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Optimization of Calcination Temperature for Superior Electrochemical Performance in Single-Crystal $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$

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Abstract

With properties such as excellent energy-storage performance and large specific discharge capacity ($\sim 180 \text{ mAh g}^{-1}$), nickel-rich $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM) has become one of the important research systems of cathode materials in advanced and energy-dense lithium-ion batteries. Attributed to the elimination of grain boundaries and other structural defects in Ni-rich single-crystal layered cathodes, they exhibit superior electrochemical performance in terms of cycling stability. The solid-phase method is commonly used to prepare single-crystal material is mostly a particle aggregation of “quasi-single-crystal”, the need for ball milling or air flow pulverization and other ways to obtain a standard single-crystal. Good single crystals can be successfully prepared without further ball milling treatment using the molten salt process. In this paper, single-crystal materials were prepared by setting calcination temperatures of 900 °C, 950 °C and 1000 °C. The influence of calcination temperature during the molten-salt synthesis process on the electrochemical characteristics of the cathode materials were systematically examined. The obtained data reveal that the single-crystal material $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (SC-950) synthesized at the calcination condition of 950 °C has the most outstanding electrochemical performance. The material delivered first-cycle specific discharge capacities of 179.4 and 95.8 mAh g^{-1} at 0.1 C and 5 C, respectively. In addition, capacity retention performance of 91.3% and 87.1% were maintained after 200 cycles at current rates of 1 C and 5 C, respectively.

Keywords: $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$, Lithium-ion batteries, Ni-rich cathode materials, Molten salt method, Calcination temperature

Introduction

Nowadays, the problems of global warming and shortage of non-renewable resources have become more and more serious, and humanity urgently needs to research and develop new energy sources, countries around the world are also increasingly focusing on going green and actively developing new renewable resources [1–3]. Lithium-ion batteries (LIBs) as newly developed type of green and environmentally friendly battery, have developed rapidly and become the mainstay of new energy materials in the future on account of their long-term cycling stability, enhanced safety performance, superior energy density and reduced environmental impact [4–6]. Among them, the ternary nickel-rich layered cathode material $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ ($x + y + z = 1$, $x \geq 0.6$, NCM) has become a material with considerable application potential benefiting from its outstanding specific discharge capacity (180 mA h g^{-1}), excellent energy density, and excellent balance of performance and safety[7–10].

Although NCM cathode materials have been commercialized, they are prone to electrochemical degradation and capacity reduction, mainly because their grains are secondary polycrystalline spheres formed through the aggregation of multiple primary single-crystal particles [11]. With the internal cycling of the cell, the volume expansion direction and constriction direction of the primary particles will change, the stress-strain anisotropy of the primary particles is caused by the randomly oriented grain boundaries, which makes the NCM spherical secondary particles susceptible to cracking, and ultimately leads to the lattice distortion and the generation of grain boundary cracks [12–14]. Electrolytes can penetrate into these cracks, leading to further crack enlargement and unwanted side reactions such as transition metal migration, which ultimately give rise eventually leading to deteriorated electrochemical performance and capacity degradation. [15–16]. Therefore, material structure design [17–19], elemental doping [20–21], surface modification [22–26] and other such methods have been devised to solve the problem. Among them, the reduction of grain boundaries by preparing large-diameter primary particles, single crystals (SC), is a very effective and promising solution [27–30].

Currently, a variety of methods exist for synthesizing single-crystal NCM cathode materials, including molten salt synthesis, solid-state synthesis under high-temperature conditions and co-precipitation. The high-temperature solid-phase method entails thoroughly blending the precursor

with a lithium source via techniques like grinding, and then calcining the mixture at temperatures between 800 and 1000 °C to produce single-crystal particles. The co-precipitation method employs the principle of co-precipitation reactions, where metal salt solutions of Ni, Co, and Mn are combined with precipitant solutions (NaOH and NH₄OH). By adjusting the pH value, a precursor for the ternary material (e.g. Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂) is synthesized. The starting material is subsequently combined with a lithium source (Li₂CO₃ or LiOH·H₂O) and calcined at elevated temperature to yield a single-crystal material. The molten salt method entails blending the precursor, lithium source, and a cosolvent (e.g., Li₂SO₄ and NaCl, etc.). By introducing the cosolvent, the growth environment of the particles is modified, shifting the reaction from a solid-phase to a liquid-phase process. This facilitates ion diffusion and directly yields standard single-crystal particles. Wang et al.[31] prepared SC-NCM622 samples by a molten salt-assisted method, and the obtained SC-NCM622 has the effect of inhibiting Li⁺/Ni²⁺ antisite defects, suppressing intergranular microcracks and mitigating undesirable phase evolution, thereby reinforcing the crystal structure stability.

In this study, we employed the binary molten salt method utilizing LiOH-H₂O-Li₂SO₄ to synthesize single crystal materials. Calcination temperature plays a vital role in the molten-salt synthesis process, significantly influencing the synthesis of the obtained materials. To clarify the role of calcining temperature on the morphology, particle size, and electrochemical characteristics of single crystals, three various calcining temperatures (900 °C, 950 °C and 1000 °C) were set for the preparation of single crystals during the experiments. The role of temperature in regulating the crystal morphology, dimensions, and electrochemical characteristics of the materials was examined experimentally to identify the optimal calcination system. This work offers a novel technique for the fabrication of Ni-rich layered ternary cathode materials with a single-crystal structure.

Experimental section

Materials fabrication

Fig. 1 illustrates the synthesis process of NCM622. The precursor Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂, lithium source LiOH-H₂O (1:1.5 molar ratio to precursor) and cosolvent Li₂SO₄ (1:6 molar ratio to LiOH-H₂O) were dispersed in 20 mL of absolute ethanol. The mixture underwent sufficient grinding treatment until complete evaporation of ethanol, followed by drying. Subsequently, the dried product underwent calcination in an atmosphere filled with oxygen at temperatures of 900 °C, 950 °C, and

1000 °C for 10 h under quartz tube-furnace conditions. After cooling with the furnace, the product underwent centrifugation and was repeatedly cleaned with deionized water until achieving neutrality. The sample was subjected to drying at 80 °C for 10 h in an oven and underwent calcination at 700 °C in flowing oxygen for 6 h. Finally, the material was thoroughly ground, and the final product, single crystal NCM 622 was obtained by sieving the powder using a 325-mesh sieve. The single crystal NCM622 prepared at calcination temperatures of 900 °C, 950 °C and 1000 °C is respectively represented as SC-900, SC-950 and SC-1000.

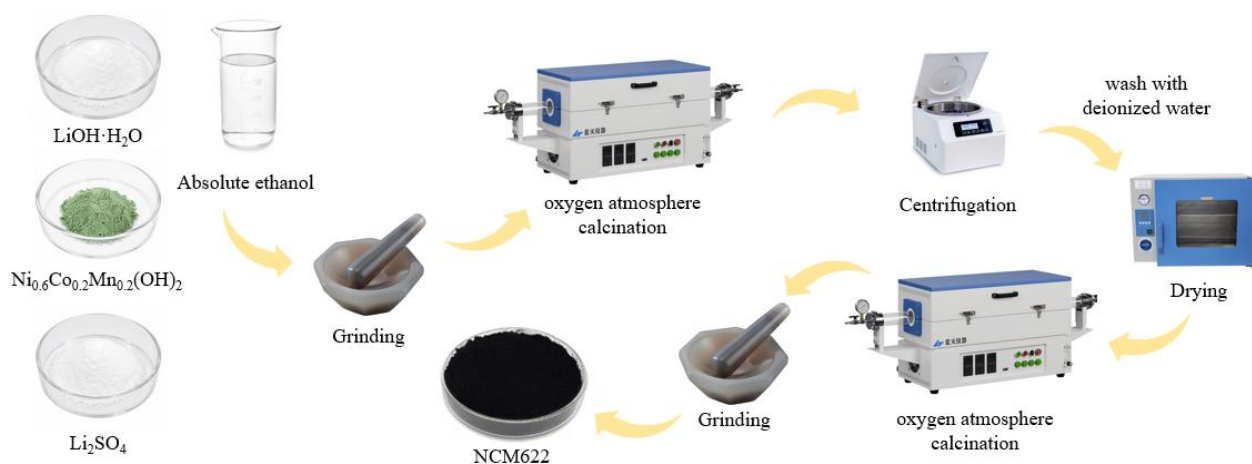


Fig. 1 Schematic diagram of the NCM622 synthesis process

Materials analysis and characterization

The structural and crystallographic features of the obtained samples were investigated by X-ray diffraction analyzer (XRD, Rigaku SmartLab 3 kW). A Cu K α radiation source was employed, with a measurement extent of 10° to 90° and a scanning speed of 10° min⁻¹. Subsequently, the acquired data underwent Rietveld refinement analysis utilizing the Structural Analysis System (GSAS-II). Scanning electron microscopy (SEM, Hitachi S4800, Japan) was employed to investigate the crystal morphology and particle size of the materials. The types of elements and their amounts of each element in the single crystal samples were quantitatively carried out through analysis with ICP-OES (Mettler Toledo DSC 3+, USA). The microstructure of the tested materials was analyzed using Transmission electron microscope (TEM, JEM-F200, Japan). The TEM images were further processed and analyzed with Gatan Digital Micrograph software. The single crystal materials synthesized in the study underwent qualitative and quantitative analysis through X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA) for characterization of elemental types, their signal strengths, and chemical valences. Analysis and fitting of the XPS spectra were undertaken

using XPS PEAK software.

Electrochemical measurement of materials

The slurry, consisting of 88% by weight monocrystalline NCM622, 6% by weight polyvinylidene fluoride (PVDF), 6% by weight acetylene black, and a proper quantity of N-methyl-1,2-pyrrolidone (NMP), was uniformly mixed and applied to aluminum foil, which serves as the cathode collector. Subsequently, the coated foil was subjected to vacuum drying treatment at 80 °C for 10 h, followed by cutting into electrode sheets measuring 14 mm in diameter, each electrode possessing an active material mass per unit area in the ranging from 5 to 7 mg cm⁻². The prepared electrode sheets were employed as the cathodes in CR2032 coin-type half-cells. Lithium metal plates were employed as the counter electrode. The cathode and counter electrode are divided by a separator Celgard 2400 diaphragm. They are immersed in the electrolyte of 1.0 M LiPF₆ dissolved in a mixed solvent of DMC: DEC:EC (1:1:1). The batteries were fabricated in an atmosphere filled with argon and subsequently charged and discharged using the LAND Battery Test System at varying current densities (1 C = 200 mAh g⁻¹), charge–discharge measurements were conducted between 2.7 and 4.3 V at 25 °C. Electrochemical characterization by cyclic voltammetry was conducted on an electrochemical workstation (CHI 760e) over a voltage interval of 2.5–4.5 V. Furthermore, electrochemical impedance spectroscopy quantifications were performed with an AC perturbation amplitude of 5 mV over a frequency extent from 10 mHz to 100 kHz.

Results and discussion

Characterization of structural and morphological

The composition of phases and the structure in the single-crystal NCM622 samples were examined using X-ray diffraction along with Rietveld refinement. Fig. 2 illustrates the relevant XRD patterns and the outcomes of the Rietveld refinement. Each of the diffraction peaks corresponds to a layered hexagonal α -NaFeO₂ structure characterized by the R $\bar{3}$ m space group [32,33]. In all samples, there is a significant degree of splitting between the (006)/(102) peaks and the (108)/(110) peaks, which suggests that the material features a well-structured lamellar morphology [34]. To delve deeper into the physical phase characteristics, SC-900, SC-950, and SC-1000 samples underwent refinement and analysis with the GSAS software. The corresponding lattice constants are presented in Table 1. All samples manifested R_{wp} values lower than 5%, and the fitting-derived data are in great agreement

with the experimental data indicating a low fine-tuning error and high accuracy. The c/a ratios of all samples exceeded 4.9, demonstrating a well-ordered layered structure. The I_{003}/I_{104} ratios of SC-900, SC-950, and SC-1000 are 0.95, 1.04, and 0.91, respectively, and it can be clearly seen that SC-950 has the highest I_{003}/I_{104} ratio, which suggests that the degree of mixing of $\text{Li}^+/\text{Ni}^{2+}$ cations is much lower ($\sim 4.98\%$) [35]. The reason for such variation can be explained by the following factors, on one side, the lower calcination temperature ($900\text{ }^\circ\text{C}$) resulted in incomplete diffusion of Li^+ , which was unable to occupy all the Li sites, allowing Ni^{2+} to occupy the Li sites, which resulted in a severe mixing of $\text{Li}^+/\text{Ni}^{2+}$ cations ($\sim 5.46\%$). On the other side, although the excessively high calcination temperature ($1000\text{ }^\circ\text{C}$) allowed Li^+ to diffuse sufficiently, the high temperature caused the thermodynamic entropy increase effect to take the dominant position, which caused Ni^{3+} to generate Ni^{2+} again through the defective reaction, thus exacerbating the phenomenon of the severe $\text{Li}^+/\text{Ni}^{2+}$ cation mixing ($\sim 6.37\%$). By comparison, a calcination temperature of $950\text{ }^\circ\text{C}$ yielded the optimal result, exhibiting the lowest degree of cation mixing. In addition, the lower cation mixing degree helps to strengthen the long-cycle characteristics of the obtained material, which is favorable for the subsequent electrochemical characterization testing.

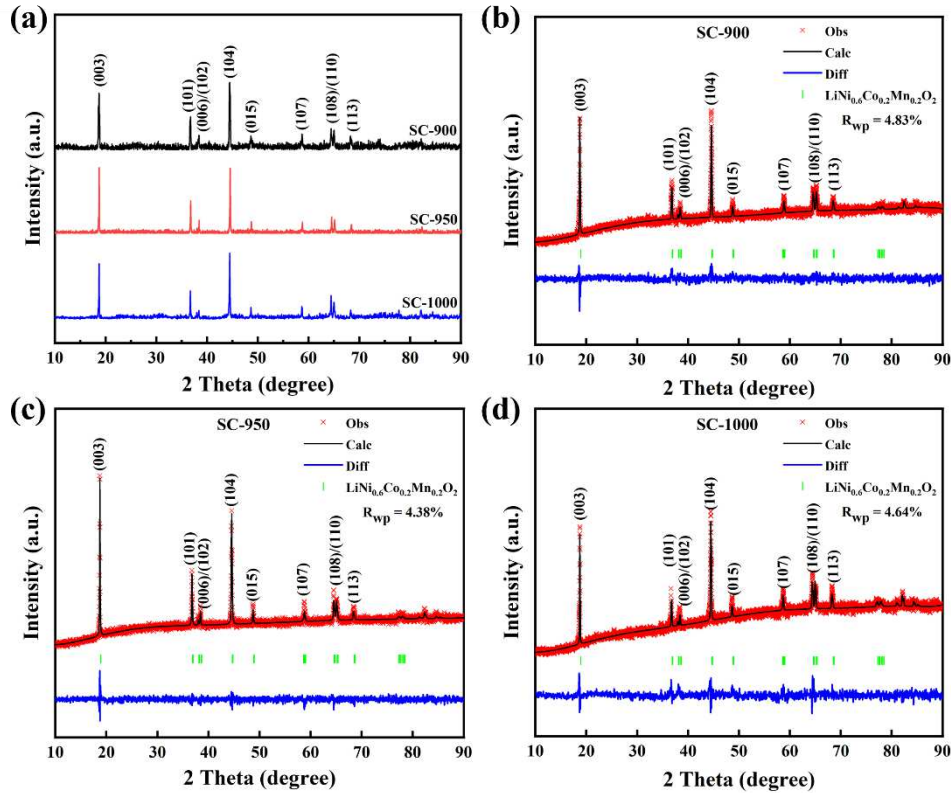


Fig. 2 XRD patterns of SC-900, SC-950, and SC-1000 (a), and corresponding Rietveld refinement profiles of SC-900 (b), SC-950 (c), and SC-1000 (d).

Table 1 Structural parameters and refinement results of SC-900, SC-950, and SC-1000 obtained from Rietveld analysis

Sample	$a / \text{\AA}$	$c / \text{\AA}$	c / a	$V / \text{\AA}^3$	I_{003}/I_{104}	Li ⁺ /Ni ²⁺ disorder (%)
SC-900	2.860	14.184	4.959	100.48	0.95	5.46
SC-950	2.863	14.218	4.966	100.94	1.04	4.98
SC-1000	2.870	14.237	4.961	101.56	0.91	6.37

The morphology and particle size of the single crystals strongly affect their electrochemical performance. The morphological features of the three samples was examined using SEM. The SEM scanning images proved that the samples SC-900, SC-950, and SC-1000 have typical single-crystal morphology, as illustrated in Fig. 3 (a-f). With increasing calcination temperature, the size of single crystal particles also increases. After calcination at 900 °C and 950 °C, the single-crystal particles showed a “hexagonal prism” morphology, with particle sizes of approximately 1.5 μm and 2 μm , and the particles continued to grow after increasing the temperature to 1000 °C, with single-crystal sizes of 3.5 μm and irregular polygonal morphology. Because the lower temperature will lead to incomplete development of single crystal particles, too high calcination temperature makes the single crystal particles over-expansion, the phenomenon of melting, and ultimately show irregular morphology. Secondly, fine particles were observed on the single-crystal particle surfaces. These particles may be the incompletely reacted Li-containing residues or their by-products, mainly Li_2SO_4 and Li_2CO_3 , during the calcination process, which may have a certain effect on the subsequent electrochemical properties. The elemental composition of the three obtained as ascertained by inductively coupled plasma measurement, with the test results presented in Table 2. As shown in Table 2, the molar ratios of Ni, Co, and Mn in all obtained samples are consistent with the theoretical ratio of 6:2:2, confirming the materials were synthesized successfully.

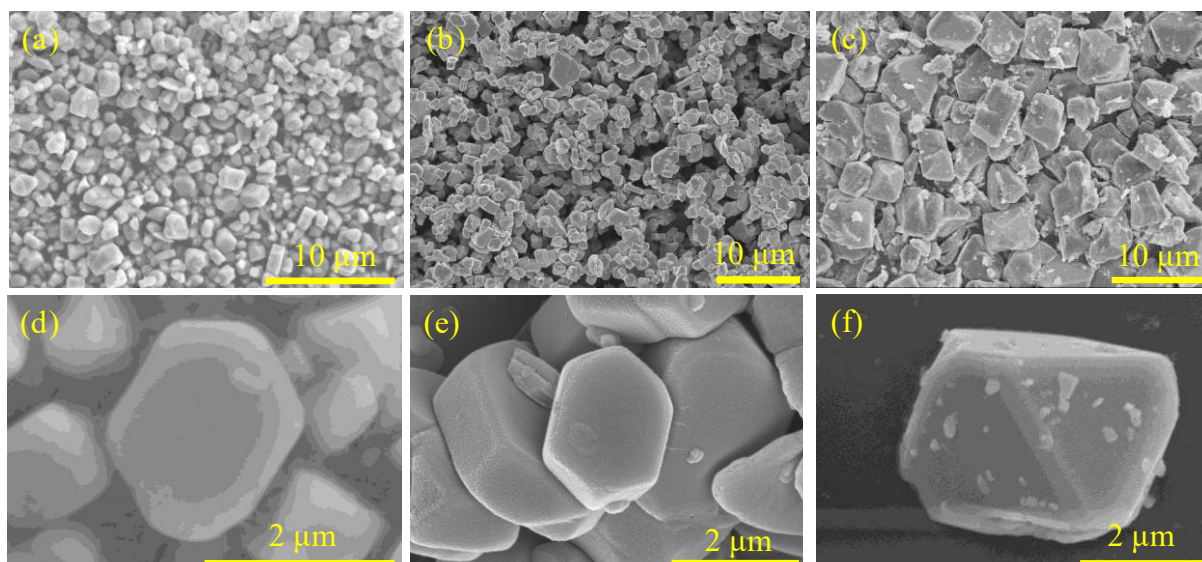


Fig. 3 SEM images and corresponding magnified views of SC-900 (a, d), SC-950 (b, e), and SC-1000 (c, f)

To further investigate the microstructure, the SC-950 sample was examined by TEM, and the resulting images were analyzed through Gatan Digital Micrograph software. The findings are presented in Fig. 4. The SC-950 sample shows a “hexagonal prism” morphology, which is consistent with the single crystal morphology observed by SEM, and the selected area shows a more distinct layer structure. The crystal plane spacing was calculated to be 0.207 nm by FFT fitting, which compares with the standard card to get the crystal plane belonging to the (104). The lamellar structure of the samples is uniformly distributed, and the other impure phases are not observed, which is conducive to promote the material's lattice stability and improve lithium-ion intercalation/deintercalation kinetics during charge–discharge cycles.

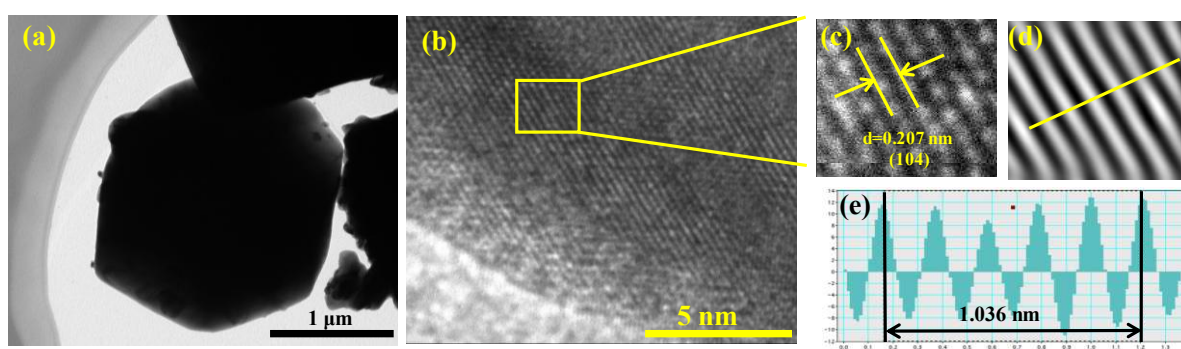


Fig. 4 TEM images and corresponding FFT patterns of SC-950

Table 2 Elemental composition of SC-900, SC-950, and SC-1000 determined by ICP

	Ni (%)	Co (%)	Mn (%)
SC-900	62.7	19.0	18.3
SC-950	62.9	19.0	18.1
SC-1000	62.9	19.1	18.0

The surface chemical element composition and valence state distribution of SC-900, SC-950, and SC-1000 samples were analyzed using X-ray photoelectron spectroscopy (XPS). Fig. 5 displays the narrow spectrum of Ni, Co, and Mn. In the Ni 2p energy spectrum, the diffraction peaks at approximately 855.1 eV and 872.7 eV represent the Ni 2p_{3/2} and Ni 2p_{1/2} orbitals, respectively. Each orbital exhibits two smaller diffraction peaks, matching with Ni²⁺ and Ni³⁺ [36]. Notably, SC-950 exhibited the lowest Ni²⁺ content. A lower Ni²⁺ concentration is associated with a decreased extent of Li⁺/Ni²⁺ cation mixing. These results indicate that SC-950 exhibits the lowest degree of cation mixing, which contributes to improved electrochemical performance and is consistent with XRD analysis. The Co 2p spectrogram shows the existence of 2 valence states (+2, +3) of Co. The diffraction peaks observed at approximately 782.1 eV and 796.5 eV match with the Co 2p_{3/2} and Co 2p_{1/2} orbitals, respectively, aligning with the characteristic peaks associated with cobalt. In contrast, the Mn 2p spectrum indicates that Mn exists predominantly in the +4 valence state. Mn promotes to the material's structure stabilization, thereby strengthening both the structural integrity and safety of the battery [37].

Table 3 Ni²⁺ and Ni³⁺ contents of SC-900, SC-950, and SC-1000 determined from XPS analysis

	SC-900	SC-950	SC-1000
Ni ²⁺ (%)	55.1	51.1	59.6
Ni ³⁺ (%)	44.9	48.9	40.4

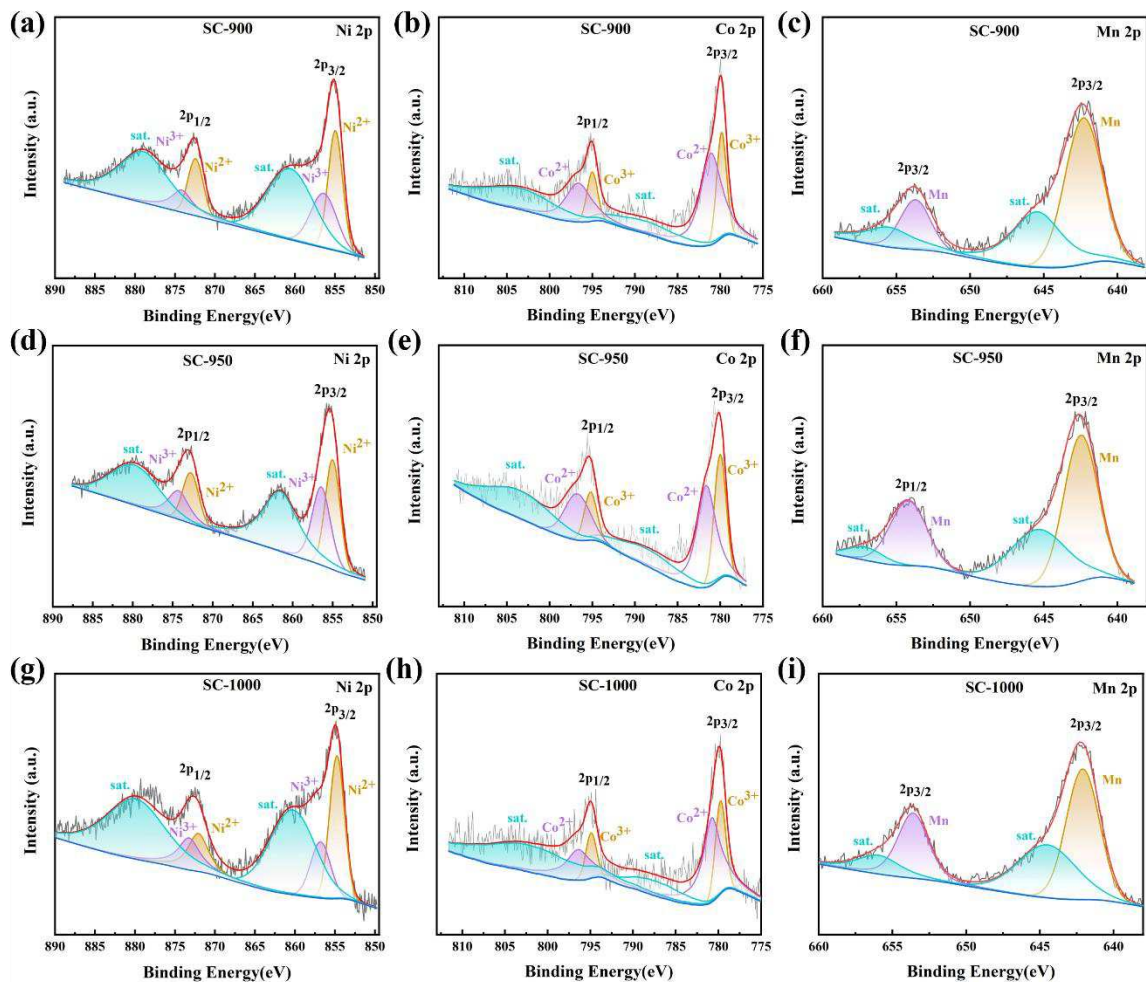


Fig. 5 XPS analysis of SC-900, SC-950, and SC-1000: Ni 2p (a, d, g), Co 2p (b, e, h), and Mn 2p (c, f, i) spectra

Performance of electrochemical

To assess how calcination temperature influences electrochemical characterization, three single-crystal materials obtained (SC-900, SC-950, and SC-1000) were employed in half-cell configurations. Galvanostatic charge–discharge experiments were performed within a voltage range of 2.7–4.3 V, with the relevant results illustrated in Fig. 6. Fig. 6(a–c) exhibits the first-cycle galvanostatic charge–discharge curves of the three obtained samples measured at various current rates. At a 0.1 C rate, the first-cycle specific discharge capacities for SC-900, SC-950, and SC-1000 were 174.6, 179.4, and 146.8 mAh g⁻¹, respectively. At a 5 C rate, the initial discharge specific capacities were 64.8, 95.8, and 46.3 mAh g⁻¹, respectively. SC-950 delivers the highest initial discharge capacity at all current rates. The enhanced electrochemical performance is likely associated with the optimized calcination temperature, which facilitates the development of a favorable single-crystal morphology and minimizes Li⁺/Ni²⁺ cation disorder.

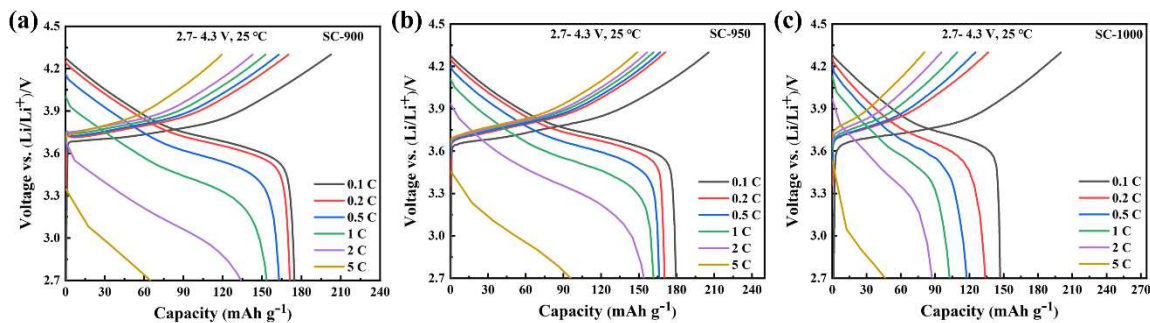


Fig. 6 Initial charge-discharge curves of SC-900 (a), SC-950 (b), and SC-1000 (c) at different current rates

To evaluate the influence of calcination temperature on the stability of structure, rate capability, and cycling performance of the materials, SC-900, SC-950, and SC-1000 were tested at different current densities. Fig. 7(a) shows that the discharge capacities of the three samples are similar at low current rates. However, notable discrepancies in specific capacities emerge at high rates, particularly at 5 C. When returning from high rate (5 C) to low rate (0.2 C), the capacity performance of the three obtained samples can still be well maintained, which indicates that they have good reversibility. The cycling performance of the single-crystal materials was investigated at current rates of 1 C and 5 C, as presented in Fig. 7(b, c). After 200 cycles at 1 C, the specific discharge capacities of SC-900, SC-950, and SC-1000 decreased from 145.3, 147.8, and 124.8 mAh g⁻¹ to 127.1, 135.0, and 97.9 mAh g⁻¹, respectively. The corresponding capacity maintenance values were 87.4%, 91.3%, and 78.4%. Following 200 cycling tests at 5 C, the discharge capacities of SC-900, SC-950, and SC-1000 decreased from 69.2, 91.7, and 49.0 mAh g⁻¹ to 59.4, 79.8, and 22.6 mAh g⁻¹, with capacity maintenance rates of 85.4%, 87.1%, and 46.1%, respectively. SC-950 demonstrates superior cycling performance, as evidenced by its higher discharge capacity, greater capacity retention, and lower capacity decay rate compared with SC-900 and SC-1000. This is due to the optimal calcination temperature of SC-950, which gives it the right particle size (~2 μm), smaller cation mixing and better structural stability. Furthermore, excessively high calcination temperatures promote overgrowth and uneven distribution of single-crystal particles while impairing the crystal structure. Conversely, insufficient calcination temperatures restrict crystal growth and yield undersized particles. As a result, both conditions adversely affect cycling stability and accelerate capacity degradation. Therefore, an appropriate calcination temperature is essential for achieving optimal electrochemical characterization.

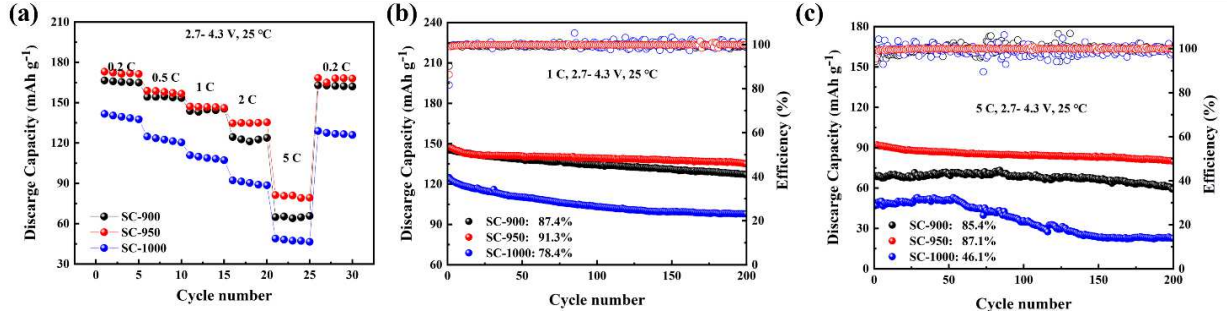


Fig. 7 Electrochemical characterization curves of SC-900, SC-950 and SC-1000 materials: Rate capacity performance (a), Cycle stability at 1 C (b) and 5 C (c)

Fig. 8 displays the cyclic voltammetry (CV) profiles of the cathode materials in the voltage span of 2.5–4.5 V. A well-defined pair of redox peaks was observed for each sample around 3.8 V and 3.6 V, signifying the taking place of a $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox reaction. Fig. 8(a) shows that SC-950 possesses sharper redox peaks, higher peak currents, and less potential difference ($\Delta V = 0.217$ V) than those of SC-900 and SC-1000, indicating that SC-950 has lower overpotential and higher electrochemical reversibility, which would be favorable for Li^+ insertion and extraction, providing a theoretical basis for higher long-cycle capacity retention of the material. Fig. 8(b)–(d) present the cyclic voltammetry (CV) curves of the three samples at scan rates of 0.10, 0.12, 0.14, 0.16, and 0.18 mV s^{-1} . With increasing scan rates, the oxidation peak shifts to higher potentials, while the reduction peak moves to smaller potentials, consistent with the expected behavior. The linear correlation between the peak current (i_p) and $v^{1/2}$ shown in Fig. 8(e) is characteristic of a diffusion-controlled electrochemical process involving Li^+ insertion/extraction mechanism.

The Randles–Ševčík equation was applied to calculate the Li^+ diffusion coefficient/:

$$i_p = (2.69 \times 10^5) n^{\frac{3}{2}} A D_{\text{Li}}^{\frac{1}{2}} v^{\frac{1}{2}} C_0$$

where i_p denotes the peak current, n represents the number of electrons transferred by each molecule during charging and discharging cycles, A indicates the area of the electrode, v specifies the scan rate, and C_0 refers to the bulk Li^+ concentration within the cathode material. The D_{Li}^+ value for SC-950 was determined to be $5.86 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, exceeding that of SC-900 ($4.01 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) and SC-1000 ($5.02 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$), thus underscoring the enhanced ion dispersion kinetics associated with SC-950.

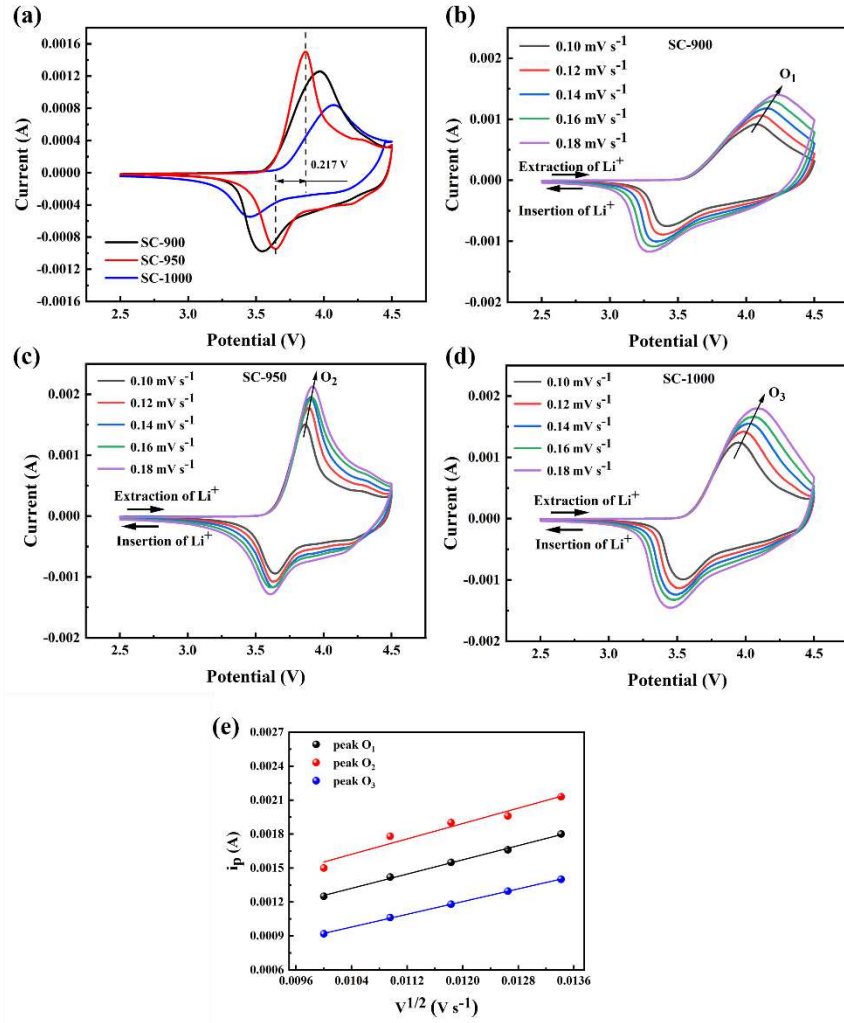


Fig. 8 CV curves of the samples at 0.1 mV s^{-1} (a); CV curves of SC-900 (b), SC-950 (c), and SC-1000 (d) at scan rates of $0.10, 0.12, 0.14, 0.16$, and 0.18 mV s^{-1} ; linear plots of i_p versus $v^{1/2}$ (e).

To further elucidate the kinetic behavior and electrochemical reaction mechanisms of the obtained materials, EIS measurements were performed and analyzed. The findings are presented in Fig. 9 and Table 4. Fig. 9(a) and 9(b) illustrate the electrochemical impedance spectroscopy results of the electrode following 1 cycle and 200 cycles, respectively. The semicircular shape seen in the high-frequency area of the Nyquist plot is indicative of the charge-transfer resistance (R_{ct}) for the electrode. In contrast, the linear portion in the low-frequency region relates to the Li^+ diffusion occurring within the electrode. The R_{ct} of SC-900, SC-950 and SC-1000 after the first cycle were 80.64 , 57.01 and 47.37Ω , respectively. After 200 cycles, the impedance of all three electrodes increased to 116.5 , 103.7 , and 108.4Ω , respectively, which could be primarily attributed to the structural degradation of the cathode material during prolonged cycling. From the values, it is easy to see that SC-950 has the lowest impedance value before and after cycling with a smaller increase, which contributes to enhanced ion diffusion and improved electrochemical kinetics. The diffusion

coefficient of lithium ions (D_{Li^+}) is linked to the diagonal of the low-frequency region and can be determined using a specific formula. As the frequency (ω) approaches 0 in the low-frequency area, the Warburg factor σ can be defined by the subsequent formula:

$$Z' = R_s + R_{\text{ct}} + \sigma \omega^{-\frac{1}{2}}$$

and the diffusion coefficient of lithium ion (D_{Li^+}) can be expressed using the following equation:

$$D_{\text{Li}^+} = \frac{1}{2} \left[\frac{V_m}{FA\sigma} \left(-\frac{dE}{dx} \right) \right]$$

however, the voltage platform exhibits in the voltage curve, so obtaining accurate values of dE/dx is challenging, the transformation leads to the following formula:

$$D_{\text{Li}^+} = \frac{R^2 T^2}{2n^4 F^4 A^2 C_{\text{Li}^+}^2 \sigma^2}$$

where R denotes the universal gas constant, T represents the absolute temperature, F indicates the Faraday constant, A specifies the electrode region, and C_{Li^+} refers to the bulk Li^+ concentration within the cathode material. The Li^+ diffusion coefficient (D_{Li^+}) of SC-950 was determined to be $2.11 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, which is higher than those of SC-900 ($5.12 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$) and SC-1000 ($4.38 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$) (Table 4). These results indicate that SC-950 exhibits a relatively high Li^+ diffusion rate, consistent with the diffusion coefficient (D_{Li^+}) obtained from cyclic voltammetry (CV) measurements. These results help explain the superior electrochemical performance of SC-950.

Table 4 Impedance parameters obtained from Nyquist plots

	SC-900		SC-950		SC-1000	
	After 1 cycle	After 200 cycles	After 1 cycle	After 200 cycles	After 1 cycle	After 200 cycles
$R_s(\Omega)$	5.96	3.97	5.26	2.42	2.28	2.47
$R_{\text{ct}}(\Omega)$	80.64	116.5	57.01	103.70	47.37	108.40
$R_{\text{CEI}}(\Omega)$	-	-	-	-	29.58	78.80
$D_{\text{Li}^+}(\text{cm}^2 \text{ s}^{-1})$	5.12×10^{-15}		2.11×10^{-14}		4.38×10^{-15}	

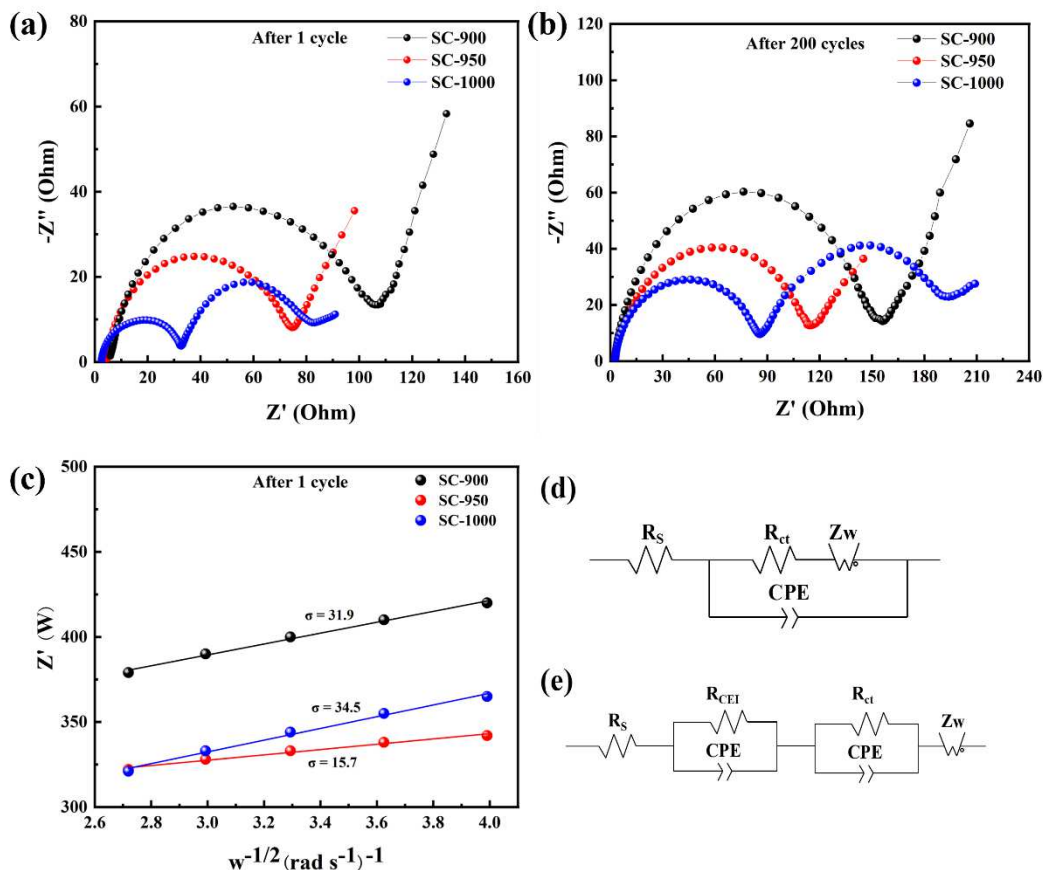


Fig. 9 Nyquist plots of the obtained samples and matching impedance spectra after 1 cycle (a) and after 200 cycles at 1 C (b); $Z'-\omega^{-1/2}$ plots (c); equivalent circuits for SC-900 and SC-950 (d) and SC-1000 (e)

Conclusion

In brief, we synthesized single-crystal NCM 622 (SC 622) cathode materials using the molten salt technique and investigated the influence of varied calcination temperatures (900 °C, 950 °C, and 1000 °C) on the structure and electrochemical characterization of the materials. The results demonstrate that calcination temperature has a significant influence on the morphology, particle size, and electrochemical performance of the material. The grain size of single-crystal particles increases with increasing calcination temperature, but too high calcination temperature leads to excessive grain growth and exacerbates $\text{Li}^+/\text{Ni}^{2+}$ cation mixing of the material, which is unfavorable for enhancing the electrochemical characterization of the material. The single crystal material synthesized through calcination at 950 °C exhibits superior crystal structure, uniform morphology, and exceptional electrochemical characterization. SC-950 delivers a high first-cycle specific discharge capacity of 179.4 mAh g⁻¹ at 0.1 C, with a capacity maintenance rate of 91.3% after 200 cycles at 1 C. Additionally, it retains 87.1% of its capacity after 200 cycles at 5 C. Hence, the optimal calcination

temperature for fabricating single-crystal NCM622 cathode materials is 950 °C. These findings present a novel approach for synthesizing single-crystal nickel-rich layered ternary cathode materials.

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