Enhanced Electrochemical Properties of Zr$^{4+}$-doped Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ Cathode Material for Lithium-ion Battery at Elevated Temperature

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The typical co-precipitation method was adopted to synthesized the Li-excess Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) series cathode materials. The influences of Zr$^{4+}$ doping modification on the microstructure and micromorphology of Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ cathode materials were studied intensively by the combinations of XRD, SEM, LPS and XPS. Besides, after the doping modification with zirconium ions, Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ cathode demonstrated the lower cation mixing, superior cycling performance and higher rate capacities. Among the four cathode materials, the Li$_{1.20}$[Mn$_{0.50}$Zr$_{0.02}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ exhibited the prime electrochemical properties with a capacity retention of 88.7% (201.0 mAh g$^{-1}$) after 100 cycles at 45 °C and a discharge capacity of 114.7 mAh g$^{-1}$ at 2 C rate. The EIS results showed that the Zr$^{4+}$ doping modification can relieve the thickening of SEI films on the surface of cathode and accelerate the Li$^+$ diffusion rate during the charge and discharge process.

Recently, the Li-excess Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (0.6Li$_2$MnO$_3$$\cdot$0.4LiNi$_{0.50}$Co$_{0.20}$Mn$_{0.30}$O$_2$) materials have attracted much study as cathodes for LIBs owing to the high specific discharge capacity (up to 250 mAh g$^{-1}$) and less cost$^{(1)}$. With further research, people have discovered that the Li$_3$MnO$_3$ phase (one of the components in the Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$) will be activated and participate in the electrochemical reactions only when the cell voltage is charged to exceed 4.5 V$^{(4)}$. However, the high working voltage will cause some drawbacks, such as severe capacity degradation and poor thermal stability, which restrict the practical applications, especially in EV and HEV$^{(5)}$. Moreover, when the batteries have been used in the high temperature circumstance, the side reaction between the cathode and electrolyte will be more severe in comparison with the traditional cathode materials, such as LiCoO$_2$ or LiNi$_{0.50}$Co$_{0.20}$Mn$_{0.30}$O$_2$ owing to the high working voltage for the Li-excess Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ materials$^{(6)}$.

To maintain the stability of the cathode at high temperature, considerable effort has been made to resolve the intrinsic defects. For example, the surface coating modification can effectively protect the cathode from reacting with the electrolyte and retard the thickening of SEI film during cycling. In addition, the suppression of the layered-to-spinel transformation for the Li-excess cathode materials can be obtained by the compact coating layer, leading to the improved electrochemical properties$^{(8-12)}$. The ion doping modification can stabilize the cathode crystal structure and suppress the layer structural damage$^{13,14}$. However, the surface coating modification technology has been complicated and the coating effect demonstrates to be difficult to control, while the ion doping modification shows the easy accessibility and obvious synthetic efficiency$^{15}$. Therefore, the ion doping modification has been regarded as the competitive method to enhance the electrochemical properties of the Li-excess Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ materials.

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Numerous studies have shown that the Zr$^{4+}$ doping modification can effectively enhance the cyclical stability and rate capacity of cathodes. For example, when Zr$^{4+}$ was doped into the LiCoO$_2$ by using the ultrasonic spray pyrolysis method, the LiCo$_{0.99}$Zr$_{0.01}$O$_2$ delivered the discharge capacity of 108 mAh g$^{-1}$ at 1 C in the voltage range of 3.0–4.2 V after 50 cycles, while the un-doped sample rapidly dropped down to 23 mAh g$^{-1}$ at the same condition$^{16}$. When the LiNi$_{0.52}$Zr$_{0.08}$Mn$_{0.40}$O$_2$ was doped modification with Zr$^{4+}$ by solid-state method reaction, the Li$_{1.20}$[Mn$_{0.52}$Zr$_{0.08}$Co$_{0.08}$]O$_2$ demonstrated the much more enhanced rate capability than that of the LiNi$_{0.52}$Mn$_{0.40}$O$_2$ by the suppression of electrode polarization$^{17}$. While the radius of Zr$^{4+}$ (0.072 nm) is larger than those of Mn$^{3+}$ (0.053 nm), Ni$^{2+}$ (0.069 nm), Co$^{3+}$ (0.0685 nm) in the transition-metal layer, the Zr$^{4+}$ adulteration will expand the diffusion path of Li$^+$ insertion/extraction, leading to the improved electrochemical properties. On the other hand, the bond energy of Zr–O has found to be stronger than those of Ni–O Co–O and Mn–O, which will contribute to stabilizing the structure of cathode$^{18}$. Based on the above evidence, Zr$^{4+}$ will be an attractive doping element to dope into the Li-excess Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ and enhance the electrochemical properties.

In the work, the Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) series samples have been synthesized via using carbonate co-precipitation method. And then the combination of microstructural, particle morphology and electrochemical properties has been surveyed to evaluate the influence of different Zr$^{4+}$ doping contents into Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ cathode.

Experimental

The Li-excess Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) series cathode materials were synthesized via using the carbonate co-precipitation method to synthesize the carbonate precursors, followed by sintering with LiOH·H$_2$O powder at high temperatures to obtain the cathode materials. The typical synthesis route has been shown as follows: (1) The stoichiometric amounts of MnSO$_4$·H$_2$O, NiSO$_4$·6H$_2$O, CoSO$_4$·7H$_2$O and Zr(NO$_3$)$_4$·5H$_2$O were dissolved in distilled water to obtain a transparent solution; (2) Then the appropriate amount of NH$_3$·H$_2$O, as chelating agent and Na$_2$CO$_3$, as precipitant, were dropped into the above solution to make the metal ions deposit uniformly; (3) The acquired [Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]CO$_3$ precursors were washed, with deionized water until the impurities eliminate completely; (4) Then the stoichiometric amount of [Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]CO$_3$ precursors and an excess 3 wt.% amount of LiOH·H$_2$O powder were mixed uniformly, followed by pre-heated at 500°C for 6 h and finally calcined at 950°C for 12 h in tube furnace to acquire the Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples.

To investigate the influence of the Zr$^{4+}$ doping on the crystal structure of Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$, the XRD measurement were carried out by using Rigaku RINT2400 X-ray diffractometer with Cu Kα radiation in the 10° ≤ 2θ ≤ 80°, accompanied by a step size of 0.02° and a count time of 10.0s. Rietveld refinement of the cathode powder diffraction patterns were performed by using the GSAS/EXPGUI program. The morphologies of Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) were observed by using scanning electron microscopy (SEM, Ultra 55, Zeiss) and high-resolution transmission electron microscopy (TEM, FEI Titan G2 60–300) equipped with energy-dispersive X-ray spectroscopy (EDX, Oxford) to test the elemental distributions of cathode material (x = 0.02). The particle size was measured by using laser particle size Analysis (LPS, TOOLSO, 2005A). The chemical states of the doping element were determined by using X-ray photoelectron spectroscopy (XPS, Perkin Elmer PHI 1600). And the XPS spectra were fitted by using XPSPEAK software. The elemental composition, i.e. Ni, Co, Mn and Yb, was detected by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer, iCAP 6000). Phase transformation studies of original and cycled Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.02) were carried out using a micro–Raman spectrometer (LabRAMHR Evolution, HORIBA).

The electrochemical properties of Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples were measured by using galvanostatic charge and discharge with the coin cell of type CR2025. The coin cells were assembled by using the GSAS/EXPGUI program. The morphologies of Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples, 10 wt.% carbon black and 5 wt.% polyvinylene fluoride were evenly mixed to form the cathode slurry; Then the slurry was casted onto Al foil by using a smudge stick and dried at 110°C for 12 h in vacuum drying oven, followed by squeezed and punched into a circular disc with d = 12 mm; (3) The as-prepared cathode plate, the lithium metal plate as anode, the Celgard 2400 as the separator and 1 M LiPF$_6$ dissolved in EC/DMC at mass ratio of 1:1 as the electrolyte were assembled in an argon-filled glove box to form the coin cells. The Galvanostatic charge-discharge tests were carried out by using a Land CT2001A (Wuhan, China) tester.

The cells were charged and discharged in the voltage range of 2.0 to 4.8 V at the different current densities (1C = 250 mAh g$^{-1}$). In addition, the CHI660D workstaton was used to perform the electrochemical impedance spectroscopy (a frequency range from 0.01 Hz to 100 kHz and perturbation amplitude of 5 mV) and the cyclic voltammogram (a voltage range from 2.0 V to 4.8 V with a scanning rate of 0.1 mV s$^{-1}$).

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples. The as-prepared samples have mainly demonstrated the typical XRD patterns of the hexagonal α-NaFeO$_2$ structure with the space group R-3m (the LiMO$_2$ features), except for the weak super lattice peaks between 20° and 25°, which are related to the Li$_2$MnO$_3$ phase, corresponding to the monocline unit cell C2/m$^{19,20}$. In addition, the distinct splitting of (006)/(102) and (018)/(110) peaks have indicated that the as-prepared cathode materials have formed a well-developed hexagonal layered structure$^{21}$. Besides, to further investigate the cation mixing between the Ni$^{2+}$ and Li$^+$ in the LiMO$_2$ main phase, the Rietveld refinement of the diffraction patterns was performed based on the R-3m (used for LiNi$_{0.50}$Co$_{0.20}$Mn$_{0.30}$O$_2$ phase) and C2/m (used for Li$_2$MnO$_3$ phase), as is shown in Fig. 1. And the structural parameters obtained from the refinement for the Li$_{1.20}$[Mn$_{0.52}$–Zr$_{x}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples are listed in Table 1. It can be seen that with the Zr$^{4+}$ doping content increasing, the lattice parameters a and c of LiNi$_{0.50}$Co$_{0.20}$Mn$_{0.30}$O$_2$ phase have gradually
rised owing to the larger radius of Zr$. The larger lattice parameters $a$ and $c$ will contribute to enhancing the Li$^+$ diffusion rate during the charge and discharge process$^{29,30}$. Besides, the $c/a$ ratio is related to the cation mixing and a high ratio represents the well cation ordering has been formed$^{29}$. It can be observed the Zr$^{4+}$-doped samples deliver the higher $c/a$ ratio than that of the un-doped cathode, indicating the cation mixing of the as-prepared samples has been improved after the Zr$^{4+}$ doping. Besides, according to the reports of J.R. Dahn$^{24,25}$, the nominal formula of Li$_{1.20}$[Mn$_{0.52}$Zr$_{0.00}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ can be assumed as [Li$_{1−x}$Ni$_{x}$][Li$_{1.20}$Zr$_{0.00}$Ni$_{0.20}$Co$_{0.08}$]O$_2$. The GSAS/EXPGUI program has been adopted to calculate the refined lattice structural data of as-prepared samples, as is shown in Table 1. It is clear that the amount of Ni in Li site for the Zr$^{4+}$-doped samples is lower than that of the pristine Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ sample. And when the Zr$^{4+}$ doping content aggrandizes, the amount of Ni in Li site first decreases from 0.059 to 0.041 and 0.032, then increases to 0.039, the Li$_{1.20}$[Mn$_{0.52}$Zr$_{0.02}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ has demonstrated the optimal cation ordering. The lower cation mixing will not only suppress formation of spinel-like phase, but also improve the layered structure stability, finally contribute to enhancing the cyclic performance. Besides, the occupancy of Zr cations in 3b-site are respectively 0, 0.012, 0.019 and 0.031 with the Zr$^{4+}$ doping contents increasing, indicating the molar ratio for Zr$^{4+}$ doping can be designed experimentally. The Zr$^{4+}$ doping can enlarge the lattice parameters, which facilitates Li-ion diffusion and subsequently enhances the high-rate capability.

Figure 2 shows the SEM images of the Li$_{1.20}$[Mn$_{0.52}$Zr$_{0.00}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) samples. The as-prepared samples are composed of numerous crystallites with a diameter of 200~700 nm. All particles present the similar morphology of rock-like grains without obvious aggregation. In addition, with the Zr$^{4+}$ doping content increasing, the crystal particles surface become more smooth and the size of the particles become larger, which implies the crystallinity of the particles can be enhanced after the Zr$^{4+}$ doping. To further analyze the influence of the Zr$^{4+}$ doping on the cathode particles size, the size distribution of the Li$_{1.20}$[Mn$_{0.52}$Zr$_{0.00}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) samples have been measured, as is shown in Fig. 3. It is obvious that the size of $D_{50}$ gradually aggrandizes when the Zr$^{4+}$ doping content increases, as is shown by the arrows, which is in good consistent with the observation of SEM images. A small amount of doped Zr ions may form continuous grain boundary phases in the Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ particles. These continuous grain boundary phases could enhance the mass diffusion transport at grain boundaries, finally promote the grain growth of Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$. And the well crystallization will help to ameliorate the electrochemical properties of cathode. Besides, the STEM images of Li$_{1.20}$[Mn$_{0.52}$Zr$_{0.02}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ and corresponding elemental maps of Ni, Mn, Co and Zr is shown in Fig. 4. The Fig. 4 demonstrates that not only the Ni, Co and Mn atoms have been distributed homogeneously, but also the doping element Zr atom have been evenly distributed in the cathode particles rather than segregated on the oxide surface, indicating the Zr$^{4+}$ doping technology has obtained the obvious synthetic efficiency. Based on the above analysis, it has proved that the Zr$^{4+}$ has been successfully doped into the Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ cathode material with uniform dispersion. The uniform dispersion of Zr dopant will make the function of Zr$^{4+}$ doping modification more stability, which may be ready to provide a better cycling performance to some extent.

Figure 5 shows X-ray photoelectron spectroscopy (XPS) results of Zr, Mn, Ni and Co for the Li$_{1.20}$[Mn$_{0.52}$Zr$_{0.00}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.02$) samples. In Fig. 5(a), the obvious peaks at the binding energies of 184.9 eV and 182.6 eV are assigned to Zr 3$d_{3/2}$ and Zr 3$d_{5/2}$, respectively, which corresponds to the Zr-O bonds at the state of Zr$^{4+}$28. In Fig. 5(c), the obvious peaks at the binding energies of 854.2 eV is assigned to Ni 3$d_{3/2}$, which corresponds to the oxidation state of Ni$^{2+}$ and Ni$^{3+}$ after fitting, respectively$^{29,30}$. Besides, it can be calculated that the relative content of Ni$^{2+}$ decreased after zirconium doping owing to the reduction of cation mixing degree. Compared with the pristine Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$, the binding energies of Mn$_{2p}$ and Co$_{2p}$ peaks for Li$_{1.20}$[Mn$_{0.52}$Zr$_{0.02}$Ni$_{0.20}$Co$_{0.08}$]O$_2$, have no obvious changes, indicating the chemical properties of the Mn and Co elements have not been changed after the Zr$^{4+}$ doping modification.
Table 1. Structural parameters obtained from the refinement by the Rietveld method of the X-ray diffraction data recorded for the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples.

| Sample | Lattice parameters | Cations occupancy (%) | Reliability factors |
|--------|--------------------|------------------------|---------------------|
|        | LiNi$_{0.50}$Co$_{0.20}$Mn$_{0.30}$O$_2$ phase | Li$_2$MnO$_3$ phase |                     |
|        | a(Å) | c(Å) | c/a | a(Å) | b(Å) | c(Å) | at. Li/Ni occ. | 3b Ni/Li occ. | 3b Mn occ. | 3b Zr occ. | $R_p$ (%) | $R_w$ (%) | $\chi^2$ |
| x = 0  | 2.8483 (2) | 14.2154 (1) | 4.9907 | 4.9812 (1) | 8.5582 (1) | 5.0542 (1) | 1.141/0.059 (2) | 0.141/0.059 (2) | 0.518 (2) | 0 | 0.082 (2) | 7.88 | 9.16 | 1.59 |
| x = 0.01 | 2.8515 (2) | 14.2357 (2) | 4.9925 | 4.9820 (2) | 8.5588 (1) | 5.0549 (1) | 1.159/0.041 (3) | 0.159/0.041 (2) | 0.509 (3) | 0.012 (3) | 0.079 (2) | 8.53 | 9.58 | 1.75 |
| x = 0.02 | 2.8531 (1) | 14.2469 (2) | 4.9939 | 4.9825 (1) | 8.5592 (2) | 5.0552 (1) | 1.168/0.032 (2) | 0.168/0.032 (3) | 0.500 (3) | 0.019 (2) | 0.081 (3) | 8.21 | 9.62 | 1.69 |
| x = 0.03 | 2.8539 (1) | 14.2522 (2) | 4.9934 | 4.9818 (1) | 8.5586 (2) | 5.0547 (1) | 1.161/0.039 (2) | 0.161/0.039 (2) | 0.491 (2) | 0.031 (1) | 0.078 (2) | 7.32 | 8.93 | 1.50 |

Figure 2. SEM images of the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples.

Figure 3. Size distribution of the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples.
To acquire the elements composition of Li$_{1.20}$[Mn$_{0.52}$−$x$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples, the ICP test was adopted and the results is demonstrated in Table 2. The measurement values of Ni, Co, Mn and Zr elements content are approximately equal to the theoretical analysis values, indicating that the molar ratios for Ni, Co, Mn and Zr elements have been synthesized in accordance with the experimental requirements.

Figure 6 shows the initial charge-discharge curves of the Li$_{1.20}$[Mn$_{0.52}$−$x$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) samples in the voltage range of 2.0~4.8 V at 0.1 C rate. All samples have demonstrated the similar charge curve for the two typical charge steps. The first step of charging process exists in the potential region from 2.0 V to 4.5 V, corresponding to the Li$^+$-extraction from layer LiNi$_{0.50}$Co$_{0.20}$Mn$_{0.30}$O$_2$ component and the oxidation of Ni$^{2+}$ to Ni$^{4+}$ and Co$^{3+}$ to Co$^{4+}$.$^{31,32}$ For the second step, all samples exhibit a long voltage plateau at about 4.5 V, where the irreversible Li$^+$ extract and oxygen release from the Li$_2$MnO$_3$ phase.$^{33,34}$ Table 3 shows the initial cycle electrochemical data of Li$_{1.20}$[Mn$_{0.50}$Zr$_{0.02}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ (x = 0, 0.01, 0.02, 0.03) cathodes at 0.1 C rate in the voltage range of 2.0~4.8 V. With the Zr$^{4+}$ doping content increasing, the initial charge capacities of as-prepared samples gradually decline owing to the electrochemical inactive of doped Zr$^{4+}$, While the discharge capacities first enhance and then decrease and the Li$_{1.20}$[Mn$_{0.50}$Zr$_{0.02}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ sample delivers the highest discharge capacity of 272.4 mAh g$^{-1}$. In addition, the lowest irreversible capacity loss for the Li$_{1.20}$[Mn$_{0.50}$Zr$_{0.02}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ sample has promoted the highest initial coulombic efficiency, which indicates that the Zr$^{4+}$ doping can restrain the release of oxygen from the Li$_2$MnO$_3$ and decrease the irreversible capacity loss. Compared to the bonds break energy values for the $\Delta H_{\text{f298}}$(Ni-O) = 391.6 kJ mol$^{-1}$, $\Delta H_{\text{f298}}$(Co-O) = 368 kJ mol$^{-1}$ and $\Delta H_{\text{f298}}$(Mn-O) = 402 kJ mol$^{-1}$, the Zr-O delivers the higher bonds break energy value of $\Delta H_{\text{f298}}$(Zr-O) = 760 kJ mol$^{-1}$, therefore with the Zr$^{4+}$

**Figure 4.** STEM images of Li$_{1.20}$[Mn$_{0.50}$Zr$_{0.02}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ and corresponding elemental maps of Ni, Mn, Co and Zr.
doping, the oxygen release of the Zr\textsuperscript{4+}-doped samples will face more resistance than the un-doped sample, subsequently the irreversible capacity loss has been suppressed\textsuperscript{17}.

Figure 7 shows the rate capabilities of the Li\textsubscript{1.20}[Mn\textsubscript{0.52−x}Zr\textsubscript{x}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2} (\(x=0, 0.01, 0.02, 0.03\)) samples with various current densities in the voltage range of 2.0~4.8 V. Obviously, the Li\textsubscript{1.20}[Mn\textsubscript{0.52−x}Zr\textsubscript{x}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2} (\(x=0.01, 0.02, 0.03\)) samples have all demonstrated the higher discharge capacities than those of the pristine Li\textsubscript{1.20}[Mn\textsubscript{0.52}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2} sample delivers the optimum rate capacity. In addition, with current density increasing, the superiority has become particularly evident, indicating the advantage of Zr\textsuperscript{4+} doping on the rate capacity of Li\textsubscript{1.20}[Mn\textsubscript{0.52}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2} is much more significant at high rate. As is seen in Table 4, the discharge capacity of the Li\textsubscript{1.20}[Mn\textsubscript{0.50}Zr\textsubscript{0.02}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2} is only 8.8 mAh g\textsuperscript{−1} higher than that of the bare Li\textsubscript{1.20}[Mn\textsubscript{0.52}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2}. However when the current density enhances to 5 C rate, the bare sample shows a discharge capacity of 86.6 mAh g\textsuperscript{−1} and this value is increased to 105.3, 114.7 and 108.6 mAh g\textsuperscript{−1} for the Li\textsubscript{1.20}[Mn\textsubscript{0.52−x}Zr\textsubscript{x}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2} (\(x=0.01, 0.02, 0.03\)) samples, respectively. The superior rate capacity of the Zr\textsuperscript{4+}-doped samples have mainly been attributed to the fast Li\textsuperscript{+} migration speed during the charge and discharge process. One reason is that with the Zr\textsuperscript{4+} doping, the larger lattice parameters of the Zr\textsuperscript{4+}-doped samples have contributed to enhancing the Li\textsuperscript{+} diffusion speed. Besides, the better crystallization property of the Zr\textsuperscript{4+}-doped samples will also help to strengthen the conductivity ability of ions and electrons during the charge-discharge process.

Figure 8 shows the cycling performance of the Li\textsubscript{1.20}[Mn\textsubscript{0.52−x}Zr\textsubscript{x}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2} (\(x=0, 0.01, 0.02, 0.03\)) samples at 0.5 C rate in the voltage range of 2.0~4.8 V at room temperature (25 °C). It can be observed that the Zr\textsuperscript{4+}-doped samples have delivered the higher discharge capacity than that of the bare Li\textsubscript{1.20}[Mn\textsubscript{0.52}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2}. And after 100 cycles, the corresponding capacity retentions still maintain 86.9%, 88.5%, 90.4% and 88.7%, respectively. It has proved that the Zr\textsuperscript{4+} doping modification can enhance the specific capacity and cycling performance of the Li\textsubscript{1.20}[Mn\textsubscript{0.52}Ni\textsubscript{0.20}Co\textsubscript{0.08}]O\textsubscript{2} cathode, owing to the lower cation mixing and faster Li\textsuperscript{+} migration speed for the Zr\textsuperscript{4+}-doped samples. Besides, the discharge voltage plateau will gradually decrease during the cyclic process, owing to the enlargement of polarization and the formation of spinel-like phase for cathode materials\textsuperscript{35}. It can be observed that the discharge voltage drops to lower plateau for...
the all cathodes after different cycles, as the arrows pointed in Fig. 9. Table 5 shows the declining value of voltage plateau between 1st and 100th ($\Delta V$) for the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) samples and with the Zr$^{4+}$ doping contents increasing, the $\Delta V$ values are 0.298, 0.259, 0.211 and 0.236 V, respectively. The smaller $\Delta V$ values of the Zr$^{4+}$-doped cathodes have indicated that the Zr$^{4+}$ doping modification can improve the layered structural stability by restraining the cation mixing between the Ni$^{2+}$ and Li$^{+}$ and the formation of spinel-like phase. While the smaller $\Delta V$ values of Zr$^{4+}$-doped cathodes will contribute to maintaining the high power output of cells.

| Sample | Theoretical molar ratio | Measurement molar ratio |
|--------|-------------------------|-------------------------|
|        | Mn | Ni | Co | Zr | Mn | Ni | Co | Zr |
| $x = 0$ | 0.540 | 0.130 | 0.130 | 0 | 0.542 | 0.129 | 0.129 | 0 |
| $x = 0.01$ | 0.530 | 0.130 | 0.130 | 0.010 | 0.533 | 0.129 | 0.128 | 0.010 |
| $x = 0.02$ | 0.520 | 0.130 | 0.130 | 0.020 | 0.518 | 0.131 | 0.130 | 0.021 |
| $x = 0.03$ | 0.510 | 0.130 | 0.130 | 0.030 | 0.512 | 0.128 | 0.131 | 0.029 |

Table 2. Relative contents of Ni, Co, Mn and Zr in the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) samples.

Figure 6. Initial charge-discharge curves of the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) samples in the voltage range of 2.0~4.8 V at 0.1 C rate.

Figure 7. Rate capabilities of the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) samples with various current densities in the voltage range of 2.0~4.8 V.
The inhomogeneity phase of the ZrO₂ existed in the compound can hinder the Li-intercalation/deintercalation process at high temperature, the cathodes have suffered from the attack of HF, dissolution of the Mn ions, structural change and decomposition of electrolyte on the cathode surface. While the stronger total metal–oxygen bonding for the Zr₄⁺ doped Li₁.2₀[Mn₀.5₂Ni₀.2₀Co₀.0₈]O₂ samples exhibit the discharge capacity of 180.2, 190.7 and 176.9 mAh g⁻¹ respectively, corresponding that the capacity retention first enhance from 86.3% to 88.7% and then decline to 86.5%. As for the bare Li₁.2₀[Mn₀.5₂Ni₀.2₀Co₀.0₈]O₂, the discharge capacity decreases acutely to 172.5 mAh g⁻¹ with the capacity retention of only 82.8%. During the charge-discharge process at high temperature, the cathodes have suffered from the attack of HF, dissolution of the Mn ions, structural change and decomposition of electrolyte on the cathode surface. While the stronger total metal–oxygen bonding for the Zr⁺⁺⁺ doped samples can contribute to stabilizing the structure of cathode during cycling, leading to the improved cycling performance. However, when the Zr⁺⁺⁺ doping content reaches to 0.03, the cycling performance of Li₁.2₀[Mn₀.5₂Ni₀.2₀Co₀.0₈]O₂ is not as good as that of the Li₁.2₀[Mn₀.5₀Zr₀.₀₂Ni₀.₂₀Co₀.₀₈]O₂ for that the inhomogeneity phase of the ZrO₂ existed in the compound can hinder the Li⁺⁺⁺ intercalation/deintercalation from the cathode.

To further understand the influence of Zr⁺⁺⁺ doping on the electrochemical properties of Zr⁺⁺⁺ doped Li₁.2₀[Mn₀.5₂Ni₀.2₀Co₀.0₈]O₂, the electrochemical impedance spectroscopy (EIS) for the four samples have been acquired, as is shown in Table 7. In the 1st cycle, the Rₛ values of Zr⁺⁺⁺ doped Li₁.2₀[Mn₀.5₂Ni₀.2₀Co₀.0₈]O₂ are lower respectively, corresponding to the impedance of Li⁺⁺⁺ migration across the SEI film (Rₛ) and CPEₛ, the impedance of charge transfer (R₉, and CPE₉) and the impedance of Li⁺⁺⁺ ion migration in the cathode (Zₛ). The corresponding equivalent circuit in Fig. 10(c) is used to simulate the Nyquist curves and the corresponding Rₛ, R₉ and Rₛ values can be acquired, as is shown in Table 7. The 1st cycle, the Rₛ values of Zr⁺⁺⁺ doped Li₁.2₀[Mn₀.5₂Ni₀.2₀Co₀.0₈]O₂ are lower...
than that of the bare one, therefore the superior initial discharge capacity can be obtained for the Zr$^{4+}$-doped Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$, which is in consistency with the results of Table 3. With the cycles going on, the SEI film will thicken, causing the increase of the $R_{sf}$ value. After 30 cycles, with the Zr$^{4+}$ doping contents increasing, the Zr$^{4+}$-doped Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$ samples deliver the $R_{sf}$ values of 445.8, 363.1 and 428.8 Ω respectively, corresponding that the $\Delta R_{sf}$ values first enhance from 287.1 to 210.8 and then drop to 284.9 Ω. As for the bare Li$_{1.20}$[Mn$_{0.52}$Ni$_{0.20}$Co$_{0.08}$]O$_2$, the $R_{sf}$ value rise promptly to 544.5 Ω, with the $\Delta R_{sf}$ value of 371.4 Ω. It indicates the samples after the Zr$^{4+}$ doping can relieve the thickening of SEI films on the surface of cathode, which contributes to decreasing the Li$^+$ migration resistance across the SEI films and enhancing the electrochemical properties.

Besides, the Li$^+$ diffusion rate ($D_{Li^+}$) in the cathode can be calculated using the following equations$^{41}$:

Figure 8. Cycling performance of the Li$_{1.20}$[Mn$_{0.52}$−$x$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x$ = 0, 0.01, 0.02, 0.03) samples at 0.5 C rate in the voltage range of 2.0~4.8 V at 25 °C.

Figure 9. Discharge profiles of the Li$_{1.20}$[Mn$_{0.52}$−$x$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x$ = 0, 0.01, 0.02, 0.03) samples from 2.0 V to 4.8 V at 0.5 C rate in the 1st, 30th, 60th and 100th cycles.
Figure 10. Cycling performance of the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) at 0.5 C rate in the voltage range of 2.0–4.8 V at 45 °C.

Figure 11. Nyquist plots of the Li$_{1.20}$[Mn$_{0.52-x}$Zr$_x$Ni$_{0.20}$Co$_{0.08}$]O$_2$ ($x = 0, 0.01, 0.02, 0.03$) samples at a charge state of 4.5 V in the 1st, 30th cycles and (e) the equivalent circuit used to fit the measured impedance spectra.
\[ \tau = +D \Delta F n AC (1) \]

\[ \tau_{\omega} = +ZR R (2) \]

where, \( F, n, A, C R \) is gas constant, \( T \) is the absolute temperature, \( F \) represents the Faraday constant, \( n \) is the number of electrons per molecule during oxidation, \( A \) corresponds to the area of the electrode-electrolyte interface, and \( C \) is the concentration of lithium ion, respectively. Besides, \( \tau_{\omega} \) is the Warburg coefficient of the bulk cathode, which can be calculated by the Eqs (2). Thereinto, the \( Z_{re} \) is the real part of impedance, \( \omega \) is the angular frequency and Fig. 12 shows the plots comparison of \( Z_{re} \) vs. \( \omega^{-1/2} \) for the Li\(_{1.20}[Mn_{0.52-x}Zr_{x}Ni_{0.20}Co_{0.08}]O_{2} \) (\( x = 0, 0.01, 0.02, 0.03 \)) samples after 30 cycles. Thus \( \tau_{\omega} \) can be obtained from the linear fitting of \( Z_{re} \) vs. \( \omega^{-1/2} \).

**Table 6.** Capacity retention and discharge capacity of Li\(_{1.20}[Mn_{0.52-x}Zr_{x}Ni_{0.20}Co_{0.08}]O_{2} \) (\( x = 0, 0.01, 0.02, 0.03 \)) at 0.5 C rate in the voltage range of 2.0–4.8 V at 45 °C.

| Sample | Initial discharge specific Capacity (mAh g\(^{-1}\)) | 100th Specific discharge capacity (mAh g\(^{-1}\)) | 100 cycles capacity retention (%) |
|--------|-----------------------------------------------|-----------------------------------------------|-------------------------------------|
| \( x = 0 \) | 208.3 | 172.5 | 82.8 |
| \( x = 0.01 \) | 221.8 | 191.4 | 86.3 |
| \( x = 0.02 \) | 226.6 | 201.0 | 88.7 |
| \( x = 0.03 \) | 218.0 | 188.5 | 86.5 |

**Table 7.** The simulated data of the Li\(_{1.20}[Mn_{0.52-x}Zr_{x}Ni_{0.20}Co_{0.08}]O_{2} \) (\( x = 0, 0.01, 0.02, 0.03 \)) cathodes at 4.5 V from EIS spectra using the equivalent circuit shown in Fig. 11(e).

| Sample | Cycle number | \( R_{s} (\Omega) \) | \( R_{d} (\Omega) \) | \( R_{ct} (\Omega) \) | \( \Delta R_{sf} (\Omega) \) |
|--------|--------------|----------------|----------------|----------------|----------------|
| \( x = 0 \) | 1st | 7.9 | 173.1 | 23.52 | 371.4 |
| 30th | 8.5 | 544.5 | 54.64 | 287.1 |
| \( x = 0.01 \) | 1st | 7.5 | 158.7 | 22.05 | 210.8 |
| 30th | 7.4 | 445.8 | 45.23 | 284.9 |
| \( x = 0.02 \) | 1st | 6.9 | 152.3 | 18.99 | 21.47 |
| 30th | 6.6 | 363.1 | 348.7 | 21.47 |
| \( x = 0.03 \) | 1st | 6.4 | 143.9 | 21.47 | 21.47 |
| 30th | 8.3 | 428.8 | 47.29 | 21.47 |

**Figure 12.** Plots comparison of \( Z_{re} \) vs. \( \omega^{-1/2} \) for the Li\(_{1.20}[Mn_{0.52-x}Zr_{x}Ni_{0.20}Co_{0.08}]O_{2} \) (\( x = 0, 0.01, 0.02, 0.03 \)) samples after 30 cycles.
respectively, higher than that (7.63 × 10^{-15} \text{ cm}^2 \text{ s}^{-1}) of the pristine electrode. Therefore, the Zr^{4+}-doped Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2 samples have demonstrated the superior rate capacity.

Figure 13 shows the Raman spectra of original and cycled Li_{1.20}[Mn_{0.52}Zr_{0.02}Ni_{0.20}Co_{0.08}]O_2 (x = 0, 0.02) (100 cycles at 45 °C). The Raman band at 427 cm\(^{-1}\) corresponds to the monoclinic Li_{1.20}MnO_2 phase, which can be observed in the spectrum of original Li_{1.20}[Mn_{0.52}Zr_{0.02}Ni_{0.20}Co_{0.08}]O_2 (x = 0) (100 cycles at 45 °C) and disappear in the cycled electrode in Fig. 13(b) owing to the disappearance of the monoclinic Li_{1.20}MnO_2 component after cycling.45 Besides, the other two significant Raman bands at 481 and 593 cm\(^{-1}\) for the Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2 (481 and 593 cm\(^{-1}\) for the Li_{1.20}[Mn_{0.52}Zr_{0.02}Ni_{0.20}Co_{0.08}]O_2 (x = 0) owing to the Zr^{4+} doping) belong to the bending \(E_1\) and stretching \(A_{3g}\) modes, respectively45 in Fig. 13(a). After 100 cycles, the Raman bands at 593 cm\(^{-1}\) for the Li_{1.20}[Mn_{0.52}Zr_{0.02}Ni_{0.20}Co_{0.08}]O_2 (x = 0, 0.02) have both shifted to higher values, indicating the cathode structure transformation from the layered to defect spinel structure.45 The Raman band for the Li_{1.20}[Mn_{0.52}Zr_{0.02}Ni_{0.20}Co_{0.08}]O_2 (x = 0, 0.02) has shifted from 593 to 602 cm\(^{-1}\) after 100 cycles, much lower than that of the pristine Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2 (from 593 to 615 cm\(^{-1}\)). Therefore, the Zr^{4+} doping have restrained the layered-to-spinel phase change of Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2 during cycling, forming the superior electrochemical properties by Zr doping.

Conclusions
In order to enhance the electrochemical properties of Li-excess Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2, the different contents of Zr^{4+} have been doped into the pristine Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2. After the Zr^{4+} doping, the cation mixing between Li^{2+} and Ni^{2+} has been lowered and the cathode particles have been aggrandized. In comparison with the pristine cathode, the Zr^{4+}-doped Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2 samples have demonstrated the more stable cycling performance and higher rate capacities. Especially at high temperature (45 °C), the Zr^{4+} doping modification has delivered the more obvious superiority. After 100 cycles, with the Zr^{4+} doping contents increasing, the Zr^{4+}-doped Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2 samples exhibit the capacity retentions of 86.3%, 88.7% and 86.5% respectively, larger than that (82.8%) of the bare Li_{1.20}[Mn_{0.52}Ni_{0.20}Co_{0.08}]O_2. The stronger total metal–oxygen bonding for the Zr^{4+}-doped samples has mainly contributed to stabilizing the structure of cathode and improving the cycling performance. The Zr^{4+} doping modification has provided a potential approach to enhance the electrochemical properties of the Li-excess cathodes for Li-ion battery.

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Author Contributions
Y. Lu conceived and designed this work, M. Pang and S. Shi assisted the experiments. Q. Ye did the XRD refinement, Z. Tian did the SEM, LPS and XPS test and T. Wang performed the electrochemical properties measurement. Y. Lu wrote the manuscript. All authors discussed the results on the manuscript and reviewed the manuscript.

Additional Information
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