

Effects of Washing and Heat-treatment on Structure and Electrochemical Charge/Discharge Property of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Powder

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Abstract: The effect of washing on electrochemical properties of Ni-rich layered cathode $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder is widely known, but few literatures have reported thoroughly. Primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders processed by deionized water and heat-treatment at different temperatures in a paralleling time was explored for the first time. Significant changes of structure, morphology and electrochemical charge/discharge property of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode were detected comprehensively. Mechanism of washing and heat-treatment on the structure and electrochemical charge/discharge property and the rate performance were studied. XRD patterns show the $I_{(003)}/I_{(104)}$ value of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders decreases and the volume turns smaller after being washed and heat-treated. FT-IR spectra confirm the existence of lithium carbonate, and nickel compounds and their relative changes in the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders. The specific capacity and rate performance of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders were carried out before and after washing and heat-treatment. The capacities of primitive sample and treated samples remain 88.87%, 87.21%, 85.43% and 87.80% after 30 cycles, respectively.

Key words: $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder; washing and heat-treatment; charge/discharge; capacity

As one of the most promising cathode materials used in small battery from electronic equipment to hybrid electric vehicle, layered Ni-rich $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder has been studied extensively for its high specific capacity and low cost with respect to LiCoO_2 powder in recent years^[1-3]. Some scientific articles have reported that there exist two kinds of space group in Ni-rich cathode materials including a layered hexagonal phase with an $R\bar{3}m$ of electro-activity and a spinel phase or rock-salt type with an $Fm\bar{3}m$ of electro-inactivity^[4-5]. The preparation of layered Ni-rich $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder with outstanding cycle-ability, high capacity and energy for wide usage is extremely significant. Ohzuku, *et al*^[6] mentioned that LiNiO_2 which was washed with deionized water to remove excess LiOH or Li_2O and obtained almost perfect structure as $\text{LiNi}_2\text{O}_2\text{S}$ prepared by other methods without washing, but the electrochemical reactivity was difficult to examine probably due to washing by deionized water. Washing can improve the cycling performance and structural stability of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ material in electrode, though with a slight negative effect on the capacity^[7]. Majumder, *et al*^[8]

reported that the retention of undesired secondary Lithium carbonate phase in the preparation of layered Ni-rich cathode $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder should be responsible for the relatively lower discharge capacity of the material. Lithium carbonate, approximately 10 nm in thickness, was found on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder which formed by exposing to air during storage, and it severely reduced the accessible capacity and the rate performance^[9]. Lithium compounds are usually excessive in preparing $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder to recuperate the evaporation of Li-ion^[10-16], but this brings undesired residual lithium compounds which may decrease properties of target product^[8-9]. Washing and heat-treatment can remove the impurities like Li_2O , LiOH and Li_2CO_3 that generated in the preparation or storage of layered Ni-rich cathodes. However, there is no special-purpose involved in how to deal with lithium compounds in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder. Therefore, it's necessary to study whether washing and heat-treatment can resolve the problem and would not change the structure, morphology and electrochemical charge/discharge property of $\text{LiNi}_{0.8}\text{Co}_{0.15}$

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$\text{Al}_{0.05}\text{O}_2$ powder.

1 Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder was prepared by sintering fully mixture of $\text{LiOH}\cdot\text{H}_2\text{O}$ and precursor $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{OOH}$, prepared by co-precipitation method, at molar ratio of 1.02:1. The sintering procession includes a pre-sintering stage at 550°C for 4 h and a high temperature sintering at 750°C for 15 h. The primitive sample was obtained after the two sintering stages, which labeled as M1. Secondly, 20 g M1 was placed into beaker with 200 mL deionized water and under constantly stirring with a magnetic stirrer for 0.5 h and suction-filtered to get the moist M1. Finally, The N1, N2 and N3 powders were obtained after heated the moist M1 at 100°C , 250°C and 500°C for 2 h, separately.

Water content tester (Coulometer KF Titrator, mettler toledoC20) was used to determine the content of water in M1, N1, N2 and N3, respectively. TG-DSC (NETZSCH STA 449C) was used to monitor the changes of primitive sample and moist M1 occurred in the procession from room temperature to 500°C . FT-IR spectrum (Nicolet 6700) was used to confirm the changes of samples. X-ray diffraction (XRD, Rigaku D) measurement using $\text{Cu K}\alpha$ radiation was used to identify the crystalline structure of the powders. The scanning electron microscope (SEM, Sirion 200) was used to observe the morphology of particles before and after treated. Electrochemical charge/discharge test were performed to try to find out the capacities and rate performance of primitive sample and treated samples. Electrochemical charge/discharge procedures using the cathode with a mixture of 80wt% $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder, 10wt% carbon black and 10wt% polyvinylidene fluoride (PVDF), and the electrolyte was 1.0 mol/L $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$ (1:1:1, volume ratio). Preliminary cell tests were done using 2023 coin-type cell with Li metal as an anode and the procession carried out between 2.8 V and 4.5 V for primitive sample and 2.8 V and 4.3 V for treated samples at room temperature.

2 Results and discussion

2.1 Water content and TG-DSC curve analysis

Table 1 shows the water content of primitive sample M1 and treated samples N1, N2, N3. The water content of N1 is higher than those of the other samples, especially higher much than that of N3. This is because that the heat-treated temperature of N3 is higher than that of others, so that water molecular in N3 can be evaporated more

completely. Primitive sample's water content is 500.16×10^{-6} , which is higher than the samples heat-treated at 250°C and 500°C , whose quantities are 257.95×10^{-6} and 207.74×10^{-6} , respectively.

TG-DSC curves of primitive sample and moist samples from room temperature to 500°C at heating rate of $5^\circ\text{C}/\text{min}$ are given in Fig. 1. The moist sample shows greater loss about 1.25wt% in mass compared with primitive sample about 0.65wt% throughout the procession. The moist sample shows a relatively obvious endothermic peak at 220.9°C with respect to the smooth curve of primitive simple, which is consistent to the decomposition reaction of nickel hydroxide and produce nickel oxide and water^[17-18]. Therefore, washing of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder with deionized water can generate nickel hydroxide, which would have effect on electrochemical property of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder.

2.2 X-ray diffraction and SEM analysis

Fig. 2 shows the XRD patterns of the primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder M1 and treated samples N1,

Table 1 Water content of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3)

Samples	M1	N1	N2	N3
Water content/ $(\times 10^{-6})$	500.16	1552.45	257.95	207.74

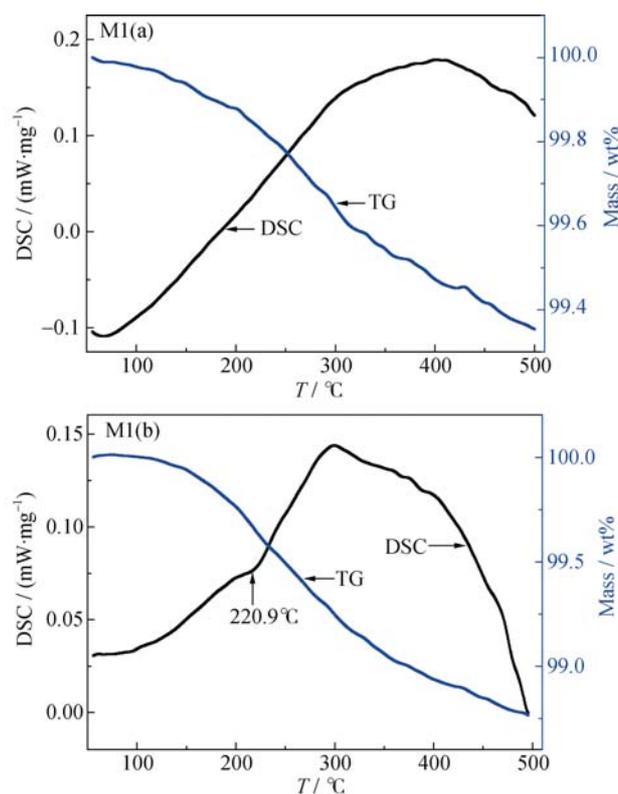


Fig. 1 TG-DSC curves of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder M1 (a) and moist M1 (b)

N2, N3 and the card of PDF 87-1562. All patterns show the structure of a layered hexagonal phase with an $R\bar{3}m$ space group. The (006)/(012) and (018)/(110) peaks in all patterns separate apparently implying that all $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders have the layered structure which plays a vital positive role in electrochemical properties^[4]. As Morales^[5], Ohuzuku^[4], and Reimers^[19] reported that maximum $I_{(003)}/I_{(104)}$ value, c/a ratio and minimum R value, which calculated from $(I_{(006)}+I_{(012)})/I_{(101)}$, corresponding to minimum disorder of Li^+ in 3a site and Ni^{3+} in 3b site and the order of layered structure in some degree to evaluate the electrochemical property of Ni-rich cathode powders. Especially, they are electrochemical inactivity when $I_{(003)}/I_{(104)} < 1.0$, but the point of 1.0 should be reconsidered when Co and Al elements were doped in LiNiO_2 and occupied almost 20% ingredient which leads to the intensity of peaks changed.

Table 2 shows the structural and lattice parameters obtained from the XRD patterns. The c/a ratios of all samples almost keep steady as seen from Table 2, but it obviously shows that staple changes happened in c axis. Integrated intensity ratio of the $I_{(003)}/I_{(104)}$ shift to smaller with the heat-treated temperature rising, but the ratio of Sample N2 is consistent with Sample M1. However, the R values become bigger with the heat-treated temperature rising, but the R value of Sample N1 is consistent with Sample N2. As to unit cell volume, it becomes smaller from primitive sample M1 to N3 and the variable quantity between M1 and treated samples is much larger than that among themselves. The situation may result from the temperature is too low to cause a quite obviously changes in crystal structure for other samples. Consequently, volume, c/a ratio and $I_{(003)}/I_{(104)}$ of Sample N2 and M1 are all bigger than that of N1 and N3 after heat-treating which implies that Sample M1 and N2 probably perform better in electrochemical properties.

Fig. 3 shows SEM images of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3). There are no obvious changes between the samples before and after washing and heat-treatment. All $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders still keep spherical morphology and the sizes of particles are about 15 μm .

2.3 Fourier transformation infrared spectrum analysis

As supplementary information to XRD analysis, FT-IR spectra of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3) are shown in Fig. 4. Every curve occupies a absorption band near 1640 cm^{-1} ($\delta_{\text{H}_2\text{O}}$ mode) and a broad band around 3430 cm^{-1} (stretching vibration of hydrogen bond) and a relatively weak intensity at 436 cm^{-1} (Ni–O stretching vibration) except N2, which corresponds to the absorption bands of nickel hydroxide^[20-21] implying $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder can combine with water and produce trace nickel hydroxide on the surface. But there are only two bands at 1640 cm^{-1} and 3430 cm^{-1} in N2 indicating that the presence of partial water is in the form of absorbed water and formed hydrogen bond between the layers other than free water molecular. The strong band at 517 cm^{-1} which corresponding to the hydroxyl groups' lattice vibration of water molecular is consistent with the analysis of water content before. The band at 2340 cm^{-1} and 2360 cm^{-1} are assigned to carbon dioxide stretching mode, which are background spectrum during FT-IR detection. The band at 560 cm^{-1} belongs to the Ni^{3+} -O stretching frequency with bands at 1640 cm^{-1} and 3430 cm^{-1} indicating the existence of nickel oxide hydroxide^[21-23]. The existence of nickel hydroxide and nickel oxide hydroxide implying that water molecular

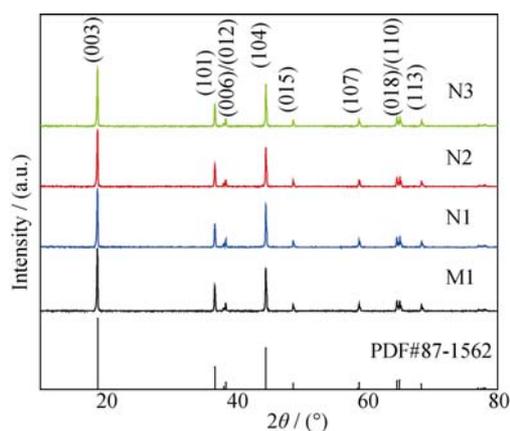


Fig. 2 XRD patterns of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3)

Table 2 Lattice constant, c/a ratio, $I_{(003)}/I_{(104)}$, R , and V of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3)

Samples	a/nm	c/nm	c/a	$I_{(003)}/I_{(104)}$	R	$V/(\times 10^{-5}, \text{nm}^3)$
M1	0.2868	1.4183	4.945	1.18	0.40	1.0101
N1	0.2867	1.4177	4.945	1.16	0.42	1.0091
N2	0.2867	1.4180	4.946	1.18	0.42	1.0092
N3	0.2867	1.4178	4.945	1.11	0.44	1.0090

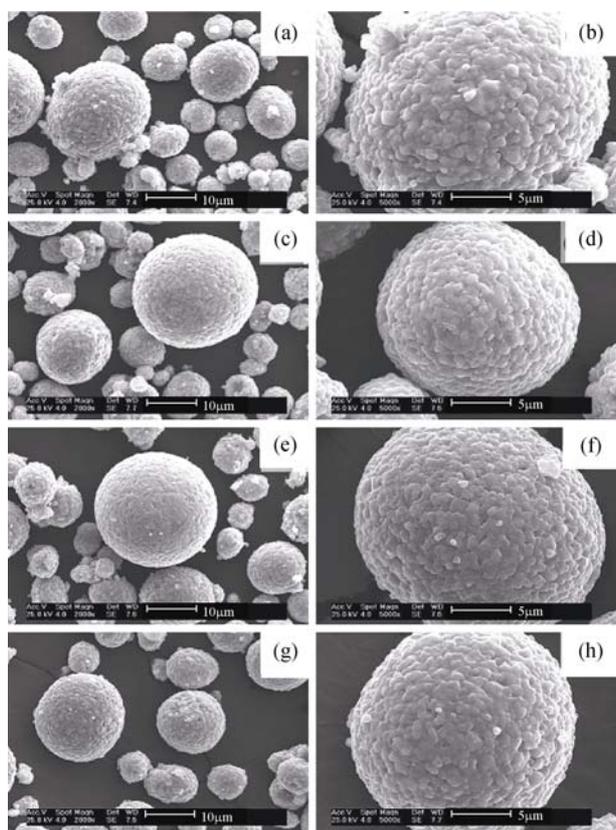


Fig. 3 SEM images for primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder M1 (a, b) and treated samples N1 (c, d), N2 (e, f) and N3 (g, h)

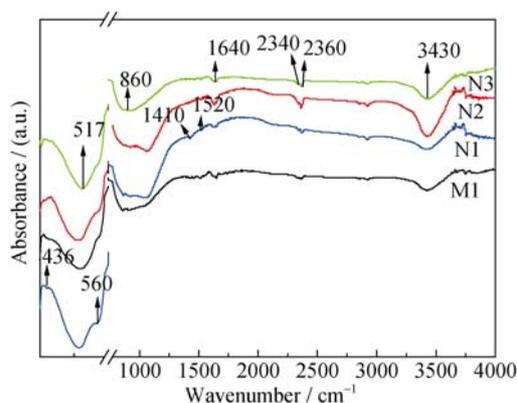


Fig. 4 FT-IR spectra of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3)

not only combine Ni^{2+} ion on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, but also bonding with Ni^{3+} ion in the bulk by penetrating into the interlayer of structure^[24]. Three bands at 860 cm^{-1} , 1410 cm^{-1} and 1520 cm^{-1} correspond to the absorption frequencies of lithium carbonate^[25]. The primitive sample M1 exists trace lithium carbonate may originate from preparation of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder that is high alkalinity and easily absorb water and carbon dioxide to produce lithium carbonate on the surface. However, the curve for N1 shows relatively noticeable intensity of lithium carbonate absorption bands with respect to other samples indicating that $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder washed

and heat-treated at relatively low temperature can produce lithium carbonate, nickel hydroxide and nickel oxide hydroxide much easier.

2.4 Charge/discharge test and rate performance

Fig. 5 compares the initial and the 30th charge/discharge curves at $0.2C$ of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3). The initial discharge capacities of primitive and treated samples performed differently indicating that $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode powders are affected after watering and heat-treating. The initial discharge capacity of primitive powder M1 is 179.99 mAh/g , which is higher than that of watered and heat-treated samples at $100\text{ }^\circ\text{C}$, $250\text{ }^\circ\text{C}$ and $500\text{ }^\circ\text{C}$ for 160.56 mAh/g , 174.82 mAh/g and 166.57 mAh/g in Fig. 5(a), and the capacities remain 88.87% , 87.21% , 85.43% and 87.80% after 30 cycles in Fig. 5(b), respectively.

According to the analysis before, primitive powder M1 performs best among the samples. N2 and N3 perform better than N1 owing to the decomposition of nickel compounds with heat-treatment. Lattice parameters of N3 become smaller making it hard to be by Li^+ intercalation/de-intercalation compared with N1. Relatively high quantity of lithium carbonate and nickel compounds impurities on the surface of

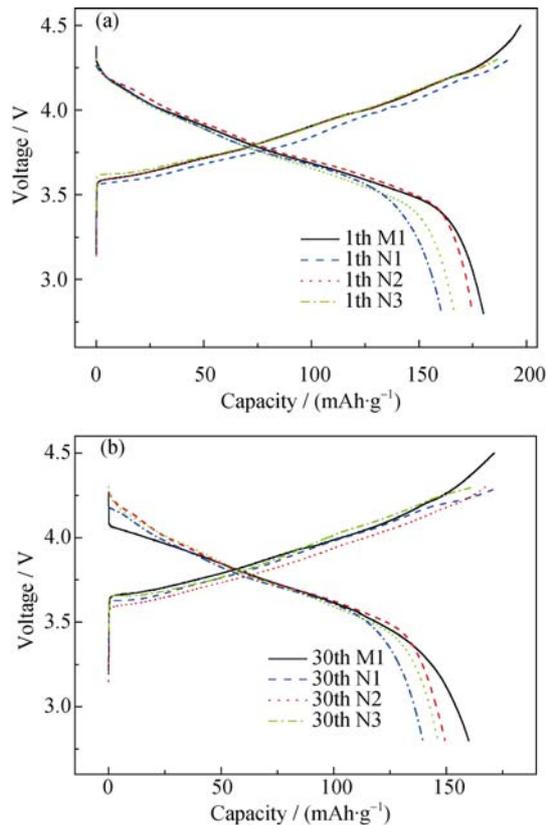


Fig. 5 Initial (a) and the 30th cycle (b) charge and discharge curves at $0.2C$ of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3)

powder intensively affect order of $\text{Li}^+/\text{Ni}^{3+}$ and lead to instability of layered structure of N1 which cause the degradation of capacity^[7-8].

From the results of rate performance in Fig. 6, we find that the discharge capacity of M1 drops from 206.63 mAh/g, at a constant current density of 0.1C, to 153.32 mAh/g of 0.5C. On the other hand, the discharge capacities of treated samples drop from 181.71 mAh/g, 191.87 mAh/g and 187.36 mAh/g, at a constant current density of 0.1C, to 128.39 mAh/g, 144.24 mAh/g and 142.09 mAh/g of 0.5C, respectively. The capacity of N1 fades severely at 0.5C and keeps lower position compared with others. This is impacted by its large amount of impurities of lithium carbonate and nickel compounds. The capacity of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder M1 and treated samples N1, N2, N3 remained 74.20%, 70.66%, 75.18% and 75.84%, respectively after 30 cycles. Therefore, it can be concluded that washing and heat-treatment makes crystal structure of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode unstable and can be destructed much easier during charging/discharging, and it also decreases the capacity of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode and structural stability during charging procession for Li-ion de-intercalation.

3 Conclusions

We compared the changes about XRD patterns, SEM photographs, FT-IR spectra, charge/discharge capacity and rate performance of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder M1 and treated samples N1, N2, N3, and discussed the mechanism of washing and heat-treatment to the structure and electrochemical properties. The $I_{(003)}/I_{(104)}$ value of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders decreased after washing and heat-treatment. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders contained more water will produce nickel compounds and react with carbon dioxide to produce lithium carbonate much easier. The capacity of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder M1

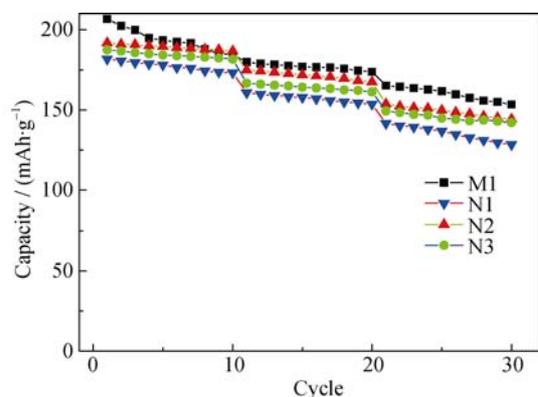


Fig. 6 Rate performances of primitive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder (M1) and treated samples (N1, N2, N3)

and treated samples N1, N2, N3 remained 74.20%, 70.66%, 75.18% and 75.84%, respectively after 30 cycles of rate performance. It can be confirmed that the decrease of structural stability and discharge capacity of samples are caused by lithium carbonate and nickel compounds during the procession of Li-ion intercalation/de-intercalation of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode, and samples containing more water would produce lithium carbonate and nickel compounds much easier, paving the way of optimizing the preparation process of ternary cathode material.

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洗涤和热处理对 LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ 正极材料结构和电化学充放电性能的影响

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摘 要: 用去离子水将原始的 LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ 正极材料进行洗涤并分别在不同温度下处理相同的时间, 讨论了 LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ 正极材料结构、形貌以及电化学充放电性能的变化, 同时探讨了洗涤和热处理对材料结构、电化学充放电性能以及倍率性能影响的机理。XRD 分析表明: 在洗涤和热处理之后, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ 正极材料的 $I_{(003)}/I_{(104)}$ 比值以及晶胞体积均有变小; 傅里叶红外光谱分析表明: 在洗涤和热处理之后, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ 正极材料中形成了碳酸锂、镍化合物杂质及其相关变化。同时对洗涤和热处理前后 LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ 正极材料容量和倍率性能进行测试。容量测试结果表明: 原始样品以及处理后样品在 30 圈循环之后容量保持率分别为 88.87%、87.21%、85.43%和 87.80%。

关键词: LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ 正极材料; 洗涤和热处理; 充放电; 容量

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