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Green and low-cost synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode material for Li-ion batteries

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Abstract

A spherical $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) cathode material is synthesized from the precursor $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ obtained through a co-precipitation method using potassium sodium tartrate for the first time as a chelating agent. X-ray diffraction analysis proves that the as-prepared NCA is a hexagonal phase with perfectly ordered layered structure. Scanning electron microscope study shows that the morphology and size of NCA remain nearly the same as those of the precursor. Clear crystal lattice fringes arranged along the (003) plane can be found in transmission electron microscope images. The NCA material exhibits excellent electrochemical properties with initial charge/discharge capacities of 245.6/204.4, 201.2/196.3, 189.0/182.2 and 177.3/171.4 $\text{mAh}\cdot\text{g}^{-1}$ at 0.1, 0.2, 0.5 and 1.0 C, respectively, and charge/discharge capacity retentions of 91.9%/91.5% after 100 cycles at 0.5 C in the voltage range of 2.8-4.3 V (vs. Li/Li⁺).

Keywords: Energy storage and conversion ; Functional; Nickel-rich lithium cobalt oxide; Potassium sodium tartrate; Green synthesis

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1. Introduction

Owing to the advantages in gravimetric capacity, rate capability and capital cost, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) has found relatively widespread commercial applications as a cathode material, for instance, in Panasonic batteries for Tesla electric vehicles [1-3]. To further enhance the electrochemical properties of NCA, various strategies have been proposed. Especially, lots of synthetic methods, such as spray drying [4], cation exchange [5], spray pyrolysis [6], sol-gel [7], solution combustion [8] and co-precipitation [9-14] have been used to prepare NCA with improved electrochemical properties. Among all of the above-mentioned methods, co-precipitation has been generally recognized as the best industrialization method due to its absolute merits with respect to homogenous elemental distribution, well-controlled spherical morphology, good fluidity and high tap density. In a typical co-precipitation route, a mixed sulphate solution of Ni^{2+} , Co^{2+} and Al^{3+} , NaOH solution and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution acted as the metal ions source, the precipitant and the chelating agent, respectively. Considering the environmental pollution caused by ammonia, 5-sulfosalicylic acid [11] and ethylenediaminetetraacetic acid (EDTA) [12] was explored as the complexing agents to synthesize NCA. However, the utilization of such expensive chelating agents is unfavorable for the industrialization of NCA. Therefore, a cheap and green complexing agent should be developed to prepare NCA.

Potassium sodium tartrate tetrahydrate ($\text{C}_4\text{H}_4\text{O}_6\text{KNa} \cdot 4\text{H}_2\text{O}$) is usually applied in the fields of plating and electroless plating based on its low cost and strong complexing ability with different metal ions including Al^{3+} , Ni^{2+} and Co^{2+} . Thus, in this work, $\text{C}_4\text{O}_6\text{H}_4\text{KNa} \cdot 4\text{H}_2\text{O}$ was firstly used as a chelating agent to synthesize the spherical $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$. Moreover, NCA prepared from this precursor was characterized by the physical and electrochemical methods.

2. Experimental

Stoichiometric amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were dissolved in deionized water with a molar ratio of 0.8:0.15:0.05 for $\text{Ni}^{2+}:\text{Co}^{2+}:\text{Al}^{3+}$. Then $\text{C}_4\text{H}_4\text{O}_6\text{KNa} \cdot 4\text{H}_2\text{O}$ was dissolved in a $1 \text{ mol} \cdot \text{L}^{-1}$ aqueous solution of metal sulphates. The mixed solution and $3 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution were simultaneously pumped into a continuous stirred tank reactor. The pH value, temperature, stirring speed and velocity of flow were strictly controlled. After the reaction for 12 h, the precipitate was thoroughly washed with deionized water and then dried at $100 \text{ }^\circ\text{C}$ for 15 h in a vacuum oven to yield $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$. After the precursor was mixed with 5% excess $\text{LiOH} \cdot \text{H}_2\text{O}$, the mixture was sintered at $750 \text{ }^\circ\text{C}$ for 12 h in flowing oxygen atmosphere to obtain NCA.

The structure and morphology of the sample were examined by X-ray diffraction (XRD, D/max-r A type Cu K_α , 40 kV, 300 mA), scanning electron microscopy (SEM, SU 3500) and transmission electron microscope (TEM, Tecnai G12), respectively. The contents of lithium, nickel, cobalt and aluminium of the sample were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 4300DV).

Coin-type CR2025 cells assembled in an argon filled glove box were used for the electrochemical testing of samples. The cell consisted of a lithium anode, a NCA cathode, a Celgard 2400 separator and an electrolyte of 1 mol L^{-1} LiPF_6 in EC-DMC-EMC (1:1:1, volume ratio) solution. The cathode was composed of NCA, acetylene black and PVDF binder (8:1:1, weight ratio) on an aluminum foil. The charge-discharge tests were performed at a desired C rate in the range of 2.8-4.3 V (vs. Li/Li^+) at $25 \text{ }^\circ\text{C}$ on a LAND CT2001A battery testing system (China). **The thermal stability of NCA was investigated using differential scanning calorimetry (DSC) on TA Q600**

from 100 to 350 °C at a rate of 5 °C · min⁻¹ in a nitrogen environment. The DSC samples were prepared in the glove box from the disassembled cells which were charged at different states of charge (SOC) after cycling five times at 0.1 C.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the precursor Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂ prepared by the co-precipitation method using C₄H₄O₆KNa·4H₂O as the chelating agent. It is seen that the diffraction peak positions of the precursor match well with the standard spectrum of JCPDS #01-1047. The XRD pattern of NCA synthesized from the precursor is presented in Fig. 1(b). Obviously, all the diffraction peaks of the as-prepared NCA can be indexed to the pure α-NaFeO₂ hexagonal phase without any impurity. Furthermore, the perfectly ordered layered structure of the product is corroborated by the strong peak splitting of (006)/(012) and (018)/(110), high values of the *c/a* (~4.95) and *I*₍₀₀₃₎/*I*₍₁₀₄₎ (~1.33) ratios, and the low *R*-factor (*R*-factor = (*I*₍₀₀₆₎+*I*₍₀₁₂₎)/*I*₍₁₀₁₎) of 0.39 [14].

The SEM images of the precursor and NCA are displayed in Fig. 2. As shown in Fig. 2(a), the spherical precursor powders with the size of 5-8 μm in diameter are comprised of primary needle-like particles. The morphology and size of NCA remain nearly the same as those of the precursor, except for the change of primary particles appearance into cylindrical form (Fig. 2(b)). This indicates that Ni_{0.8}Co_{0.15}Al_{0.05}(OH)₂ and NCA prepared using C₄H₄O₆KNa·4H₂O as the chelating agent maintain the morphology of the corresponding products obtained with NH₃·H₂O [14]. Additionally, the composition analysis of NCA measured by ICP-AES shows that the molar ratio for Ni:Co:Al is 0.801:0.149:0.051, which is close to the targeted stoichiometry.

Fig. 3 exhibits the TEM images of NCA, where clear lattice fringes with the interplanar distance of 0.47 nm can be observed. The value corresponds to the *d*-

spacing of the (003) plane derived from Bragg equation (XRD pattern found in Fig. 1b). This suggests again that NCA can be prepared using $C_4H_4O_6KNa \cdot 4H_2O$ as the chelating agent.

Both the initial charge/discharge curves at various C -rates and the cycle-life curve at 0.5 C of the sample are demonstrated in Fig. 4. Although the electrochemical polarization becomes severer with the increase of the C -rate, the sample exhibits good rate performance (Fig. 4(a)). The charge/discharge capacities at 0.1, 0.2, 0.5 and 1.0 C are found to be 245.6/204.4, 201.2/196.3, 189.0/182.2 and 177.3/171.4 $mAh \cdot g^{-1}$, with the corresponding efficiencies of 83.2%, 97.6%, 96.4% and 96.7%, respectively. The cycle-life test at 0.5 C in Fig. 4(b) indicates that the charge/discharge capacities decreases from 189.0/182.2 to 173.7/166.8 $mAh \cdot g^{-1}$ after 100 cycles with the corresponding capacity retentions of 91.9%/91.5%, and the charge-discharge efficiency of each cycle maintains about 96%. Fig. 4(c) illustrates the DSC curves of charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ as a function of x ($0 < x < 0.64$) in the presence of the electrolyte (The composition of the fully delithiated cathode was $Li_{0.36}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (100% SOC), based on the discharge capacity.). At 0% SOC, no obvious exothermic peak can be observed. As the SOC increases, the exothermic peak shifts to lower temperature with increasing heat generation. At 100% SOC, the sample exhibits an exothermic peak at 231.8 $^{\circ}C$ with heat generation of 550.6 $J \cdot g^{-1}$ which is related to oxygen generation from the decomposition of the cathode by reaction with the electrolyte [15]. These data are comparable to those of the reported NCA synthesized using other chelating agents [11-15]. However, this synthetic approach is more cost-effective and environment-friendly in the preparation of NCA compared to other co-precipitation methods, since the use of the 5-sulfosalicylic acid, EDTA and ammonia can be avoided.

4. Conclusions

$C_4H_4O_6KNa \cdot 4H_2O$ is successfully used for the first time as the chelating agent in the co-precipitation method to prepare the precursor $Ni_{0.8}Co_{0.15}Al_{0.05}(OH)_2$. The NCA material synthesized from the precursor possesses spherical morphology and perfectly ordered layered structure. This is beneficial to its electrochemical properties with initial charge/discharge capacities of 245.6/204.4, 201.2/196.3, 189.0/182.2 and 177.3/171.4 $mAh \cdot g^{-1}$ at 0.1, 0.2, 0.5 and 1.0 C, respectively, and charge/discharge capacity retentions of 91.9%/91.5% after 100 cycles at 0.5 C.

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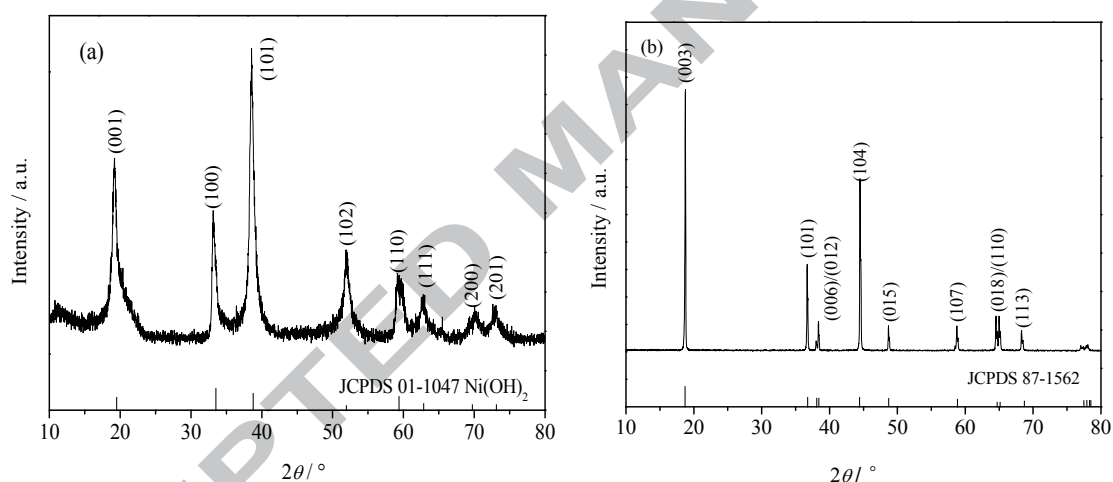


Fig. 1 XRD patterns of (a) $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ and (b) NCA.

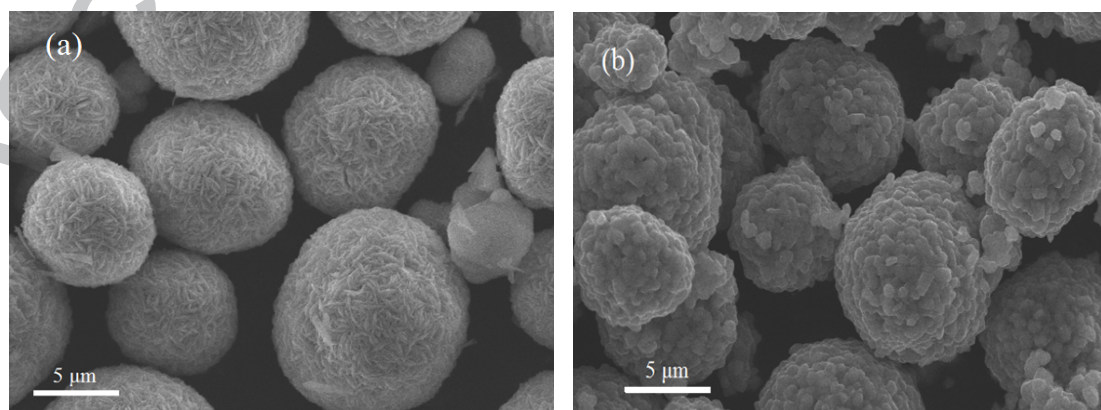


Fig. 2 SEM images of (a) $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ and (b) NCA.

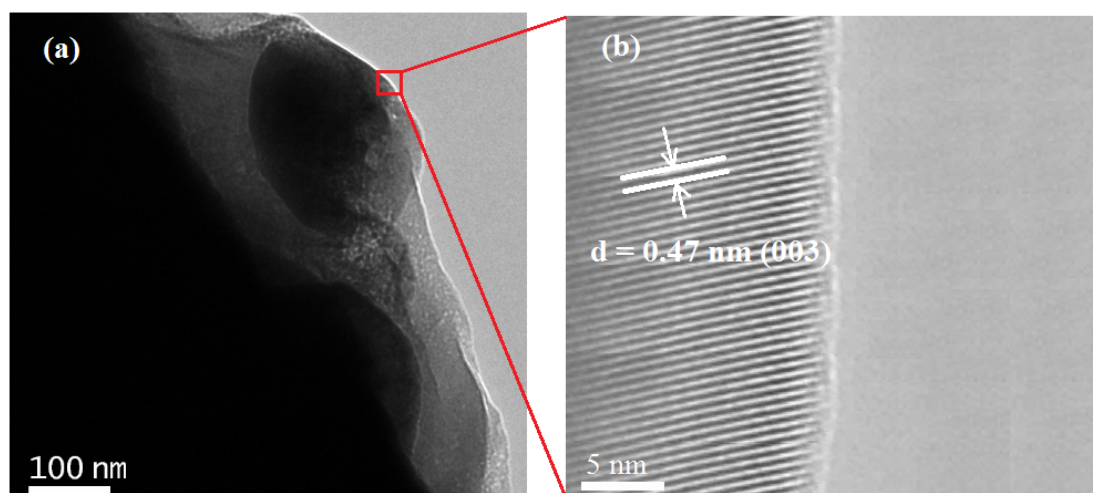


Fig.3 TEM images of NCA, (b) is the magnified image of the red frame region of (a).

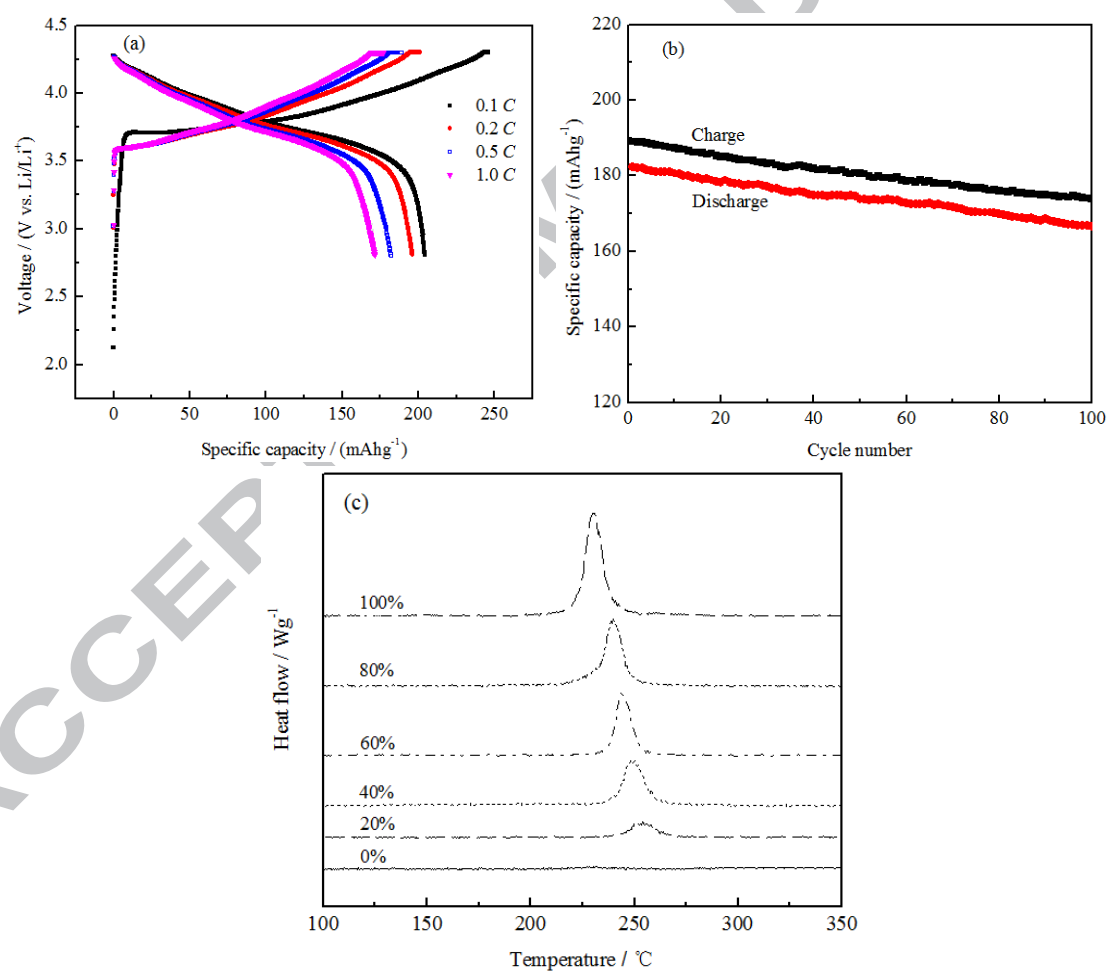


Fig. 4 (a) Initial charge/discharge curves at various C -rates, (b) cycle-life curves at 0.5 C and (c) DSC curves of NCA at different states of charge.

Highlights

> $C_4H_4O_6KNa \cdot 4H_2O$ is used as a chelating agent to prepare $Ni_{0.8}Co_{0.15}Al_{0.05}(OH)_2$.

- > NCA prepared from this precursor shows excellent electrochemical properties.
- > This synthetic approach is more cost-effective and environment-friendly.

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