in 200 PC differential scanning calorimeter (NETZSCH, Germany) with a temperature scan rate of 5°C min^{-1} .

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the prepared powders $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0, 0.02$) calcined at 950°C . All prepared powder can be indexed to the hexagonal $\alpha\text{-NaFeO}_2$ structure with a space group of $R\bar{3}m$. Partial Zr doping did not change the host structure based on the XRD patterns. It can be observed from Fig. 1 that there is a split between (1 0 8)/(1 1 0) peaks, indicating that the partial Zr-doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ was successfully synthesized without change of the host structure. The Rietveld refinement was performed to determine the crystal structure of the prepared $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ [4]. The space group of $R\bar{3}m$ was chosen as the best structure model. The Rietveld refinement patterns of the $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ was shown in Fig. 2. The calculated lattice constants and unit cell volume of $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ are summarized in Table 1.

Table 1
Structural parameters obtained from Rietveld refinement of $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ and Zr-doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$

The amount of Zr	a (Å)	c (Å)	Ni^{2+} in Li layer (%)	R_{wp} (%)
Zr=0	2.8806	14.2825	6.5	11.3
Zr=0.02	2.8804	14.2899	5.8	11.7

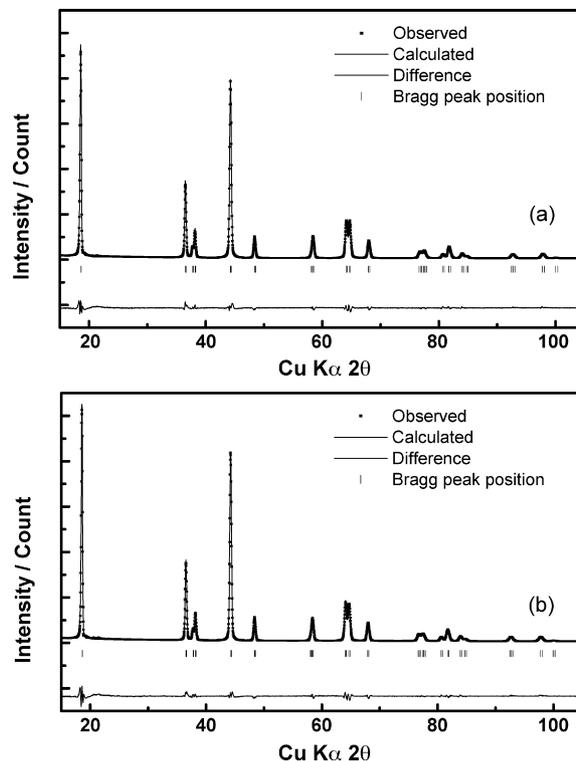


Fig. 2. Rietveld refinement XRD patterns of the prepared (a) without Zr doping $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ and (b) Zr-doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$.

The refinements resulted in good fit between the observed and the calculated patterns. As Zr was doped, the lattice constant (a) the $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}]\text{O}_2$ slightly decreased from 2.8806 \AA ($x=0$) to 2.8804 \AA ($x=0.02$). On the other hand, lattice constant (c) increased from 14.2825 \AA ($x=0$) to 14.2899 \AA ($x=0.02$). In order to determine the cationic mixing in Li layer, Ni^{2+} ion amount in Li layer was determined based on the Rietveld analysis shown in Table 1. When Zr was doped in the structure of the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$, Ni^{2+} amount in Li layer was reduced from 6.5% ($x=0$) to 5.8% ($x=0.02$). The Rietveld analysis suggested that Zr doping may suppress the cation mixing in Li layer [5].

Fig. 3 is the SEM image of the prepared $[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}](\text{OH})_2$ ($x=0$ and 0.02) and $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.1}\text{Mn}_{0.45-x}]\text{O}_2$ ($x=0$ and $x=0.02$). As seen from Fig. 3(a) and (b) the $[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x](\text{OH})_2$ ($x=0$ and 0.02) particle have a spherical shape with the average particle size of less than $10 \mu\text{m}$ in a diameter. After firing at high temperature (950°C) with Li_2CO_3 , the obtained $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0$ and $x=0.02$) particles still maintained the spherical shape and the similar particle size to the prepared precursor (Fig. 3(c) and (d)). The $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0$ and $x=0.02$) consists of the submicron sized-primary particles.

The electrochemical properties of the Zr-doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0$ and $x=0.02$) initially evaluated by galvanostatic charge and discharge at a constant current of 40 mA g^{-1} in the voltage range of 3.0–4.6 V.

Fig. 4 shows the initial charge and discharge curves of the $\text{Li}/\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0$ and $x=0.02$) cells in the voltage range of 3.0–4.6 V. The $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$

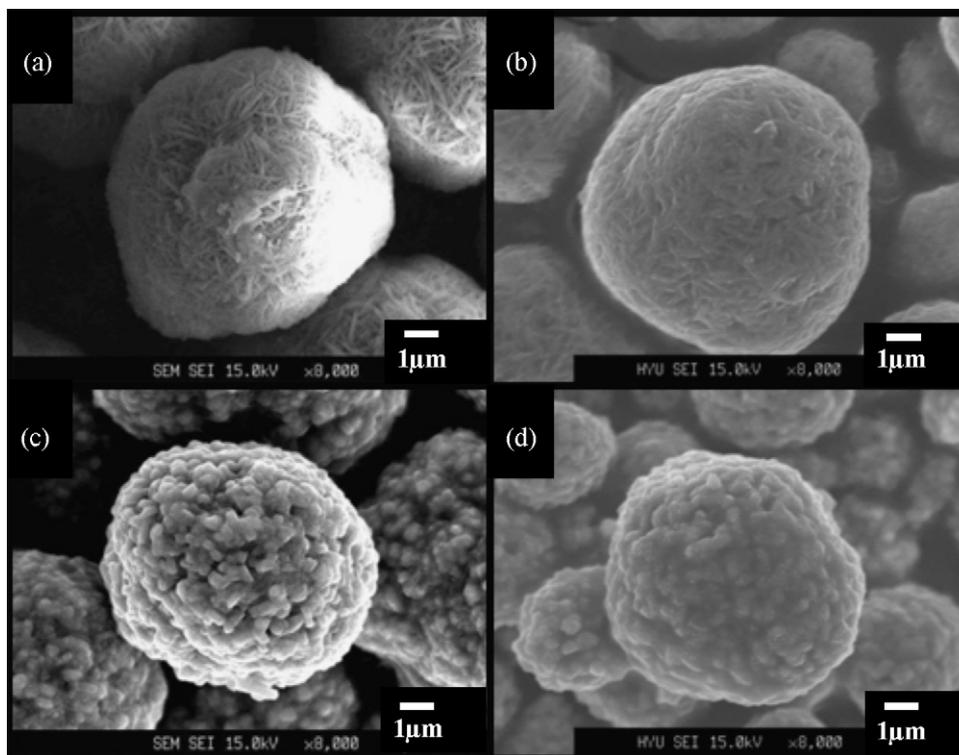


Fig. 3. SEM images of (a) $[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}](\text{OH})_2$, (b) $[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}](\text{OH})_2$, (c) $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ and (d) $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$.

($x=0$) and $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0.02$) cells delivered an initial discharge capacity of 187 mAh g^{-1} and 179 mAh g^{-1} , respectively. The overall voltage profile of all $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0$ and 0.02) are similar in the test voltage range.

The $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}\text{Zr}_{0.02}]\text{O}_2$ cell initially delivered lower capacity (179 mAh g^{-1}) than that of the $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$. However, the Zr-doped material exhibits better cycling performance over the 80 cycles. The capacity retention of the Zr-doped electrode is about 96% of the initial capacity at 80th cycle (91% for $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$) as shown in Fig. 5.

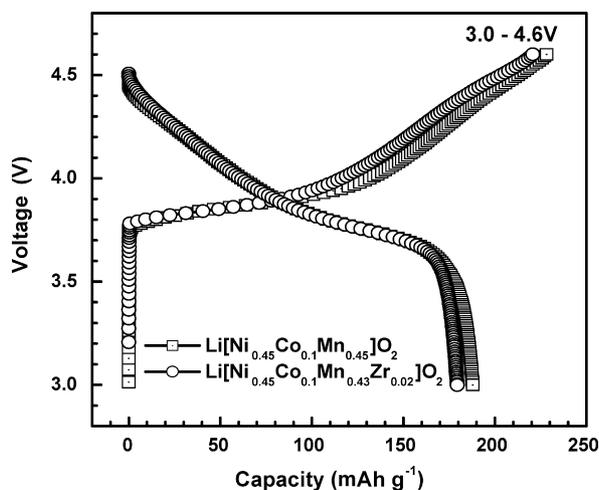


Fig. 4. Initial charge–discharge curves of the prepared (a) $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ and (b) $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$ coin cell in the voltage range of 3.0–4.5 V.

The thermal stability of the $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}]\text{O}_2$ ($x=0$ and $x=0.02$) was evaluated by DSC (differential scanning calorimetry). Fig. 6 shows the DSC traces of $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.5}]\text{O}_2$, and $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$ in the charged state of 4.6 V. The $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$ shows better thermal stability than $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$. $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ shows the major exothermic peak at 251.1°C . The major exothermic peak was shifted to 289.4°C for the Zr-doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0.02$). For $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ a small exothermic reaction was observed before the major exothermic reaction. In terms of peak temperature and the amount of heat (ΔH), Zr-doped material can be considered as thermally more stable than undoped material ($\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$) [6].

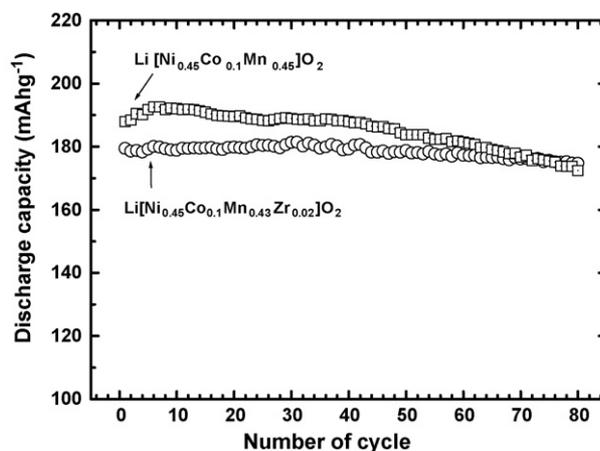


Fig. 5. The specific capacity vs. number of cycle for $\text{Li}/\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0$ and $x=0.02$) cells in the voltage range of 3.0–4.6 V.

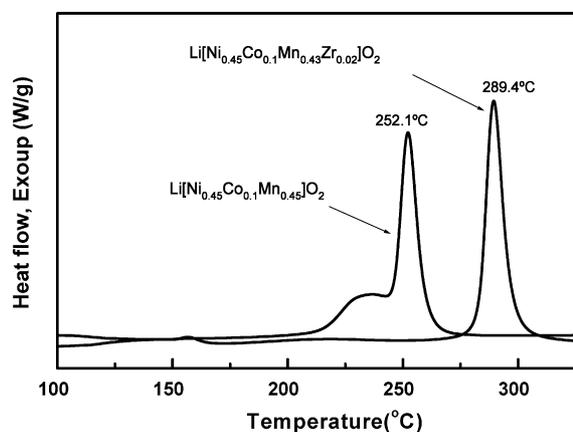


Fig. 6. DSC traces of the delithiated $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0$ and $x=0.02$) at 4.6 V, scan rate = 5°C min^{-1} .

4. Conclusion

$\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0, 0.02$) was synthesized via co-precipitation method. To improve the electrochemical performance and thermal stability, Zr was partially doped into $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$. Partially Zr-

doped $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45-x}\text{Zr}_x]\text{O}_2$ ($x=0.02$) shows better cycling performance and stable thermal stability. The major exothermic reaction was delayed from 252.1°C to 289.4°C . Also, the overall heat generated from exothermic reaction was reduced by 38% (4238 J g^{-1} for $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$ and 2690 J g^{-1} for $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.43}\text{Zr}_{0.02}]\text{O}_2$).

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