INTRODUCTION

Lithium-ion batteries (LIBs) have been widely utilized as the large-scale power sources of electric vehicles, electronic devices, and stationary energy storage.\(^1\)\(^-\)\(^4\) Especially in recent years, owing to the rapid growth of electric vehicles, the demand for LIBs has increased dramatically.\(^5\)\(^,\)\(^6\) In order to increase the endurance mileage and reduce the cost of electric vehicles, the energy density and the cost of LIBs should be further optimized.\(^7\)\(^-\)\(^11\) However, the capacity of the commercialized cathode materials, such as lithium cobalt oxides (LiCoO\(_2\)), lithium iron phosphate (LiFeO\(_4\)), lithium manganese oxide (LiMn\(_2\)O\(_4\)), and LiNi\(_x\)Co\(_y\)Mn\(_{1-x-y}\)O\(_2\) (\(x < 0.6\)), has almost reached maximum value. Therefore, nickel-rich cathode materials, including LiNi\(_x\)Co\(_y\)Mn\(_{1-x-y}\)O\(_2\) (\(x \geq 0.6\)) and \(\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2\), have caught more and more attention because of the higher specific capacity and relatively low cost.\(^12\)\(^,\)\(^13\) Unfortunately, there are still significant drawbacks in the commercial practice of this cathode material. Owing to the large energy barrier in the oxidation from Ni\(^{2+}\) to Ni\(^{3+}\) and...
the similar ionic radius of Ni\(^{2+}\) (0.69 Å) and Li\(^+\) (0.76 Å). Li\(^+\)/Ni\(^{2+}\) cation mixing can be easily formed in nickel-rich cathode materials.\(^\text{14}\) Meanwhile, a large amount of Ni\(^{4+}\) is formed during highly delithiated process. The strong oxidizing ability of Ni\(^{3+}\) not only induces the pernicious side reactions between cathode materials and electrolyte, but also causes irreversible structural rearrangement from the original layered phase to the disordered layered in the bulk and to NiO-like rock-salt phases on the surface. Moreover, nickel-rich cathode materials occur in multiple phase transformation during charge and discharge processes, leading to mechanical stress and the pulverization of material particles.\(^\text{15}\) Consequently, nickel-rich cathode materials generally show a gradual fading of capacity and structural stability during cycling.

Cathode materials as the most important part of LIBs account for over 40 percent of the total cost.\(^\text{16}\) This situation can lead to the heavy use of valuable metals, such as Ni and Co. However, the resource reserves of these metals are limited, and the price of them is going up with the increasing demand.\(^\text{17,18}\) Meanwhile, spent LIBs are potentially hazardous due to the presence of flammable electrolyte and toxic elements.\(^\text{19-21}\) Therefore, it is necessary to develop suitable routes to regenerate spent LIBs. The typical recycling strategies for spent LIBs can be classified into two categories: pyrometallurgy and hydrometallurgy process.\(^\text{22}\) The hydrometallurgy process is considered to be the most promising route for the recycling of spent LIBs on account of high recovery rate, lower temperature, and desirable efficiency.\(^\text{23}\) It is noted that the leaching solution during hydrometallurgy process contains not only valuable metals mentioned before but also some impurities, such as Cu, Fe, and Al.\(^\text{24}\) It is worth noting that the complete separation of them leads to additional cost and complex operations.

Remarkably, many researches have proved that appropriate metal doping can improve the structural stability and the electrochemical properties of cathode materials.\(^\text{25,26}\) Chen et al.\(^\text{27}\) reported that Li[(Co\(_{0.3}\)Ni\(_{0.5}\)Fe\(_{0.2}\)]O\(_2\) delivered lower cation mixing, better reversible capacity, and higher electrical conductivity and excellent electrochemical properties. Liu et al.\(^\text{29}\) declared that Li\(_2\)Mn\(_{0.55}\)Ni\(_{0.15}\)Fe\(_{0.3}\)O\(_2\) showed stable layered structure and well-crystallized particle surface with pristine cathode material. The electrochemical performance of Li\(_2\)Mn\(_{0.55}\)Ni\(_{0.15}\)Fe\(_{0.3}\)O\(_2\) was significantly improved. The effect of Cu doping on cathode material has also been reported by many researchers. Wang et al.\(^\text{30}\) synthesized Cu-substituted LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) cathode material by coprecipitation method. The results indicated that cycling performance at high cutoff voltage was improved due to the change of surface composition and structure. Wu et al.\(^\text{24}\) reported that appropriate Cu had a positive impact on the rate property and capacity retention in synthesizing LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) cathode material. However, studies on Cu- and Fe-doped Ni-rich cathode material are seldom reported.

To make full use of Cu and Fe during the regeneration of spent LIBs, the impact of Cu and/or Fe substitutions on the Ni-rich cathode material must be systematically studied. In this paper, a series of Cu- and/or Fe-doped LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) cathode materials were prepared by spray pyrolysis and high-temperature solid-state method. The effect of Cu and/or Fe substitution on the structure and electrochemical performance of LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) was discussed in detail.

2 | EXPERIMENTAL

2.1 | Synthesis

LiNi\(_{0.8-x-y}\)Co\(_{0.15}\)Al\(_{0.05}\)Cu\(_{x}\)Fe\(_{y}\)O\(_2\) samples were synthesized by spray pyrolysis and high-temperature solid-state method. The precursor solution was prepared by dissolving a certain amount of NiCl\(_2\)-6H\(_2\)O, CoCl\(_2\)-6H\(_2\)O, AlCl\(_3\)-6H\(_2\)O, and CuCl\(_2\)-2H\(_2\)O in distilled water. The concentration of total metal ions was 1.0 mol L\(^{-1}\). A 1.75 MHz ultrasonic nebulizer was applied to aerosolize the precursor solution. The droplets stream was carried into a 3-zone vertical furnace with an oxygen flow rate of 4 L min\(^{-1}\). The pyrolysis temperature was maintained at 750°C. The resulting oxide precursors were collected at the exit of the reactor. After that, the precursors were thoroughly blended with Li\(_2\)CO\(_3\) in a molar ratio of 1:1.05. The mixtures were sintered at 480°C for 5 hours and 750°C for 15 hours under flowing oxygen at a heating rate of 5°C min\(^{-1}\). The prepared LiNi\(_{0.8-x-y}\)Co\(_{0.15}\)Al\(_{0.05}\)Cu\(_{x}\)Fe\(_{y}\)O\(_2\) samples with different Cu and/or Fe doping content were labeled as (NCA) \(x = y = 0\), (NCAC) \(x = 0.01, y = 0\), (NCAF) \(x = 0, y = 0.002\), and (NCACF) \(x = 0.008, y = 0.002\).

2.2 | Sample characterization

The powder X-ray diffraction (XRD, Rint-2000, Rigaku) using CuK\(_{α}\) radiation was used to identify the crystalline phase of the samples. XRD data were collected in the 2θ angle range from 10 to 90. Rietveld refinement was performed using the GSAS program. The microstructures and the element distribution of the samples were examined by scanning electron microscopy (SEM, JEOL, JSM-5612LV) coupled with energy dispersive X-ray spectroscopy. The composition of as-prepared samples was examined by an inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS intrepid XSP, Thermo Electron Corporation). The
information of surface chemical valence state was got by X-ray photoelectron spectroscope (XPS, VG Multilab 2000).

2.3 | Electrochemical measurement

The electrochemical properties of the as-prepared samples were identified using a two-electrode coin-type cell (CR2025). The working electrode was fabricated with the mixture of 80 wt.% as-prepared active material, 10 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride (PVDF) binder. The slurry of mixture was applied onto an aluminum foil and then dried 120°C for 4 hours. In the process of slurry coating, the quality of the active substance was controlled about 1.60 mg cm⁻² by adjusting the thickness of the coating. The resulting pole piece was punched in the form of 12-mm-diameter disks. The mixture of 1 mol L⁻¹ LiPF₆ dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) (1:1:1 in volume ratio) was employed as the electrolyte. The anode material is a round sheet of lithium metal with a diameter of 14 mm. The cells were assembled in a dry argon-filled glove box. Galvanostatic charge/discharge tests were conducted between 2.8 V and 4.3 V by a NEWARE BTS-51 battery tester. The lithium-ion diffusion coefficient was tested by a galvanostatic intermittent titration technique (GITT). Electrochemical impedance spectroscopy (EIS) was examined on a CHI 660A electrochemical workstation in the frequency range from 0.1 MHz to 0.01 Hz with a voltage amplitude of 5 mV.

3 | RESULTS AND DISCUSSION

The phase compositions of all precursors are determined by XRD. As indicated in Figure 1A, the diffraction peaks of all precursors can be indexed to NiO phase. There are no other diffraction peaks detected in XRD patterns, meaning Cu and Fe do not form signal phases during spray pyrolysis process. The morphology of all precursors is investigated by SEM, as shown in Figure S1. The results indicate that the morphology of all precursors produced by spray pyrolysis is similar, which is spherical-like particles. The particle size of all precursors is in good agreement with the designated compositions during synthesis within the limits of error.

Rietveld refinement is carried out to further investigate the effect of Cu and/or Fe substitution on the crystal structure of LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂. The analyses are performed by using a hexagonal crystal (space group: R̅₃m) as the structural model. The cationic distribution is assumed as follows: Li at the 3a sites (0, 0, 0), transition metals at the 3b sites (0, 0, 5), and O at the 6c site (0, 0, z) [31,32]. The total occupation of 3a, 3b, and 6c should be 1.0 because the lithium or oxygen vacancies are ignored. Therefore, the structural formulae of Li[Ni₀.₈−x−yCo₀.₁₅Al₀.₀₅CuₓFeₙ]O₂ is assumed to be as follows: [Li₁−x−y−zNi xo.₈−x−yCo₀.₁₅Al₀.₀₅CuₓFeₙ]O₂.

Figure 2 shows the Rietveld refinement results of as-prepared samples. The corresponding lattice parameters and atomic occupancies are summarized in Table 2. It can be observed that the fitting results are in good agreement with experimental patterns. The values of reliability factors Rwp and Rp are relatively low, indicating that the structural model of Rietveld refinement is suitable. It is noted that the cation mixing is suppressed after Cu and/or Fe substitution. The amount of Ni²⁺ occupied in Li layer of NCAC, NCAF, and NCAF is 0.0178, 0.0213, and 0.0136, while this amount of NCA is 0.0239. The diffusion of Li⁺ will be hindered when Ni²⁺ enter into Li layer, which leads to reduction in electrochemical performance of cathode materials. In addition, the lattice parameters of a-axes and c-axes are increased after Cu and/or Fe substitution. The reason for this expansion can be attributed to the fact that the ionic radius of Cu²⁺ (0.73 Å) and Fe³⁺ (0.64 Å) is larger than that of Ni³⁺ (0.56 Å). It has been reported that the lattice parameter of c-axes has a significant effect on the activation barrier for Li⁺ migration. Hence, it can be expected that Cu and/or Fe substitution is beneficial to the improvement of electrochemical performance and crystal structure stability of Li[Ni₀.₈−x−yCo₀.₁₅Al₀.₀₅CuₓFeₙ]O₂.

X-ray photoelectron spectroscope (XPS) is applied to gain information about the composition and valence state of chemical elements on the surface of materials. Only Ni 2p₃/₂ is fitted for the XPS experiment because the fitting results can completely meet the requirement of experimental analysis. Figure 3 shows the XPS spectra of Ni 2p₃/₂ and corresponding fitting curves. It can be observed that a main peak and a satellite peaks of Ni 2p₃/₂ are detected at 855.19 eV and 862.26 eV, respectively. The Ni 2p₃/₂ can be well fitted by two peaks at 855.63 eV for Ni³⁺ and 854.64 eV without destroying the layered structure. Figure S2 shows the SEM images of as-prepared cathode materials. It can be seen that the spherical-like particles of the precursors have been fractured during the sintering process, leaving an irregular morphology. Similarly, there is no significant difference between all samples. The chemical formulas of the as-prepared samples are analyzed by ICP-AES, as shown in Table 1. The results indicate that the analyzed chemical formula for all samples is in good agreement with the designated compositions.
for Ni$^{2+}$, indicating the valence state of Ni is a mixture of Ni$^{3+}$ and Ni$^{2+}$. The results show that the relative ratio of Ni$^{3+}$ increases after Cu and/or Fe substitution. This phenomenon that the valence state of Ni on the sample surface increases after other trivalent or even higher valence ions doping is also observed by others. The ionic radius of Ni$^{2+}$ and Li$^{+}$ is similar and hence Ni$^{2+}$ can easily migrate from transition metal slabs to lithium slabs. The decreased content of Ni$^{2+}$ on the surface is conducive to reducing the cation mixing degree of cathode material, which is consistent with the Rietveld refinement results.

Figure 4A presents the initial charge-discharge curves of the as-prepared samples under a current density of 18 mA g$^{-1}$ (0.1 C) between 2.8 and 4.3 V (vs Li$^{+}$/Li). During the charging process, the voltage of battery is first charged to 4.3 V by constant current. Then, battery is charged by constant voltage until reaching the cutoff current. The results demonstrate that the initial charge-discharge curves of all samples are similar. The initial discharge capacity of NCA, NCAC, NCAF, and NCACF is 201.18, 197.59, 198.80, and 195.16 mA h g$^{-1}$, respectively. It can be observed that the discharge capacity of all samples gradually decreases with the increased cycle number, and the Cu- and/or Fe-doped samples exhibited better cycling performance than the pristine samples. The first cycle discharge capacity of NCA, NCAC, NCAF, and NCACF is 180.24, 178.08, 178.36, and 177.52 mA h g$^{-1}$, respectively. The reason for the slightly capacity decrease for Cu- and/or Fe-doped samples has been explained as previously mentioned. After 100 cycle, the capacity retention of NCA, NCAC, NCAF, and NCACF is 86.62%, 91.12%, 89.19%, and 92.50%. It can be noted that the capacity retention of Cu- and/or Fe-doped samples significantly increase comparing with the pristine sample, and NCACF delivers the best cycling performance. One of the reasons for this distinct improvement in the cycling performance is related to the decreased cation mixing degree of Cu- and/or Fe-doped samples. The other is attributed to the suppression of the electrode polarization and structural collapse, caused by Cu and/or Fe ions doped into the transition metal layer. A series of Cu- and/or Fe-doped samples are prepared to judge the influence of doping amount on the cycling performance of LiNi$_{0.5}$Co$_{0.15}$Al$_{0.05}$O$_2$, as shown in Figure S3. The results reveal an appropriate amount of Cu and/or

---

**TABLE 1** Designated and observed chemical formulas of the as-prepared samples measured by ICP-AES

| Designated chemical formula | Analyzed chemical formula |
|-----------------------------|--------------------------|
| LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ | Li$_{1.009}$Ni$_{0.801}$Co$_{0.149}$Al$_{0.050}$O$_2$ |
| LiNi$_{0.79}$Co$_{0.15}$Al$_{0.05}$Cu$_{0.01}$O$_2$ | Li$_{1.011}$Ni$_{0.791}$Co$_{0.149}$Al$_{0.049}$Cu$_{0.011}$O$_2$ |
| LiNi$_{0.79}$Co$_{0.15}$Al$_{0.05}$Fe$_{0.002}$O$_2$ | Li$_{1.008}$Ni$_{0.801}$Co$_{0.148}$Al$_{0.049}$Fe$_{0.002}$O$_2$ |
| LiNi$_{0.79}$Co$_{0.15}$Al$_{0.05}$Cu$_{0.008}$Fe$_{0.002}$O$_2$ | Li$_{1.007}$Ni$_{0.791}$Co$_{0.149}$Al$_{0.049}$Cu$_{0.009}$Fe$_{0.002}$O$_2$ |

---

**FIGURE 1** XRD patterns of all as-prepared precursors (A) and cathode materials (B)
Fe substitution can improve the electrochemical properties of cathode materials. However, Cu- and/or Fe-doped samples deliver decreased capacity retention when the atomic ratio of Ni to Cu and Ni to Fe is lower than 79.0 and 399.0, respectively. Figure S4 shows the XRD patterns of as-prepared cathode materials. The corresponding lattice parameters are displayed in Table S1. All peaks of the XRD pattern exhibit typical layered hexagonal structure of a-NaFeO$_2$. In the XRD pattern of layered cathode materials, the intensity ratio of (0 0 3) to (1 0 4) is generally used to measure the degree of cation mixing. It is believed that the degree of cation mixing of materials is relatively small when the value of $I_{(003)}/I_{(104)}$ is greater than 1.20. Lower value of $I_{(003)}/I_{(104)}$ means higher degree of cation mixing, which is unfavorable for the electrochemical performance because the diffusion of lithium ion is hindered in the layered structure.24 When the atomic ratio of Ni to Cu and Ni to Fe is lower than 79.0 and 399.0, the value of $I_{(003)}/I_{(104)}$ is decreased compared to the pristine sample. Therefore, the cycle performance of these samples is worsened.

Differential capacity ($dQ/dV$) profiles can be carried out to deeper understand the degree of the electrochemical irreversibility and the change of crystal structure during prolonged cycles. Figure 5 shows the corresponding $dQ/dV$ curves of various cycles at 1.0 C rate between 2.8 and 4.3 V (vs Li$^+/Li$) for each sample. It can be observed

---

**TABLE 2** Results of Rietveld refinement of as-prepared samples

| Parameter | NCA | NCAC | NCAF | NCACF |
|-----------|-----|------|------|-------|
| Li1       | 0.9761 | 0.9822 | 0.9787 | 0.9864 |
| Ni1       | 0.0239 | 0.0178 | 0.0213 | 0.0136 |
| Li2       | 0.0239 | 0.0178 | 0.0213 | 0.0136 |
| Ni2       | 0.7761 | 0.7722 | 0.7767 | 0.7764 |
| $a$ (Å)   | 2.8645 | 2.8649 | 2.8647 | 2.8651 |
| $c$ (Å)   | 14.1872 | 14.1924 | 14.1891 | 14.1931 |
| $wRp$     | 6.86 | 4.75 | 5.85 | 4.37 |
| $Rp$      | 4.62 | 3.55 | 4.13 | 3.36 |
that the $dQ/dV$ curves for all samples are similar. There are three redox peaks in the curves, which are due to the multiphase transitions from hexagonal to monoclinic (H1 to M), monoclinic to hexagonal (M to H2), and hexagonal to hexagonal (H2 to H3).\(^{39}\) As the charge-discharge processes proceeded, the redox peaks for Cu- and/or Fe-doped samples are more stable than that of the pristine sample, meaning the structure stability of Cu- and/or Fe-doped samples is increased. Additionally, it can be noted that the phase transition from H2 to H3 of Cu- and/or Fe-doped samples are weakened. The phase transition from H2 to H3 corresponds to significant lattice parameters changes, resulting in the particle pulverization and cycling performance fading.\(^{40}\) Moreover, the plateaus' voltage drops of Cu- and/or Fe-doped samples in prolonged cycles are reduced, which corresponds to a decreased electrochemical polarization. The plateaus' voltage of NCA shifts 0.135 V after 100 cycles, while the plateaus' voltage of NCAC, NCAF, and NCACF is only 0.074 V, 0.106 V, and 0.062 V, respectively. Thus, it can be indicated that Cu and/or Fe doping is beneficial to improve the cycling performance and reduce the electrochemical polarization.

Figure 6A shows the rate capability of as-prepared samples from 0.1 C to 10 C between 2.8 and 4.3 V. The cells are charged and discharged at different current densities for five cycles. The discharge capacity of all samples is
decreased with the increased current densities because the electrochemical polarization became remarkable at large current densities. Obviously, there is no significant difference in the discharge capacity of all samples at low current densities. This could be ascribed to the fact that Cu and/or Fe doping leads to the slight decrease in the discharge capacity. Hence, the discharge capacity loss caused by electrochemical polarization is not reflected. However, the capacity for all the samples displays obvious differences at 5 C and 10 C rate. For instance, the discharge capacity at 10 C rate of NCAC, NCAF, and NCACF is 123.10, 113.2, and 143.12 mA h g\(^{-1}\), while the NCA sample exhibits only 81.12 mA h g\(^{-1}\). The corresponding discharge curves of each sample at different current densities are presented in Figure 6B-D. The NCA sample delivers the larger discharge voltage plateau drop compared with Cu and/or Fe doping samples, implying that the electrochemical polarization is inhibited by Cu and/or Fe doping especially at large current densities. Therefore, it indicated that Cu and/or Fe doping can improve rate capacity and suppress the electrochemical polarization.

The process that lithium ions are embedded and released in cathode materials is an ion diffusion process. The Li\(^+\) diffusion coefficient largely determines the reaction rate and also affects the overall performance of the battery. The determination of Li\(^+\) diffusion coefficient is of great significance to study the electrochemical properties of the cathode materials. Thus, galvanostatic intermittent titration technique (GITT) based on chronopotentiometry is applied to confirm the Li\(^+\) diffusion coefficient of each sample under an approximate thermodynamic equilibrium condition.\(^\text{41}\) The \(D_{\text{Li}^+}\) can be calculated with Equation (1):

\[
D_{\text{Li}^+} = \frac{4}{\pi} \left( \frac{m_B V_m}{M_B S} \right)^2 \left( \frac{\Delta E_s}{\tau \left( dE_r/d\tau \right)} \right)^2 \left( \tau \ll L^2 / D_{\text{Li}^+} \right) \tag{1}
\]

where \(m_B\) stands for the mass of the active material (g), \(V_m\) and \(M_B\) stand for the molar volume and molecular weight of the samples, \(S\) stands for the area of the electrode, \(\tau\) stands for the time duration during the current pulse, \(\Delta E_s\) stands for

![Figure 5](image-url)
the difference in the steady-state cell voltage in a single-step GITT test, and $L$ stands for the length of Li$^+$ ions diffusion.

The fourth discharge cycle of each sample is depicted in Figure 7A-D. All samples are discharged for 10 minutes under a galvanostatic current of 0.1 C and then remain stationary for 50 minutes to reach a quasi-steady state. This process repeats between 2.8 and 4.3 V. A typical GITT profile for each sample during a single GITT test step is showed in FIGURE 6.

FIGURE 6  Rate capacity of as-prepared samples at different C-rates and the corresponding discharge curves of (A) NCA, (B) NCAC, (C) NCAF, and (D) NCACF

FIGURE 7  (A-D) GITT curves of the as-prepared samples between 2.8 and 4.3 V, (E-F) applied current pulse vs voltage for a single titration step, (I-L) linear fit of the voltage vs the square root of time ($t^{1/2}$) with different pulse currents
Figure 7E-H. Different parameters ($E_0$, $E_s$, $E_\tau$, $\Delta E_s$, $\tau$, etc) are schematically labeled in the diagram. The responding potential ($E$) as a function of $\tau^{1/2}$ for the single GITT curve is represented in Figure 7I-L. It is noted that there is a straight-line trend between $E$ and $\tau^{1/2}$; thus, the Equation (1) can be simplified as Equation (2):\[ \text{Equation (2)} \]

\[
D_{Li^+} = \frac{4}{\pi \tau} \left( \frac{m_p V_m}{M_p S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_r} \right)^2 \left( \tau \ll L^2/D_{Li^+} \right)
\]

Based on Equation (2), the Li$^+$ diffusion coefficient calculated from GITT as a function of voltage is shown in Figure 8. It can be seen that all as-prepared samples have similar curves, and the Li$^+$ diffusion coefficient of Cu and/or Fe doping samples is higher compared with the pristine sample. The value of the chemical diffusion coefficient is sharply increased till about 3.7 V, and then, the value almost keeps stable. The highest Li$^+$ diffusion coefficient of NCAC, NCAF, and NCACF is about $9.97 \times 10^{-10}$, $5.24 \times 10^{-10}$, and $2.25 \times 10^{-9}$ cm$^2$ s$^{-1}$, while the NCA sample exhibits $4.65 \times 10^{-10}$ cm$^2$ s$^{-1}$. The results confirm that Cu and/or Fe doping can improve the chemical diffusion coefficient of Li$^+$. The reason for the improving of Li$^+$ diffusion coefficient can attribute to decrease cation mixing after Cu and/or Fe doping. Hence, the electrochemical polarization of Cu and/or Fe doping samples can be suppressed, resulting in an improvement in discharge rate and cycling performance.

In addition to calculating the Li$^+$ diffusion coefficient of each sample with GITT test, electrochemical impedance spectroscopy (EIS) is used to study the effect of Cu and/or Fe substitution on the interfacial electrochemistry and reaction kinetics of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$. As shown in Figure 9, both the EIS plots consist of two semicircles. The small break in the high frequency region is attributed to the solution resistance ($R_s$). Two semicircles in high and mid/low frequency region are assigned to the surface interface resistance ($R_{int}$) and the charge transfer resistance ($R_{ct}$). It is noted that the resistance of Cu and/or Fe doping samples is smaller than that of the pristine sample, indicating that the electrochemical performances are improved after Cu and/or Fe doping. The impedance parameters estimated by using the equivalent circuit model are showed in Table 3. It can be seen that the values of $R_s$, $R_{int}$, and $R_{ct}$ are decreased after Cu and/or Fe doping. The values of $R_{int}$ and $R_{ct}$ for NCA after 1 cycle are 265.12 and 381.25 $\Omega$, respectively. However, the same values for NCACF after 1 cycle are only 160.14 and 150.47 $\Omega$. Therefore, it can be indicated that Cu and/or Fe doping can facilitate lithium-ion migration and reduce the charge transfer resistance. During charge and discharge process, lithium-ion diffusion coefficient and charge transfer impedance are the main reasons for electrochemical polarization. The decrease in lithium-ion diffusion coefficient and the increase in charge transfer impedance will increase the electrochemical polarization during this process. According to the results of GITT and EIS tests, the lithium-ion diffusion coefficient of Cu- and/or Fe-doped samples increases while the electrochemical transfer impedance decreases compared with the pristine sample. Hence, the electrochemical polarization of Cu- and/or Fe-doped samples decreased during charge and discharge process. When lithium-ion batteries are charged and discharged under high C-rate, the electrochemical polarization has a more significant impact on the electrochemical performance of the samples. Therefore, the electrochemical performance of Cu- and/or Fe-doped samples is effectively improved under high C-rate because Cu and/or Fe doping can increase the lithium-ion diffusion coefficient and decrease the charge transfer impedance of the samples.

In order to explore the structure stability of as-prepared samples, XRD is introduced to the identify the crystalline phase of postcycled samples. All cathode electrodes are taken out at discharged state after 100 cycles. The postcycled cathode electrodes are immersed in DMC for 20 minutes, and then, the aluminum foil is removed. Figure 10 shows the XRD patterns of as-prepared...
samples before and after 100 cycles at 1.0 C between 2.8 and 4.3 V. The results show that the strength of the diffraction peaks of all samples decreases after cycling, indicating that all samples show different degrees of irreversible phase transition during the cycling process. The diffraction peak strength of Cu- and/or Fe-doped samples is higher than that of the pristine sample, meaning that the structural stability of the doped material is improved. The change of peak position before and after cycling can also be used to reflect the change degree of crystal structure. As can be seen from the partial enlarged figure, the (0 0 3) peak position of all materials after cycling is shifted to a lower angle. After Cu and/or Fe doping, the shifted value of (0 0 3) peak is smaller, indicating that Cu and/or Fe doping can effectively inhibit the structural collapse of cathode materials. In order to further study the structure change at the surface of the postcycled samples, XPS is used to determine the valence state of Ni on the surface, as shown in Figure S5. The position and strength of Ni peak are changed compared with the pristine sample due to the adverse reaction of the samples with the electrolyte and the formation of phosphorus and fluorine compounds on the surface of the postcycled samples. The results show that the content of Ni$^{3+}$ on the surface of all samples decreases. It can attribute to the partial transformation from layered structure to rock-salt structure on the surface of the cathode material during the cycling process. However, the content of Ni$^{3+}$ on the surface of the doped sample is higher than that of the pristine sample, indicating that Cu and/or Fe doping can improve the stability of the surface structure of the cathode material.

4 CONCLUSION

Cu- and/or Fe-substituted LiNi$_{0.8-x}$Co$_{0.15}$Al$_{0.05}$Cu$_x$Fe$_y$O$_2$ cathode materials were successfully prepared by spray pyrolysis and high-temperature solid-state method. Combining ICP, XRD, XPS, and Rietveld refinement tests, the results indicate that Cu and/or Fe doping can reduce Li/Ni disorder degree and enlarge the lattice parameters, which is helpful to promote the diffusion of lithium ion. Cu- and/or Fe-doped samples deliver superior capacity retention when the atomic ratio of Ni to Cu and Ni to Fe is greater than 79.0 and 399.0, respectively. The rate capability of Cu- and/or Fe-doped samples is also improved. In

![XRD patterns of as-prepared samples before and after 100 cycles at 1.0 C between 2.8 and 4.3 V (vs Li$^+/Li$)](image)

| Samples  | $R_e$ (Ω) | $R_{ef}$ (Ω) | $R_{ct}$ (Ω) | $R_{ef} + R_{ct}$ (Ω) |
|---------|----------|-------------|-------------|----------------------|
| NCA     | 6.71     | 265.12      | 381.25      | 646.37               |
| NCAC    | 3.49     | 193.35      | 160.12      | 373.57               |
| NCAF    | 5.45     | 198.43      | 331.38      | 529.81               |
| NCACF   | 2.71     | 160.14      | 150.47      | 310.61               |
addition, \(dQ/dV\), GITT, EIS, XRD, and XPS studies confirm that Cu and/or Fe substitution can increase the \(Li^+\) diffusion coefficient and structure stability, while the electrochemical polarization and the interface resistance of cathode materials are decreased. It is concluded that appropriate Cu and/or Fe substitution is beneficial to improve the electrochemical performance of \(LiNi_{0.8}Co_{0.15}Al_{0.05}O_2\). Therefore, it makes sense to selectively separate Cu and Fe during the regeneration of spent lithium-ion batteries, resulting in the reduction of additional cost and complex operations.

ACKNOWLEDGMENTS

We thank the financial supporting from the National Natural Science Foundation of China (51874360, 51674296), the Innovation and Entrepreneurship Project of Hunan Province, China (2017GK5010, 2018GK5026), and the Program of Huxiang Young Talents (2019RS2002).

ORCID

Jiexi Wang https://orcid.org/0000-0001-7398-5566

REFERENCES

1. Ge X, Li X, Wang Z, et al. Facile synthesis of NaVPO F/C cathode with enhanced interfacial conductivity towards long-cycle and high-rate sodium-ion batteries. Chem Eng J. 2019;357:458.
2. Pan W, Peng W, Yan G, et al. Suppressing the voltage decay and enhancing the electrochemical performance of Li Mn Co Ni O by multifunctional \(Nb_2O_5\) coating. Energy Technol. 2018;6(11):2139.
3. Wu L, Zheng J, Wang L, et al. PPy-encapsulated SnS\(_2\) nanosheets stabilized by defects on TiO\(_2\) support as durable anode material for lithium ion battery. Angew Chem Int Ed. 2019;58(3):811.
4. Cao W, Wang SL, Fernandez C, Zou CY, Yu CM, Li XX. A novel adaptive state of charge estimation method of full life cycling lithium-ion batteries based on the multiple parameter optimization. Energy Sci Eng. 2019;7:1544.
5. Kim M, Kim D, Wen Y, et al. High rate Li-Ion batteries with cation-disordered cathodes. Joule. 2019;3(4):1064.
6. Peng X, Chen S, Garg A, Bao N, Panda B. A review of the estimation and heating methods for lithium-ion batteries pack at the cold environment. Energy Sci Eng. 2019;7(3):645.
7. Fu C, Li G, Luo D, Li Q, Fan J, Li L. Nickel-rich layered microspheres cathode: lithium/nickel disordering and electrochemical performance. ACS Appl Mater Interfaces. 2014;6(18):15822.
8. Zhu YH, Yuan S, Bao D, et al. Decorating waste cloth via industrial wastewater for tube-type flexible and wearable sodium-ion batteries. Adv Mater. 2017;29(16):1603719.
9. Ma J-L, Meng F-L, Xu D, Zhang X-B. Co-embedded N-doped carbon fibers as highly efficient and binder-free cathode for Na-O batteries. Energy Storage Mater. 2017;6:1.
10. Ma J-L, Zhang X-B. Optimized nitrogen-doped carbon with a hierarchically porous structure as a highly efficient cathode for Na-O batteries. J Mater Chem A. 2016;4(25):10008.
11. Wang Z, Zhu K, Hu J, Wang J. Study on the fire risk associated with a failure of large-scale commercial LiFePO\(_4\)/graphite and LiNi Co Mn O/graphite batteries. Energy Sci Eng. 2019;7(2):411.
12. B.W. J, Structural and electrochemical investigation of LiNi Co M O (M = Al, Al + Mg, Al + Mg + Fe) synthesized by solid state method. Ionics. 2008;14(6):501.
13. Woo SW, Myung ST, Bang H, Kim DW, Sun YK. Improvement of electrochemical and thermal properties of Li[Ni Co Mn] O positive electrode materials by multiple metal (Al, Mg) substitution. Electrochim Acta. 2009;54(15):3851.
14. Zhong X, Li X, Bao Z, et al. Enhanced electrochemical performance of LiNi Co Mn O cathode materials obtained by atomization co-precipitation method. Ceram Int. 2015;42(1):644.
15. Zhao J, Wang Z, Wang J, et al. Anchoring K in Li sites of LiNi Co Al O cathode material to suppress its structural degradation during high-voltage cycling. Energy Technol. 2018;6(12):2358.
16. Xi Z, Wang Z, Yan G, et al. Hydrometallurgical production of LiNi Co Al O cathode material from high-grade nickel matte. Hydrometallurgy. 2019;186:30.
17. Zhong H-X, Li K, Zhang Q, et al. In situ anchoring of Co S nanoparticles on N and S co-doped porous carbon tube as bifunctional oxygen electrolyt catalysts. NPG Asia Mater. 2016;8(9):e308.
18. Zhong HX, Wang J, Zhang Q, et al. In situ coupling FeM (M = Ni, Co) with nitrogen-doped porous carbon toward highly efficient tri-functional electrolyt catalyst for overall water splitting and rechargeable Zn-Air battery. Adv Sustain Syst. 2017;1(6):1700020.
19. Ku H, Jung Y, Jo M, et al. Recycling of spent lithium-ion battery cathode materials by ammoniacal leaching. J Hazard Mater. 2016;313:138.
20. Perez E, Andre ML, Navarro Amador R, et al. Recovery of metals from simulant spent lithium-ion battery as organophosphate coordination polymers in aqueous media. J Hazard Mater. 2016;317:617.
21. Zhu YH, Yin YB, Yang X, et al. Transformation of rusty stainless-steel meshes into stable, low-cost, and binder-free cathodes for high-performance potassium-ion batteries. Angew Chem Int Ed. 2017;56(27):7881.
22. Hu J, Zhang J, Li H, Chen Y, Wang C. A promising approach for the recovery of high value-added metals from spent lithium-ion batteries. J Power Sources. 2017;351:192.
23. Gao W, Zhang X, Zheng X, et al. Lithium carbonate recovery from cathode scrap of spent lithium-ion battery: a closed-loop process. Environ Sci Technol. 2017;51(3):1662.
24. Wu ZJ, Wang D, Gao ZF, Yue HF, Liu WM. Effect of Cu substitution on structures and electrochemical properties of Li[NiCo Mn] O as cathode materials for lithium ion batteries. Dalton Trans. 2015;44(42):18624.
25. Zhang M, Hu G, Liang L, et al. Mg-Al-B co-substitution LiNi Co Mn O cathode materials with improved cycling performance for lithium-ion battery under high cutoff voltage. Electrochim Acta. 2016;190:264.
26. Wang R, Li X, Wang Z, Han Z. Electrochemical analysis graphite/electrolyte interface in lithium-ion battery: p-Toluenesulfonyl isocyanate as electrolyte additive. Nano Energy. 2017;34:131.
27. Cheng C, Chen F, Yi H. Synthesis and electrochemical properties of layered Li(Fe Ni ) O as a cathode material for lithium-ion batteries. Miner Met Mater Soc. 2015;44(10):3738.
28. Samarasingha PB, Wijayasinghe A, Behm M, Dissanayake L, Lindbergh G. Development of cathode materials for lithium ion rechargeable batteries based on the system Li(Ni Mn Co T ) M O , (M = Mg, Fe, Al and x = 0.00–0.33). Solid State Ionics. 2014;268:226.
29. Liu X, Huang T, Yu A. Fe doped Li Mn N Fe O (x ≤ 0.1) as cathode materials for lithium-ion batteries. Electrochim Acta. 2014;133:555.

30. Wang J, Chen T. Surface composition and electrochemical behavior of LiNi Co Mn O cathode material with copper additive. Rare Met. 2012;31(4):397.

31. Zhang B, Li L, Zheng J. Characterization of multiple metals (Cr, Mg) substituted LiNi Co Mn O cathode materials for lithium ion battery. J Alloy Compd. 2012;520:190.

32. Huang Z, Wang Z, Zheng X, et al. Investigation on the effect of Na doping on structure and Li-ion kinetics of layered LiNi Co Mn O cathode material. Electrochim Acta. 2015;182:795.

33. Huang Z, Wang Z, Guo H, Li X. Influence of Mg doping on the structure and electrochemical performances of layered LiNi Co Mn Mg O cathode materials. J Alloy Compd. 2016;671:479.

34. Zhang R, Wang J, Yan G, et al. Enhancing the electrochemical and storage performance of Ni-based cathode materials by introducing spinel pillaring layer for lithium ion batteries. Solid State Ionics. 2019;332:41.

35. Zheng X, Li X, Wang Z, et al. Investigation and improvement on the electrochemical performance and storage characteristics of LiNiO-based materials for lithium ion battery. Electrochim Acta. 2016;191:832.

36. Duan J, Hu G, Cao Y, et al. Enhanced electrochemical performance and storage property of LiNi Co Al O via Al gradient doping. J Power Sources. 2016;326:322.

37. Jang B-C, Son J-T. Structural analysis of iron-doped LiNi Co Al O cathode materials for lithium-ion batteries. J Nanosci Nanotechnol. 2016;16(10):10649.

38. Chae JS, Jo MR, Kim Y-I, et al. Kinetic favorability of Ru-doped LiNi Mn O for high-power lithium-ion batteries. J Ind Eng Chem. 2015;21:731.

39. Park T-J, Lim J-B, Son J-T. Effect of calcination temperature of size controlled microstructure of LiNi Co Al O cathode for rechargeable lithium battery. Bull Kor Chem Soc. 2014;35(2):357.

40. Huang B, Li X, Wang Z, Guo H, Xiong X. Synthesis of Mg-doped LiNi Co Al O oxide and its electrochemical behavior in high-voltage lithium-ion batteries. Ceram Int. 2014;40(8):13223.

41. Zheng W, Miao S, Jie S, et al. GITT studies on oxide cathode LiNi Co Mn O synthesized by citric acid assisted high-energy ball milling. Bull Mater Sci. 2013;36(3):495.

42. Huang Z, Wang Z, Jing Q, Guo H, Li X, Yang Z. Investigation on the effect of Na doping on structure and Li-ion kinetics of layered LiNi Co Mn O cathode material. Electrochim Acta. 2016;192:120.

43. Li T, Li X, Wang Z, Guo H. A short process for the efficient utilization of transition-metal chlorides in lithium-ion batteries: A case of Ni Co Mn O and LiNi Co Mn O. J Power Sources. 2017;342:495.

44. Duan J, Dong P, Wang D, et al. A facile structure design of LiNi Co Al O as advanced cathode materials for lithium ion batteries via carbonation decomposition of NaAl(OH) solution. J Alloy Compd. 2018;739:335.

45. Cho Y, Oh P, Cho J. A new type of protective surface layer for high-capacity Ni-based cathode materials: nanoscaled surface pillaring layer. Nano Lett. 2013;13(3):1145.

SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section.

How to cite this article: Xi Z, Wang Z, Peng W, Guo H, Wang J. Effect of copper and iron substitution on the structures and electrochemical properties of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode materials. Energy Sci Eng. 2020;8:1868–1879. https://doi.org/10.1002/ese3.638