Research Article

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Improvement of long-term cycling performance of high-nickel cathode materials by ZnO coating

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Abstract: The high-nickel cathode material of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 (LNCA) has a prospective application for lithium-ion batteries due to the high capacity and low cost. However, the side reaction between the electrolyte and the electrode seriously affects the cycling stability of lithium-ion batteries. In this work, Ni^{2+} preoxidation and the optimization of calcination temperature were carried out to reduce the cation mixing of LNCA, and solid-phase Al-doping improved the uniformity of element distribution and the orderliness of the layered structure. In addition, the surface of LNCA was homogeneously modified with ZnO coating by a facile wet-chemical route. Compared to the pristine LNCA, the optimized ZnO-coated LNCA showed excellent electrochemical performance with the first discharge-specific capacity of 187.5 mA h g^{-1}, and the capacity retention of 91.3% at 0.2C after 100 cycles. The experiment demonstrated that the improved electrochemical performance of ZnO-coated LNCA is assigned to the surface coating of ZnO which protects LNCA from being corroded by the electrolyte during cycling.

Keywords: LiNi_{0.8}Co_{0.15}Al_{0.05}O_2, cathode material, ZnO coating, lithium-ion battery

1 Introduction

Since the first successful development and commercialization of lithium-ion batteries (LIBs) by Sony in Japan in 1991, LIB have received increasing attention [1]. Due to the high energy density, good cycling performance, and environmental friendliness [2], LIBs have become one of the most promising green secondary batteries in the twenty-first century [3]. As an important component of LIBs, the cathode material has much lower capacity than the anode material, accounting for the highest proportion of battery cost [4]. However, the initial Coulombic efficiency, rate capability, and cycling performance of these LiNiO_2-based cathode materials are not satisfactory, especially at an elevated temperature [5]. Therefore, research on high-capacity cathode materials plays a crucial role in the development of LIBs [6].

Among the layered materials, LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 is a promising cathode material, which is due to the combination of the advantages of high theoretical capacity and stable layered structure of LiNiO_2 [7], LiCoO_2 [8], and LiAlO_2 [9]. As the precursor of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2, Ni_{0.8}Co_{0.15}Al_{0.05}(OH)_{2}O_5 is generally prepared by coprecipitation method [10]. However, the K_{sp} of Al(OH)_3 (4.57 × 10^{-33}) is much less than that of Ni(OH)_2 (2 × 10^{-15}) and Co(OH)_2 (1.58 × 10^{-15}), meaning that the ions of Al^{3+} precipitate faster with the hydroxide, which inhibits the uniform growth of the precursor [11]. The generated precipitate will undergo a lattice change and structural collapse during the cycling [12]. In the traditional preparation process, the oxidation of Ni^{2+} was carried out during the calcination [13]. However, the agglomeration of materials could make it difficult for the internal Ni^{2+} to be oxidized to Ni^{3+}, resulting in cation mixing [14]. The radius of Ni^{2+} is very close to Li^{+}, and the 3b of Ni^{2+} will occupy the 3a of Li^{+} [15], which hinders the deintercalation of Li^{+} and further affects the cycling performance. In addition, the Ni-containing cathodes easily react with electrolyte and the transition metal ions dissolve due to HF corrosion [16]. The unstable Ni^{4+} ions in the charged state tend to transform to more stable NiO on the cathode surface,
which results in high interfacial resistance and rapid capacity decay [17]. Moreover, the oxygen is released during the structural transition, causing poor safety performance of the battery [18]. Therefore, it is urgent for us to find a new strategy to solve these problems.

Doping aluminum has been found very effective to improve durability of LIBs because it stabilizes the charge-transfer impedance on the cathode. Much more effects have been paid to solve the problem of rapid precipitation of Al3+. Trease et al. [19] used a series of techniques to measure the aluminum distribution in layered LiNi0.8-Co0.15-Al0.05O2 (NCA) to investigate the influence of aluminum doping on layer stabilization. The experimental results showed that Ni3+ ions incurred a dynamic Jahn–Teller (JT) distortion, while the Al reduced the strain associated with JT distortion by prioritizing the electron ordering of the JT long bonds of Al3+. A new aluminum source, NaAlO2, was employed by Liang et al. [20] to prepare a high-performance LNCA (LNCA-NaAlO2). NaAlO2 was hydrolyzed during the preparation of the precursor to avoid the rapid precipitation of Al3+ and the formation of flocculation precipitation. The obtained LNCA-NaAlO2 with uniform element distribution and orderly layered structure showed a high initial discharge capacity of 204.7 mA h g−1 at 0.1C and a good capacity retention of 74.1% after 200 cycles. Zhou et al. [21] also used Al2O3 as Al source to synthesize the Ni-rich precursor, Ni0.8Co0.20-Al0.03(OH)2. After optimizing the calcination conditions, LiNi0.8Co0.03Al0.03O2 demonstrated excellent electrochemical performances. Kim and Kim [22] used acetylacetone as a chelating agent to effectively control the Al reaction rate, improve the uniform distribution of Al, and more importantly, increase the average particle size and density of NCA. Both the volumetric energy and specific capacity of LIBs were increased.

Many methods have been reported to improve such instable structural of high-nickel cathode material via doping and surface coating [23,24]. Liang et al. [25] found that the SiO2 coating onto the surface of LiNi0.8-Co0.15-Mn0.05O2 can stabilize the layered structure, effectively reduce the corrosion of the cathode material by the electrolyte, and hence, improve the cycling performance. Liu et al. [26] used the pillaring effect of inactive Mg in the crystal structure to modify LiNi0.8Co0.15-Mn0.05O2 by doping Mg and obtained the improved cycling stability (high-capacity retention of 81% over 350 cycles at 0.5C).

In this work, we report the synthesis, structural characterization, and electrochemical of ZnO-coated LiNi0.8-Co0.15-Al0.05O2 cathodes. The synergistic action of Ni2+ preoxidation by (NH4)2S2O8 and the optimization of calcination temperature reduced the cation mixing of LiNi0.8-Co0.15-Al0.05O2. The solid-phase Al-doping improved the uniformity of element distribution and the orderliness of the layered structure. In addition, the surface of LiNi0.8-Co0.15-Al0.05O2 was coated with ZnO [27,28] which improved the structural stability and cycling performance. The preparation process of ZnO-coated LiNi0.8-Co0.15-Al0.05O2 is shown in Figure 1.

2 Experimental

2.1 Preparation of LiNi0.8Co0.15Al0.05O2

The NiSO4·6H2O and CoSO4·7H2O (molar ratio of 0.80: 0.15) were dissolved in deionized water to form a mixed salt solution at a concentration of 1.9 mol L−1 and added a certain amount of (NH4)2S2O8 solution. 4 mol L−1 NaOH solution and 1.5 mol L−1 NH3·H2O solution are served as the pH control agent and the chelating agent, respectively. The NH3·H2O solution is first added to a 5 L reactor, and then the salt solution and the NaOH solution are pumped together into the reactor at a flow rate ratio of 2:1 to react at 50°C for 30 h; the pH was controlled at 11.00 ± 0.02 by an online pH meter. Then, the NiO.8Co0.15(OH)2 was obtained after washing and drying. Subsequently, solid-phase Al-doping is used to prepare the LiNi0.8Co0.15Al0.05O2. The Li2CO3, Ni0.8Co0.15(OH)2, and Al(NO3)3·9H2O (molar ratio of Li:Ni:Co:Al = 1.08:0.8:0.15:0.05) were mixed and ball-milled for 5 h, then calcined at 500°C for 5 h under the oxygen atmosphere in a tube furnace to obtain the intermediate product. After that, the intermediate product is cooled to room temperature, ball-milled for 5 h, placed in the tube furnace again, and calcined at 750°C for 12 h in the oxygen atmosphere to form LiNi0.8Co0.15Al0.05O2.
2.2 Preparation of ZnO-coated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$

A certain amount of Zn(AC)$_2$·2H$_2$O was dissolved in 40 mL of ethanol, and after ultrasonic dissolution, 2 g of the LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ obtained in the above step was added under vigorous stirring for 4 h, and then increased to 65°C to evaporate the ethanol. The mixture was dried at 120°C for 12 h, and finally calcined at 450°C for 5 h to obtain ZnO-coated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ powder which could be used as cathode material. The amount of Zn(AC)$_2$·2H$_2$O added to prepare ZnO-coated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ were 1, 2, 3 wt%, and the prepared samples were recorded as Z1, Z2, and Z3, respectively, and the pristine LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ as Z0.

2.3 Materials characterization

The material structure was analyzed by X-ray powder diffractometer (XRD, Ultima type, Japan Science) at the scanning speed of 0.2° s$^{-1}$ with the scanning range of 10–80°. Thermogravimetric (TG) measurements (Netzsch-STA 449C) were conducted from room temperature to 900°C at a heating rate of 10°C min$^{-1}$ in air. The surface morphology was analyzed by scanning electron microscope (SEM, Zeiss supra 55, Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100HR, Japan).

2.4 Electrochemical measurements

The working electrodes were prepared by mixing active material, acetylene black, and PVDF at a mass ratio of 8:1:1 in N-methylpyrrolidinone solution. The slurry was coated onto the aluminum foil and dried at 110°C for 5 h. Then the coated foil was pressed and punched into 14 mm diameter disks. The electrodes were transferred to a glove box (Super 1220/750, Mikrouna Co., Ltd. China) to assemble in 2025 coin-type cells with a lithium foil counter electrode. Celgard-2400 was used as the separator and 1 M LiPF$_6$ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume ratio) as the electrolyte solution.

The galvanostatic charge and discharge cycle were conducted on CT2001A (LAND, Bart Rui Tech. Co., Ltd.) battery test system between 2.8 and 4.3 V (vs Li/Li$^+$) under different current densities. Cyclic voltammetry (CV) test was recorded on Gamry electrochemical system (Interface1010E) with a potential range of 3.0–4.3 V (vs Li/Li$^+$) at a scanning rate of 0.1 mV s$^{-1}$. Electrochemical impedance spectrum (EIS, 100 kHz to 0.01 Hz) was performed using the same electrochemical system.

3 Results and discussion

3.1 Effect of different calcination temperatures on LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$

As known, the crystal structures and microstructures of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ are also affected by the calcination temperature. Therefore, to determine the calcination temperature for preparing LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, the thermogravimetric analysis (TGA) was conducted in air for the mixture Li$_2$CO$_3$, Ni$_{0.8}$Co$_{0.15}$OH$_{1.9}$, and Al(NO$_3$)$_3$·9H$_2$O (molar ratio of Li:Ni:Co:Al = 1.08:0.8:0.15:0.05) in the temperature range from 25 to 900°C, as shown in Figure 2. The differential curve is the relationship between the temperature and the first derivative of time in the TG curve, which represents the weight loss rate. It can be seen that there is a slow weight loss from room temperature to 90°C, corresponding to a small endothermic peak (a) on the differential curve, which is due to weight loss of absorbed water on surface and crystal water of Al(NO$_3$)$_3$·9H$_2$O. A dramatic decline occurs from 190 to 270°C, corresponding to the maximum endothermic peak of the differential curve (b), mainly ascribed to the process of Ni$_{0.8}$Co$_{0.15}$OH$_{1.9}$ forming Ni$_{0.8}$Co$_{0.15}$O$_2$. From 270 to 500°C, there is a relatively slow weight loss, corresponding to the broad endothermic peak (c) on the differential curve, which is due to the thermal decomposition of Li$_2$CO$_3$ to produce Li$_2$O and release CO$_2$. With the further increase in temperature,
Al2O3 was formed by decomposition of Al(NO3)3, and finally LiNi0.8Co0.15Al0.05O2 was synthesized. The analytical curve shows that the thermal reaction of the mixture is carried out in stages. In order to obtain a positive cathode material with excellent performance, it is necessary to strictly control the calcination conditions. In addition, when the temperature is around 850°C, there is a slow weight loss, due to the volatilization of lithium, thereby, the calcination temperature cannot exceed 850°C.

Figure 3 shows the XRD patterns of the samples prepared at different calcination temperatures. All peaks are well-indexed to the R3m group and consistent with the layered structure of α-NaFeO2 [29]. Two pairs of splitting peaks, [006/102] and [108/110], in the XRD patterns correspond to the typical structural features of hexagonal layered materials [30]. None of the four samples show any impurity peaks, proving that the pure phase of LiNi0.8Co0.15Al0.05O2 for cathode material was synthesized. As the temperature rises, the intensity of the [108/110] peak and [006/102] peak increases, indicating that the increase in the calcination temperature improves the crystallinity of the samples. The lattice parameters of the four samples are shown in Table 1. It can be seen that the calcination temperature has little effect on the lattice parameters of a, c, and V, but has a certain influence on the ratio of I003/I104. In the ternary cathode material, the ratio of I003/I104 corresponds to the internal cation mixing, and the sample calcined at 750°C has the largest ratio of I003/I104, and the corresponding cation mixing is the smallest. Therefore, the calcination temperature of 750°C is the most suitable.

Figure 4 shows the cycling performance of LiNi0.8Co0.15Al0.05O2 prepared at different calcination temperatures in the voltage range of 2.8–4.3 V at 0.2C. It can be seen that the discharge capacity generally improves with the increasing calcination temperature at first, and then tends to decline. The sample synthesized at 750°C has a higher initial discharge-specific capacity of 186.8 mA h g⁻¹ with a capacity retention of 83.6% after 50 cycles, which is better than that of the samples prepared at 700°C (183.8 mA h g⁻¹, 80.5%) and 800°C (185.8 mA h g⁻¹, 78.5%). When the temperature reached 850°C, a quick capacity fading is observed (from 175.3 to 137.1 mA h g⁻¹). In summary, the experimental results prove that the sample obtained at the calcination temperature of 750°C has the best cycling performance and higher discharge-specific capacity, which is consistent with the XRD results.

### 3.2 Effect of ZnO coating on LiNi0.8Co0.15Al0.05O2

Since ZnO has relatively high electron mobility and low cost, the as-prepared LiNi0.8Co0.15Al0.05O2 was coated with ZnO to improve the structural stability and cycling performance. Figure 5a is the XRD patterns of the Z0, Z1, Z2, and Z3, showing that the XRD patterns of the four

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**Table 1: Lattice parameters of LiNi0.8Co0.15Al0.05O2 prepared at different calcination temperatures**

| Sample/°C | a/Å  | c/Å  | c/a  | V (Å × 10³) | I003/I104 |
|-----------|------|------|------|-------------|-----------|
| 700       | 2.86112 | 14.16892 | 4.9433 | 101.31       | 1.51      |
| 750       | 2.86232 | 14.16877 | 4.9421 | 101.23       | 1.79      |
| 800       | 2.86332 | 14.16965 | 4.9488 | 101.87       | 1.52      |
| 850       | 2.86375 | 14.16433 | 4.9367 | 101.53       | 1.74      |

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**Figure 3:** XRD pattern of LiNi0.8Co0.15Al0.05O2 prepared at different calcination temperatures.

**Figure 4:** Cycling performance of LiNi0.8Co0.15Al0.05O2 prepared at different calcination temperatures.
samples are basically the same. Compared with the standard XRD pattern of ZnO (Figure 5b), there is no characteristic peak of ZnO appeared in the XRD pattern of Z1, Z2, and Z3 because the amount of ZnO used in modification is very small and beyond the XRD resolution. The lattice parameters of the four samples are listed in Table 2. There is no significant change in the lattice constants for pristine (Z0) and coated samples (Z1, Z2 and Z3), indicating that the Zn\(^{2+}\) does not enter the host structure of LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\). The ratio of \(I_{003}/I_{104}\) for the coated samples is larger than that of pristine sample, indicating that ZnO-coated layer reduces the cation mixing of LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) \[31\].

Figure 6 shows the cycling performance of Z0, Z1, Z2, and Z3 at 0.2C in the voltage range of 2.8–4.3 V. It can be seen that the discharge capacity of pristine sample fades from 186.8 to 146.5 mA h g\(^{-1}\) after 100 cycles with a capacity retention of 78.4%. In contrast, the ZnO-coated samples remain 91.3, 90.2, and 86.6% for Z1, Zn2, and Z3 after 100 cycles, respectively, which demonstrates that the ZnO-coated samples have higher cyclic stability than pristine samples. The reason for the improvement of cycling performance is that ZnO-coated layer works as an isolating layer, which effectively reduces the side reactions between electrode and electrolyte, inhibits the internal collapse of the structure caused by the dissolution of transition metals \[32\], improves the structural stability of the material, and further improves the cycling performance of LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) cathode material. In addition, the thin ZnO-coated layer can improve the diffusion rate of Li\(^+\) and the conductivity of the electrode. This result will be verified by CV and EIS. However, the cycling performance of Z2 and Z3 is slightly lower than that of Z1 after 100 cycles, indicating that the thick coating will hinder the diffusion of Li\(^+\) to a certain extent.

Table 2: Lattice parameters of pristine and ZnO-coated LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) samples

| Sample | \(a/\AA\) | \(c/\AA\) | \(c/a\) | \(V (\AA^3)\) | \(I_{003}/I_{104}\) |
|--------|----------|----------|--------|----------------|-----------------|
| Z0     | 2.866232 | 14.16877 | 4.9433 | 101.31         | 1.79            |
| Z1     | 2.866239 | 14.16253 | 4.9430 | 101.37         | 1.81            |
| Z2     | 2.86210  | 14.17036 | 4.9435 | 101.46         | 1.89            |
| Z3     | 2.86256  | 14.17508 | 4.9440 | 101.57         | 1.83            |

Figure 7 is the SEM image of pristine and 1 wt% ZnO-coated LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\). The pristine sample is spherical particles with a clean surface (Figure 7a), and the secondary particles are formed by primary particle aggregation (Figure 7b). In contrast, the surface of the ZnO-coated LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) spheres became obviously rough, and there were many needle-like nano-rods and channels on the surface (Figure 4c and d), which expand the tunnels for Li\(^+\) diffusion and also stabilize the LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) frame, proving that the ZnO successfully attached to the LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) surface.

More detailed structural features of the pristine and 1 wt% ZnO-coated LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) were explored by high-resolution TEM. The pristine sample shows smooth surface and clear lattice fringes, indicating high crystallization (Figure 8a). The inter planar distance of pristine sample is about 0.47 nm (Figure 8b), corresponding to the planar distance of the (003) plane in XRD patterns \[33\]. As shown in Figure 8c and d, it is obvious that the ZnO nanoparticles are attached to the surface of the LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\), which is consistent with the result of the SEM image. As anticipated, this coating layer should improve electrochemical performances of LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) by protecting its surface from electrolyte corrosion and HF attack.

**Figure 5:** (a) XRD patterns of the pristine and ZnO-coated LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\), (b) standard XRD pattern of ZnO.
The rate performance tests of pristine and ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 were conducted under different current rates (0.2, 0.5, 1, 3, 5, 10C) in the voltage range of 2.8–4.3 V. As shown in Figure 9, at a low current rate of 0.2C, the discharge capacity of the ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 is not significantly improved. However, as the current density increases, the rate performance of ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 is obviously better than that of the pristine one. At the current rate of 10C, ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 shows a higher discharge capacity of 135 mA h g^{-1} than that of the pristine sample (115 mA h g^{-1}). In general, the ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 has ZnO protective layer, which can reduce the interfacial impedance, inhibit the electrochemical polarization, and hence improve the rate performance.

Figure 10 shows the CV of the pristine and ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 after 10 cycles with a scanning rate of 0.1 mV s^{-1} in a voltage range of 3.0–4.3 V. Those two curves show the unique redox couples of Nickel-based compounds [34]. The three pairs of redox peaks from left to right correspond to Ni^{2+/3+}, Ni^{3+/4+}, and Co^{3+/4+} [35]. In the anodic process, the peak located at about 3.76 V corresponds to phase transition from the hexagonal phase (H1) to the monoclinic phase (M), the peak at about 4.00 V corresponds to the phase transition from M to a new hexagonal phase (H2), and the peak at about 4.18 V corresponds to the phase transition from the H2 to another hexagonal phase (H3) [36]. There is no other peak in the curves of the ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2, indicating that the modification of ZnO does not affect the structure of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode material.

Figure 6: Cycling performance of the pristine and ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 samples at 0.2C.

Figure 7: SEM images of the (a and b) pristine and (c and d) 1 wt% ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 samples.
To further investigate the reasons for the improvement of rate performance, the CV measurements were performed at various scanning rates. The potential intervals ($\Delta V$) between the anodic and cathodic peaks indicate the reversibility of Li$^+$ insertion/extraction and electrode polarization [37]. As shown in Figure 11a and b, $\Delta V$ increases with the increase of the scanning rate, and when the scanning rate is 0.8 mV s$^{-1}$, the $\Delta V$ of the main peak (Ni$^{2+}$/Ni$^{4+}$, located at about 3.8 V) of ZnO-coated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ is 0.37 V, smaller than that of the pristine sample (0.43 V), which indicated that the modification of ZnO can inhibit the electrode polarization and improve the electrochemical reversibility [38]. As shown in Figure 11c and d, the linear relationship between the redox peak current ($i_p$) and the square root of

Figure 8: TEM images of (a and b) pristine and (c and d) ZnO-coated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$.

Figure 9: Rate performance of pristine and ZnO-coated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ samples.

Figure 10: CV curves of pristine and ZnO-coated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ samples at a scanning rate of 0.1 mV s$^{-1}$ in the voltage of 3.0–4.3 V.
scanning rate ($\nu^{1/2}$) is employed to calculate the Li$^+$ diffusion coefficient ($D_{\text{Li}^+}$) of the main peak ($\text{Ni}^{3+}/\text{Ni}^{4+}$, located at about 3.7 V), which is the same method used in the literature [39]. The $D_{\text{Li}^+}$ is calculated by the following equation:

$$i_p = 2.69 \times 10^7 n^{3/2} AD_{\text{Li}^+}^{1/2} C^{1/2} \nu^{1/2}$$
Table 3: EIS parameters of pristine and ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 after different cycles

| Sample                  | Cycle number | $R_s$ (Ω) | $R_t$ (Ω) | $R_{ct}$ (Ω) |
|-------------------------|--------------|-----------|-----------|---------------|
| LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 | 0            | 5.825     | 15.456    | 233.31        |
|                         | 10           | 3.164     | 12.146    | 65            |
|                         | 100          | 4.163     | 16.428    | 172.5         |
| ZnO-coated              | 0            | 4.125     | 14.943    | 151           |
| LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 | 10          | 2.823     | 6.962     | 28            |
|                         | 100          | 3.426     | 10.944    | 62.8          |

where, the $n$ is charge-transfer number, and $C^*$ is the concentration of Li$^+$ in the active material. The $D_{Li^+}$ at the oxidation peak and the reduction peak of the initial sample are $1.89 \times 10^{-10}$ and $1.47 \times 10^{-10}$ cm$^2$ s$^{-1}$, respectively, which is smaller than that of ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 (2.21 $\times 10^{-10}$ and 1.71 $\times 10^{-10}$ cm$^2$ s$^{-1}$). The diffusion control dominates the electrochemical reaction during the Li$^+$ insertion/extraction progress. Therefore, the modification of ZnO improves the rate performance.

Figure 12 shows the Nyquist plots of the pristine and ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 samples before and after 10 and 100 cycles. The equivalent circuit model of the studied system is also shown in Figure 9d. $R_s$ represents the resistance of the electrolyte, $R_t$ means the surface film resistance, $R_{ct}$ is the charge-transfer resistance [40], and $W$ is the Warburg impedance that reflects the diffusion of Li$^+$ in the solid [41].

All the fitted EIS parameters are listed in Table 3. It is noted that these two samples both show a large $R_{ct}$ value before cycling, which is caused by the inactivation of the electrodes [42]. As the cycling test begins, the $R_{ct}$ value decreases rapidly during the internal activation process [43]. However, after 100 cycles, the $R_s$ value of the pristine sample quickly increased to 172.5 Ω, which was much higher than that of after 100 cycle. However, the value of $R_{ct}$ for ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 after 100 cycles is only about 62.8 Ω, much smaller than that of the pristine one. It can be concluded from the experimental results that the ZnO-coated layer decreases the charge-transfer resistance, increases the electronic conductivity of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2, and further improves the rate performance.

### 4 Conclusion

In conclusion, we designed a novel method for the preparation of high-capacity LiNiO_2-based cathode materials.

First of all, the addition of (NH_4)_2S_2O_8 reduces the cation mixing of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 solid-phase Al-doping improves the element distribution and layered structure. Then, optimizing the calcination temperature enhances the crystallinity of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2, and the ZnO was coated on the surface of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 to improve the cycling performance. The electrochemical tests demonstrated a high reversible discharge capacity of 172.1 mA h g$^{-1}$ at 0.2C with the capacity retention of 91.3% after 100 cycles and a good rate performance at high current density. The above-mentioned improvement indicates the potential application of ZnO-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 as the cathode material for advanced LiBs.

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