



Effect of grain size of single crystalline cathode material of $\text{LiNi}_{0.65}\text{Co}_{0.07}\text{Mn}_{0.28}\text{O}_2$ on its electrochemical performance

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ABSTRACT

In this paper, single crystalline cathode materials $\text{LiNi}_{0.65}\text{Co}_{0.07}\text{Mn}_{0.28}\text{O}_2$ with different grain size are successfully prepared via controlling the key experimental parameters. Tap density, compact density, specific surface area, X-ray diffraction, scanning electron microscopy and transmission electron microscopy are performed to evaluate the effect of grain size on the physical property and electrochemical performance of single crystalline material. The electrochemical tests reveal excellent rate capability and cycle stability at the cut-off voltage of 4.5 V for the sample with grain size around 3 μm with a capacity retention of 83% while only 40% of initial capacity is retained for the sample in 9 μm . The inferior electrochemical performance of large-sized single crystalline material is attributed to the severe planar gliding, particle cracking and irreversible phase transition. A moderate grain size between 3 and 5 μm can achieve desirable physical property and electrochemical performance.

1. Introduction

In the past decades, Li-ion batteries (LIBs) have shown tremendous commercial potential in many fields, such as portable electronic devices, electrical vehicles, smart grid and etc [1]. However, the energy density and safety issue are limiting further application of LIBs in electrical vehicles. Lithium nickel-cobalt-manganese oxide ($\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$) has become one of the most promising cathode material candidates, due to its many advantages, like high specific capacity, high discharge voltage plateau and long cycle life [2–4].

Despite the merits of NCM cathode material, it still possesses certain drawbacks as following [5]. First of all, cation mixing is caused by that part of Ni^{2+} will diffuse into the Li layer because of the similar ion radius of Li^+ (0.76 Å) and Ni^{2+} (0.69 Å), consequently, resulting in structural deterioration and capacity fading during cycling [6]. Secondly, residual lithium is inevitably introduced during synthesis and storage of NCM material, which mainly exists in the form of Li_2CO_3 and LiOH , leading to gelation of slurry and battery gassing issues. NCM material undergoes irreversible phase transition from layered phase (R-3m) to spinel phase (Fd-3m) then to electrochemically inactive rock-salt phase (Fm-3m), which causes capacity decay [7]. Meanwhile, the irreversible phase transition is accompanied by oxygen evolution and transition metal

dissolution, resulting in safety issue [8]. Moreover, NCM material is usually in a secondary particle morphology, which is composed of nano-sized primary particles with different crystal orientation. The primary particles will undergo volume expansion and contraction during constant charging and discharging, thus, the anisotropic volume change leads to cracking of the aggregated secondary particles [9]. Fracture of secondary particles generates fresh surface exposed to electrolyte and the side reaction between fresh surface and electrolyte will consume more active Li^+ , resulting in capacity degradation [10,11]. What is more, in order to reach longer driving range, researchers have been working on further improving the energy density of NCM materials [12]. Elevating the upper cut-off voltage of the cathode materials can effectively increase the discharge capacity and energy density of NCM materials [13]. Nevertheless, high cut-off voltage brings new challenges for NCM materials [14]. Since NCM materials are instable at high voltage condition ($> 4.3 \text{ V vs. Li}^+/\text{Li}$), elevating the cut-off voltage will accelerate the structural deterioration, particle cracking and oxygen evolution, leading to rapid capacity fading and more severe safety issue [15].

To deal with the above-mentioned issues, in recent years, researchers developed single crystalline NCM cathode materials, which is only composed of dispersive primary particles rather than agglomerated

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secondary particles [16,17]. Due to the absence of grain boundaries, single crystalline NCM materials can avoid the intergranular cracking and suppress side reactions between electrode and electrolyte, therefore, it has excellent structural stability [18,19]. Up to now, researchers have developed various strategies to synthesize single crystalline NCM materials with different morphologies, such as high temperature calcination [20–22], molten salt method [23–25], hydrothermal method [26], spray-pyrolysis [27,28] and all-dry synthesis [29]. Furthermore, a lot of modification strategies are applied on single crystalline NCM materials to enhance their electrochemical performance, like doping [30–33], surface coating [34,35] and crystal facet manipulation [36–38]. However, the controlling of the grain size and the effect of grain size on its electrochemical properties are scarcely discussed. Previously, our group developed a facile method to synthesize single crystalline $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ and $\text{LiNi}_{0.65}\text{Co}_{0.07}\text{Mn}_{0.28}\text{O}_2$ cathode materials via assistance of SrCO_3 [38,39]. Based on the previous works, we found the key parameters and how they determine the morphology of single crystalline NCM materials, thus, it is practicable to manipulate the grain size of single crystalline cathode materials by carefully controlling these parameters. In this paper, a series of single crystalline $\text{LiNi}_{0.65}\text{Co}_{0.07}\text{Mn}_{0.28}\text{O}_2$ cathode materials with different grain size have been prepared via controlling the crucial synthesis parameters with the assistance of calcination additive and their electrochemical and physical properties are evaluated.

2. Experimental

2.1. Material synthesis

The single crystalline $\text{LiNi}_{0.65}\text{Co}_{0.07}\text{Mn}_{0.28}\text{O}_2$ cathode materials with different grain size were synthesized by a co-precipitation reaction followed by high temperature sintering similar to our previous report [40]. The precursor $\text{Ni}_{0.65}\text{Co}_{0.07}\text{Mn}_{0.28}(\text{OH})_2$ was prepared as following. The transition metal solution was obtained by dissolving $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ into de-ionized water in a molar ratio of 65:7:28. NaOH solution and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution were applied as precipitant and chelating agent, respectively. The transition metal solution, NaOH solution and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution were synchronously pumped into a 10 L constant stirring tank reactor (CSTR). The reaction pH and temperature were kept at 11.8 and 50°C. After reacting for 20 h, the precipitate was aged overnight, then washed with de-ionized water and dried in a vacuum oven for 12 h at 80°C to obtain the precursor. Next, the precursor was mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$ (99.5%, Tianqi Lithium Co., Ltd.) and nanosized SrCO_3 (99.5%, Shanghai Macklin Biochemical Co., Ltd). The mixture was sintered at 650°C for 8 h and then at 910 to 950 °C for 12 h in a tube furnace under oxygen atmosphere with a heating rate of 3°C min⁻¹. The detailed Li/TM ratio, SrCO_3 percentage and calcination temperature are listed in Supporting Information. The final products were obtained by grinding and passing through 400-mesh sieve after cooling. The products were denoted according to their measured D50 values as SC-D1, SC-D3, SC-D5, SC-D7 and SC-D9, respectively.

2.2. Characterization

A BT-9300S Laser Diffraction Particle Size Analyzer (Bettersize Instruments Ltd.) was applied to measure the D50 values of as-prepared samples. A BT-300 Tap Density Tester was used to obtain the tap density. Powder X-ray diffraction (XRD) was conducted to examine the crystal structure via a PANalytical Empyrean ($\text{Cu K}\alpha$ radiation, $\lambda_{\text{K}\alpha 1} = 1.54056 \text{ \AA}$ and $\lambda_{\text{K}\alpha 2} = 1.54439 \text{ \AA}$) at the scanning angle 2θ ranged from 10 to 80° with a scanning step of 0.02° step⁻¹. Scanning electron microscope (SEM) was performed to characterize the morphology of samples with a JEO JSM-7900F and TESCAN MIRA4 at the acceleration voltage of 5 kV. Energy dispersive X-ray spectrometer (EDS) was carried out to analyze the element distribution. The detailed morphology and structural information were observed by transmission electron microscopy

(TEM) and high-resolution transmission electron microscopy (HRTEM) images collected by a TF 20 instrument with an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) was applied to analyze the chemical valence state of each element on the surface via a Thermo Scientific K-Alpha instrument.

2.3. Electrochemical test

The electrochemical performance was tested by assembling 2025-type coin cells. The cathode slurry was prepared by mixing the as-prepared active material, conductivity agent (Super P) and binder poly(vinylidene difluoride) (PVDF) with a mass ratio of 80:10:10, then dissolved in N-methyl-2-pyrrolidone (NMP). The slurry was coated on current collector (Al foil) followed by vacuum drying at 120°C for 12h. Then the Al foil was punched to obtain disc-shaped electrodes with a diameter of 14mm. The average area mass loading density of electrode is around 3.5 mg cm⁻² and the electrode density is around 2.7 g cm⁻³. Coin cells were assembled in an Argon-filled glove box. The applied electrolyte was 1 M LiPF_6 in a mixture solvent consisted of ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC)/ethylene carbonate (EC) (EMC: DMC: EC=1:1:1 vol%), separator Celgard 2400 polypropylene films and anode lithium foil. The cycle performance and rate capability were tested on a Land battery test system (Wuhan LAND Electronic Co., Ltd.) at 25 °C in the voltage range of 2.8–4.3V and 2.8–4.5V, respectively. All cells were tested with a constant current (CC) followed by constant voltage (CV) program. Cyclic voltammetry (CV) curves were measured by a DH7000 electrochemical workstation (Donghua Test Co., Ltd.) between 2.8 and 4.5V. Electrochemical impedance spectroscopy (EIS) was collected by DH7000 electrochemical workstation in the frequency range of 100k–0.01Hz.

3. Result and discussion

The grain size of as-prepared samples was evaluated by the D50 values measured via a laser diffraction particle size analyzer and listed in Table 1. The morphologies of as-synthesized samples are obtained by field emission scanning electron microscope (FESEM), exhibited in Fig. 1. Fig. 1(a) shows the morphology of the precursor, which is in a near spherical morphology with a diameter around 4 μm. Fig. 1(b)–(f) demonstrate the morphologies of SC-D1, SC-D3, SC-D5, SC-D7 and SC-D9, respectively, in the same magnitude. Clearly, most of the primary particles of SC-D1 are in a submicron scale, in accordance with the D50 value of 1.4 μm in Table 1, which is relatively small compared to other samples. As the calcination temperature increased, the products' grain size grew larger. As shown in Table 1 and Fig. 1(c) and (d), the D50 values for SC-D3 and SC-D5 are 2.8 and 5.1 μm, respectively. To further promote particle growth, the calcination temperature and Li/TM ratio were elevated to 950 °C and 1.08, resulting in a D50 value of 7.3 μm for SC-D7. And with the SrCO_3 percentage increased to 0.5wt%, SC-D9 was synthesized with a D50 value of 9.4 μm. Moreover, it is observed that the particle surface of SC-D1, SC-D3 and SC-D5 samples is smooth while the particle surface of SC-D7 and SC-D9 is rough with a lot of fine particles. It is found that in order to obtain single crystalline NCM materials with large grain size, the harsh synthesis conditions will cause fine particles in SC-D7 and SC-D9 sample, which has been reported by others [20,21, 41]. Table 1 and Fig. 1 indicate that the grain sizes of as-prepared samples are in agreement with the designed values.

Table 1
D50 values, tap density and specific surface area of as-prepared samples.

Sample	SC-D1	SC-D3	SC-D5	SC-D7	SC-D9
D50 (μm)	1.4	2.8	5.1	7.3	9.4
Tap density (g cm ⁻³)	1.8	1.9	2.1	2.2	2.3
Compact density (g cm ⁻³)	3.2	3.2	3.3	3.4	3.4
Specific surface area (m ² g ⁻¹)	1.4	0.9	0.5	0.4	0.4

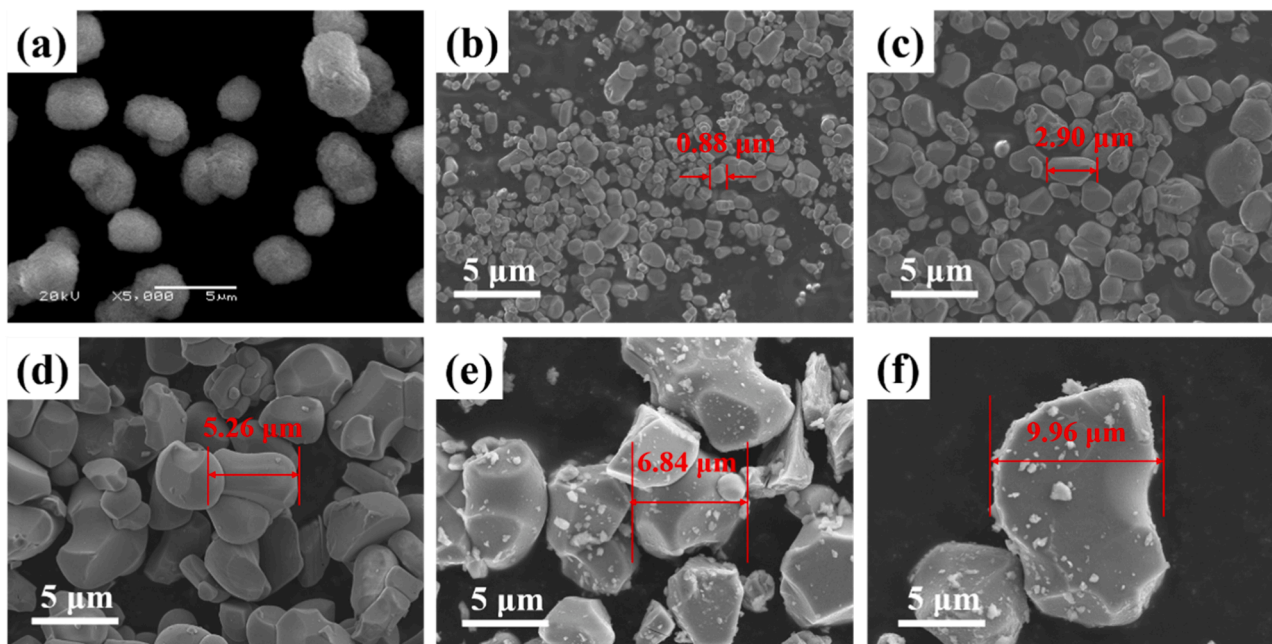


Fig. 1. SEM images of (a) precursor; (b) SC-D1; (c) SC-D3; (d) SC-D5; (e) SC-D7 and (f) SC-D9.

The tap density, compact density and specific surface area of all samples were measured and listed in Table 1 and Fig. S1. Obviously, the tap density of one sample is in a positive correlation with its grain size while the specific surface area is in a negative correlation with its grain size. The tap density of SC-D1 is only 1.8 g cm^{-3} , while that of SC-D3, SC-D5, SC-D7 and SC-D9 are 1.9, 2.1, 2.2 and 2.3 g cm^{-3} , respectively. The compact densities of as-prepared samples are also measured as 3.2, 3.2, 3.3, 3.4 and 3.4 g cm^{-3} for SC-D1, SC-D3, SC-D5, SC-D7 and SC-D9, respectively. Apparently, the tap density and compact density are gradually increased with the growing primary particles size. In contrast, SC-D1 owns the highest specific surface area of $1.4 \text{ m}^2 \text{ g}^{-1}$, and with the increasing grain size D50, the specific surface area of sample is gradually lowered, the values for SC-D3, SC-D5, SC-D7 and SC-D9 are 0.9, 0.5, 0.4 and $0.4 \text{ m}^2 \text{ g}^{-1}$, respectively. Generally, NCM cathode materials suffer from absorbing moisture from air, which may be

aggravated by the excessive specific surface area, leading to gelation during slurry preparation. It is concluded that with the increasing grain size of single crystalline material, its tap density increases while its specific surface area decreases. Thus, it is important to balance the tap density and specific surface area of single crystalline NCM material.

The crystal structure of as-prepared samples was analyzed via X-ray diffraction (XRD). Fig. 2 (a) shows the full XRD patterns of all samples, in which all diffraction peaks can be indexed into $\alpha\text{-NaFeO}_2$ structure ($R\text{-}3m$), and the clear peak splitting between (006)/(102) and (018)/(110) indicate that all samples have well-ordered layered structure [42]. The minor impurity peak located at around 30.4 degree in SC-D9 is attributed to the (111) peak of SrO (PDF#74-1227), which is the decomposition product of SrCO_3 . From the enlarged view of (003) peak, as exhibited in Fig. 2(b), it is obvious that the (003) peak gradually shifts to lower angle with the increasing grain size, indicating expansion of

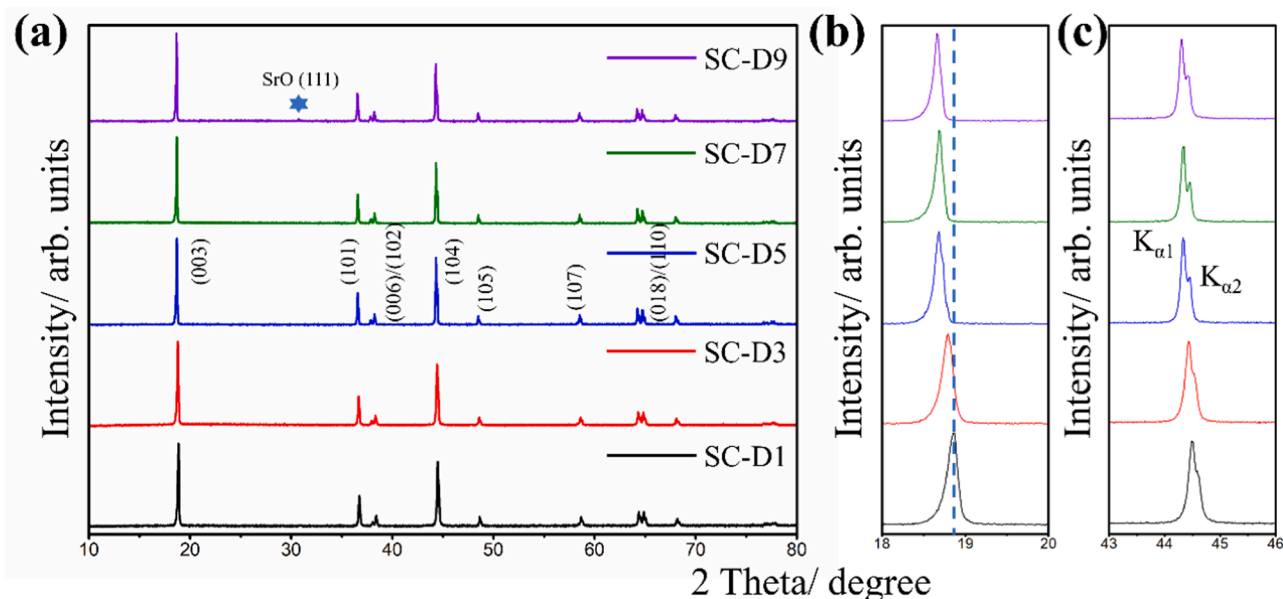


Fig. 2. (a) XRD patterns; enlarged view of (b) (003) peak and (c) (104) peak.

interplanar spacing of (003) plane, according to the Bragg's equation [43]. This phenomenon may be a result of the fact that the ionic radius of Sr^{2+} (1.18 Å) is much larger than that of the transition metal ions as well as Li ion, and with the increasing calcination temperature, more Sr^{2+} will enter the lattice of NCM material, leading to expansion of lattice fringe and enlarged lattice parameters a and c [44,45]. The enlarged view of (104) peaks is demonstrated in Fig. 2(c), where the $K_{\alpha 1}$ and $K_{\alpha 2}$ splitting appear on the spectra of SC-D5, SC-D7 and SC-D9, indicating their large grain size, in contrast, there is no obvious $K_{\alpha 1}$ and $K_{\alpha 2}$ splitting on the spectra of SC-D1 and SC-D3, in agreement with the small grain size of the two samples [20,46]. Rietveld refinement was performed on the XRD patterns of all samples, and the fitted patterns and results are showed in Fig. S2 and Table 2. In Fig. S2, the refined patterns fit well with the measured patterns, and the R_{wp} values for all samples are lower than 4%, proving good reliability of the refinement. In Table 2, the lattice parameters of a and c are gradually increased with the growing grain size, in consistency with the peak shifting of (003) peaks in Fig. 2(b). The ratio of c/a is generally applied to evaluate the layered structure, and the c/a ratio higher than 4.9 in our refinement result suggests well-ordered layered structure of all samples [47]. Moreover, the $\text{Li}^+/\text{Ni}^{2+}$ disorder rate is only 2.7% for SC-D1, while it gradually grows to 3.9%, 4.6%, 5.0% and 5.1% for SC-D3, SC-D5, SC-D7 and SC-D9 samples, respectively. The higher cation mixing may be caused by the higher calcination temperature, in order to prepare single crystalline materials with larger grain size [48].

The surface chemical valence state of as-prepared samples was tested by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 3(a), the peaks of all major elements present on the survey of as-synthesized samples. There are four peaks appeared on the Ni 2p spectra, Fig. 3 (b), where the two peaks located at the 854.6 eV and 872.3 eV are attributed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks, respectively, as well as the two satellite peaks at 860.9 eV and 879.0 eV [49]. Furthermore, the Ni $2p_{3/2}$ peak can be divided into two peaks, corresponding to Ni^{2+} and Ni^{3+} with the bind energy of 854.5 eV and 855.9 eV, respectively, indicating the co-existence of +2 and +3 valence of Ni on the surface [50]. The characteristic peaks, in Fig. 3(c), at 779.8 eV and 749.9 eV are ascribed to the Co $2p_{3/2}$ and Co $2p_{1/2}$, suggesting that cobalt mainly exists as 3+ valence [51]. Fig. 3(d) shows two peaks with the binding energy of 642.4 eV and 653.7 eV, representing the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ orbits, which indicates the Mn is mainly +4 valence [52]. In Fig. 3(e), Sr $3d_{5/2}$ and Sr $3d_{3/2}$ peaks have been detected on all samples at the binding energy of 134.6 eV and 136.5 eV, proving the existence of Sr^{2+} on the material surface [53]. The peak intensity of SC-D9 is much higher than that of the other samples, because more SrCO_3 was added to synthesize SC-D9 sample.

The electrochemical performance of as-prepared samples was tested, as shown in Fig. 4. All samples exhibit similar charge and discharge curves at the first cycle at 0.1C rate, in Fig. 4(a), and the specific discharge capacity is gradually lowered with the increasing grain size. The initial specific discharge capacities between 2.8 and 4.3 V are 183, 180, 175, 170 and 164 mAh g^{-1} for SC-D1, SC-D3, SC-D5, SC-D7 and SC-D9 sample, respectively, and their corresponding initial coulombic efficiencies are 88%, 86%, 84%, 81% and 80%, as displayed in Fig. 4(b). In Fig. 4(c) and (d), as the upper cut-off voltage reaches 4.5 V, the initial specific discharge capacities at 0.1C are increased to 202, 201, 199, 193 and 191 mAh g^{-1} for SC-D1, SC-D3, SC-D5, SC-D7 and SC-D9 sample,

respectively, with corresponding initial coulombic efficiencies of 87%, 86%, 83%, 82% and 82%. Apparently, both initial specific discharge capacity and coulombic efficiency are reduced with the increasing grain size of single crystalline cathode material. This may be a result of the sluggish kinetics caused by long Li^+ diffusion length and poor material utilization of large-sized single crystalline cathode material [20,54]. Furthermore, synthesizing large-sized single crystalline material requires higher calcination temperature, resulting in higher degree of cation mixing, which is unfavorable for the Li^+ transportation and leads to poor electrochemical performance [55]. Fig. 4(e) and (f) exhibit the cycle performance of single crystalline materials with different grain size between 2.8 and 4.3 V and 4.5 V, respectively. The specific discharge capacities at 1C are 168, 159, 156, 146 and 139 mAh g^{-1} for SC-D1, SC-D3, SC-D5, SC-D7 and SC-D9 sample, respectively. The SC-D1, SC-D3 and SC-D5 retain 88%, 92% and 92% of initial capacity after 100 cycles, however, as the grain size increased to 7 μm and 9 μm , only 85% and 77% of discharge capacities are remained for SC-D7 and SC-D9. What is more, when the cut-off voltage elevated to 4.5 V, the 1C discharge capacities are 188, 184, 182, 172 and 158 for SC-D1, SC-D3, SC-D5, SC-D7 and SC-D9 sample, respectively. SC-D3 exhibits the highest capacity retention rate of 83% after 100 cycles between 2.8 and 4.5 V, while the value for SC-D1 decreases to 77%. In contrast, the discharge capacities for SC-D5, SC-D7 and SC-D9 are rapidly declined to 58%, 52% and 40% of their initial capacities. The above-mentioned result shows that SC-D1 and SC-D3 possess better electrochemical performance even at high cut-off voltage while SC-D5, SC-D7 and SC-D9 show lower specific discharge capacity and capacity retention.

Fig. S3 exhibits the rate capability between 2.8 and 4.5 V of all samples. Clearly, SC-D1 sample shows the best rate capability among all samples, which delivers 153 mAh g^{-1} at 5C current rate. Compared with SC-D1, the discharge capacities at 5C for SC-D3, SC-D5, SC-D7 and SC-D9 samples are dramatically declined to 144, 141, 116 and 95%, respectively, and the corresponding ratios of 5C/0.1C are 75%, 71%, 71%, 60% and 50%. Therefore, it is concluded that single crystalline materials with larger grain size shows inferior rate capability, which may stem from the longer diffusion length of Li^+ and higher degree of cation mixing resulted from the high synthesis temperature [21].

Cyclic voltammetry (CV) curves were measured to evaluate the polarization of as-prepared fresh cells for the first three cycles and cells after 100 cycles between 2.8 and 4.5 V. As shown in Fig. 5(a), the oxidation peak at around 3.82 V is attributed to the phase transition from hexagonal phase H1 to monoclinic phase M, and the small peak at 4.05 V corresponds to phase transition from monoclinic phase M to hexagonal phase, H2 as well as the hexagonal phase H2 to hexagonal phase H3 at around 4.30 V [56,57]. In general, the voltage gap of redox reaction, ΔV , can be used to evaluate the reversibility of redox reaction and the polarization degree [26]. The ΔV of SC-D1 sample is 0.111 V, however, as the grain size grows, the ΔV values of SC-D3 and SC-D5 are gradually elevated to 0.120 V and 0.135 V, in Fig. 5(b) and (c). Furthermore, as demonstrated in Fig. 5(d) and (e), the voltage gap of SC-D7 and SC-D9 are drastically increased to 0.235 V and 0.312 V due to sluggish kinetics of Li^+ transport induced by their excessively large grain size and higher degree of $\text{Li}^+/\text{Ni}^{2+}$ mixing, indicating higher degree of polarization of electrochemical reactions, leading to poor electrochemical reversibility and rate capability, in consistency with the inferior electrochemical performance in Figs. 4 and 6 [58]. The cells were cycled between 2.8 and 4.5 V at 1C rate for 100 times, then the CV curves were measured and shown in Fig. 5(f). Obviously, the CV curves of SC-D1 and SC-D3 are well-preserved with sharp peaks, suggesting good electrochemical reversibility, in agreement with their excellent capacity retention at high cut-off voltage. In contrast, the CV curves of SC-D5, SC-D7 and SC-D9 show broaden redox peaks and higher degree of polarization after cycling, indicating lower electrochemical activity due to the collapse of active layered structure [59].

Electrochemical impedance spectrum (EIS) was conducted on fresh cells and after 100 cycles between 2.8 and 4.5 V, and the result was fitted

Table 2
Rietveld refinement results.

Sample	a (Å)	c (Å)	c/a	$\text{Li}^+/\text{Ni}^{2+}$ mixing (%)	R_{wp} (%)
SC-D1	2.878	14.259	4.95	2.7	3.83
SC-D3	2.881	14.263	4.95	3.9	3.76
SC-D5	2.883	14.267	4.95	4.6	3.97
SC-D7	2.884	14.274	4.95	5.0	3.88
SC-D9	2.885	14.276	4.95	5.1	3.94

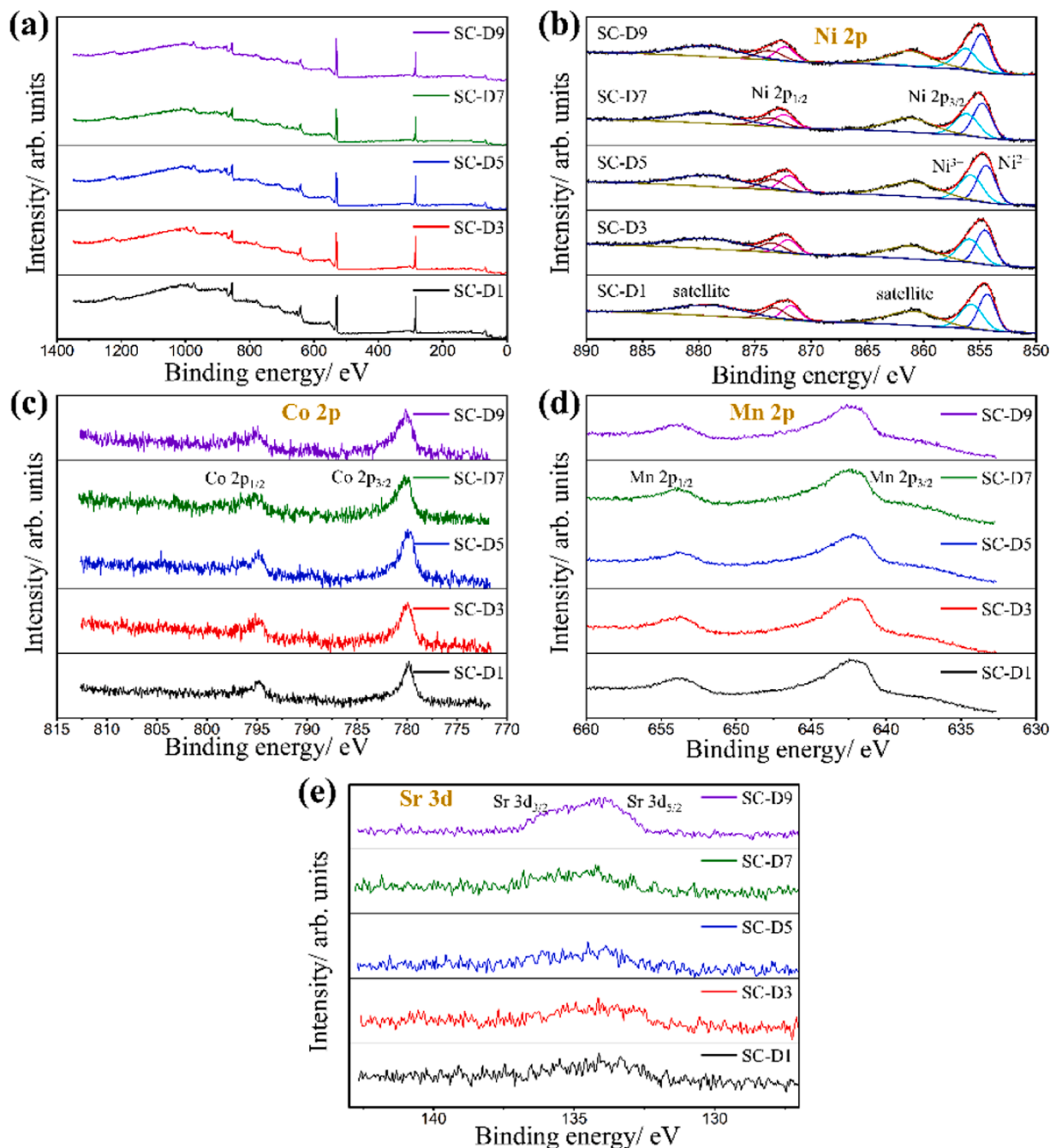


Fig. 3. XPS spectra of (a) survey; (b) Ni 2p; (c) Co 2p; (d) Mn 2p; (e) Sr 3d.

via Zview software, as shown in Fig. 6 and Table 3. In Fig. 6(a), there are a semicircle at the high frequency region and a slope at the low frequency region, representing the charge transfer resistance (R_{ct}) and Warburg impedance of Li^+ diffusion (W) in the equivalent circuit of fresh cell, respectively [60]. And at the highest frequency, the intercept of the semicircle with Z' (real axis) belongs to the internal ohmic resistance (R_s), including electrolyte resistance [61]. In Table 3, all cells have the similar R_s values, and the charge transfer resistance R_{ct} drops with the decreasing grain size, indicating that small grain size is in favor of Li^+ diffusion. Fig. 6(b) exhibits the EIS plots of cells after 100 cycles between 2.8 and 4.5 V, in which a new semicircle appears at the high frequency region (R_{sf}), which is related with the resistance of solid electrolyte interface (SEI) [62]. According to the fitting result, the R_s resistance are increased for all cells after cycling, which may be induced by the side reaction between electrode and electrolyte during cycling

[12]. Moreover, the R_{ct} values are much higher than R_s and R_{sf} for all cells, implying that the charge transfer resistance is the dominating resistance in the whole electrode [63]. Compared to the fresh cells, the R_{ct} values of cycled cells are increased a lot after 100 cycles, and the values for SC-D1, SC-D3, SC-D5, SC-D7 and SC-D9 are 112.9, 157.4, 182.5, 215.7 and 298.7 Ω , respectively. Apparently, the charge transfer resistance increases with the growing grain size, which proves that the large-sized single crystalline materials show higher resistance, leading to sluggish Li^+ diffusion and poor electrochemical performance [64].

The cells after 100 cycles between 2.8 and 4.5 V were disassembled in an Ar-filled glove box and washed with DMC to remove electrolyte, then SEM images were obtained to analyze the morphology change. In Fig. 7 (a) and (b), the particle integrity of SC-D1 and SC-D3 after 100 cycles at the cut-off voltage of 4.5 V are well-maintained without visible cracking, while only slight planar gliding can be observed, in accord with their

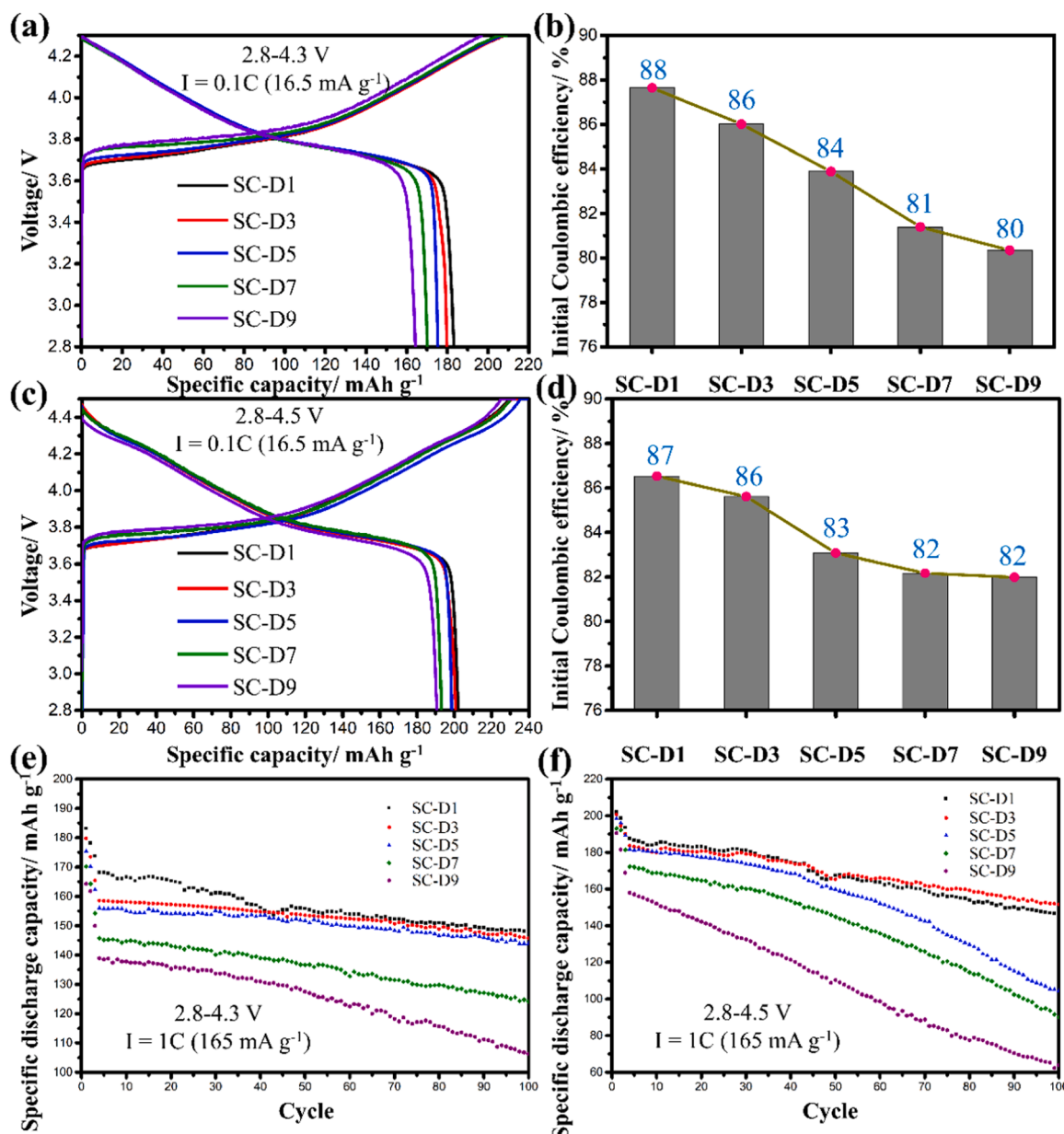


Fig. 4. Electrochemical performance of (a) charge and discharge profile of the first cycle and (b) initial coulombic efficiency between 2.8 and 4.3 V; (c) charge and discharge profile of the first cycle and (d) initial coulombic efficiency between 2.8 and 4.5 V; (e) cycle performance between 2.8 and 4.3 V; (f) cycle performance between 2.8 and 4.5 V.

outstanding cycle performance. Nevertheless, micro-cracks can be found on the particles of SC-D5 with more severe planar gliding, in Fig. 7(c). The micro-cracks on particles will generate fresh surface exposed to electrolyte and aggravate the side reactions between electrode and electrolyte, therefore, the capacity will be rapidly declined due to the loss of active material. Furthermore, more cracks were generated and developed on the particles of SC-D7 and SC-D9, as well as the severe planar gliding, in Fig. 7(d) and (f). The planar gliding occurs at high voltage that the single crystalline particle was sliced along the (003) plane. The majority of the slicing is reversible and most of the particles will recover to their original shape, however, the irreversible gliding is accumulated over cycling, and eventually generates crack opening [65]. Based on our experiments, it is found that cracking and planar gliding are less generated for the single crystalline material with smaller grain size, while the situation is much more severe for the large-sized single crystalline material. The alleviated crack generation is probably caused by the fact that the cracking is related with the grain size of single

crystalline, below the critical size, predicated to be around 3.5 μm , the cracks can be deemed as stable inside the particles [65]. The SEM images of SC-D7 and SC-D9 at larger magnification were acquired for observation in detail. As shown in Fig. 7(f) and (h), clear parallel steps and micro-crack parallel to planar gliding can be observed, which is resulted from the accumulated irreversible planar gliding over cycling. The crack generation and development are reported to be related with the formation of NiO-like rock-salt phase [66]. The rock-salt phase tends to be initiated and propagated along (003) phase, eventually developed to micro-cracking, in consistent with our observation in this paper [67]. The massive cracking and fracture of the particles of SC-D7 and SC-D9 during cycling drastically aggravate the side reaction with electrolyte and irreversible phase transition, leading to rapid capacity decline, therefore, inferior electrochemical stability. Hence, controlling the grain size of single crystalline material within a reasonable size is a key factor to improve the stability of single crystalline material.

The HRTEM images of the electrodes after 100 cycles between 2.8

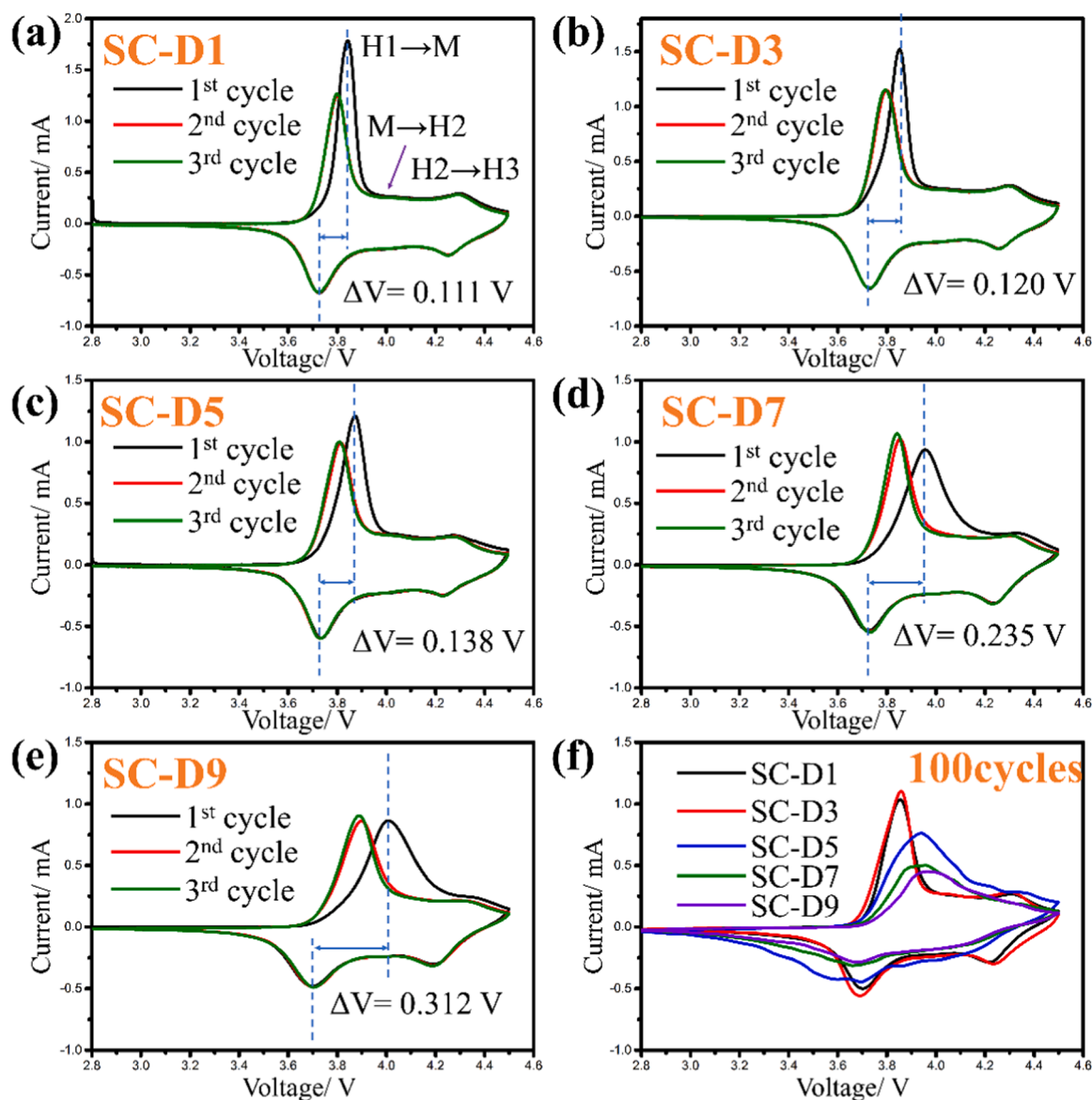


Fig. 5. CV curves of the first three cycles of (a) SC-D1; (b) SC-D3; (c) SC-D5; (d) SC-D7; (e) SC-D9; (f) CV curves after 100 cycles between 2.8 and 4.5 V.

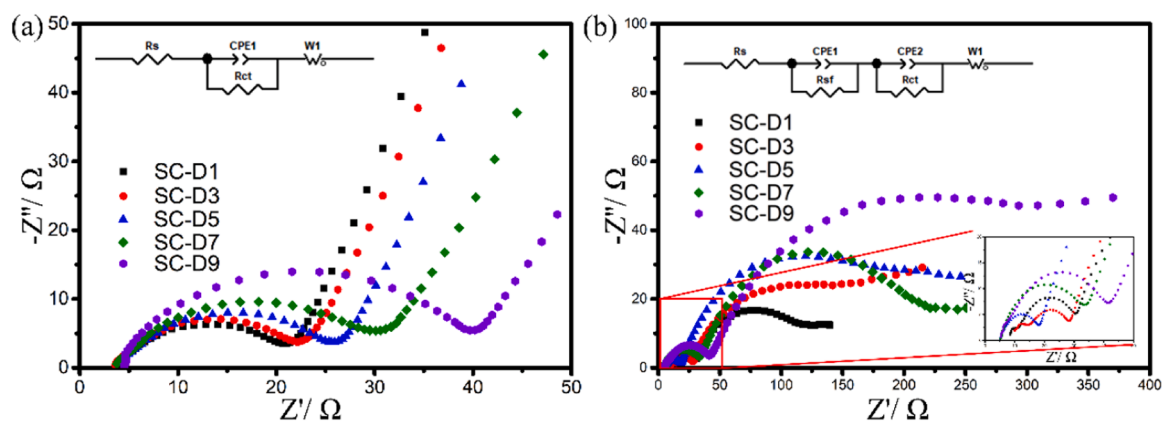


Fig. 6. EIS curves of (a) fresh cells and (b) cycled cells.

and 4.5 V for SC-D3 and SC-D9 were obtained to analyze the phase transition. In Fig. 8(a1), there are two distinct phases around the surface of SC-D3 electrode. According to the FFT images in Fig. 8(a2) and (a3),

the outer region 1 and inner region 2 can be assigned to spinel phase ($Fd-3m$) and layered phase ($R-3m$), respectively, indicating that after cycled at high voltage, irreversible phase transition from layered to spinel

Table 3

EIS fitting result for fresh cells and cycled cells.

Cell	Resistance (Ω)	SC-D1	SC-D3	SC-D5	SC-D7	SC-D9
Fresh	R_s	3.7	3.5	3.7	3.6	4.4
	R_{ct}	18	18.9	22.5	26.5	32.4
Cycled	R_s	8.3	8.0	5.3	5.3	5.0
	R_{ef}	22.5	19.8	12.3	27.8	36.8
	R_{ct}	112.9	157.4	182.5	215.7	298.7

occurred at the surface region of SC-D3, spreading around 10 nm, without rock-salt phase formed. Besides, there is not crack generated in Fig. 7(b), thus, SC-D3 possesses outstanding electrochemical stability amongst all samples. In addition, the outer region 3 in Fig. 8(b1) can be indexed into rock-salt phase ($Fm-3m$) with a depth as large as 26 nm, while two phases can be found in the inner region 4, suggesting a mixed phase of rock-salt and spinel phase. Such result reveals that the layered structure of SC-D9 sample has been severely damaged, and the irreversible phase transition from layered to spinel to rock-salt phase. The thick electrochemical inactive phase hinders the electrochemical

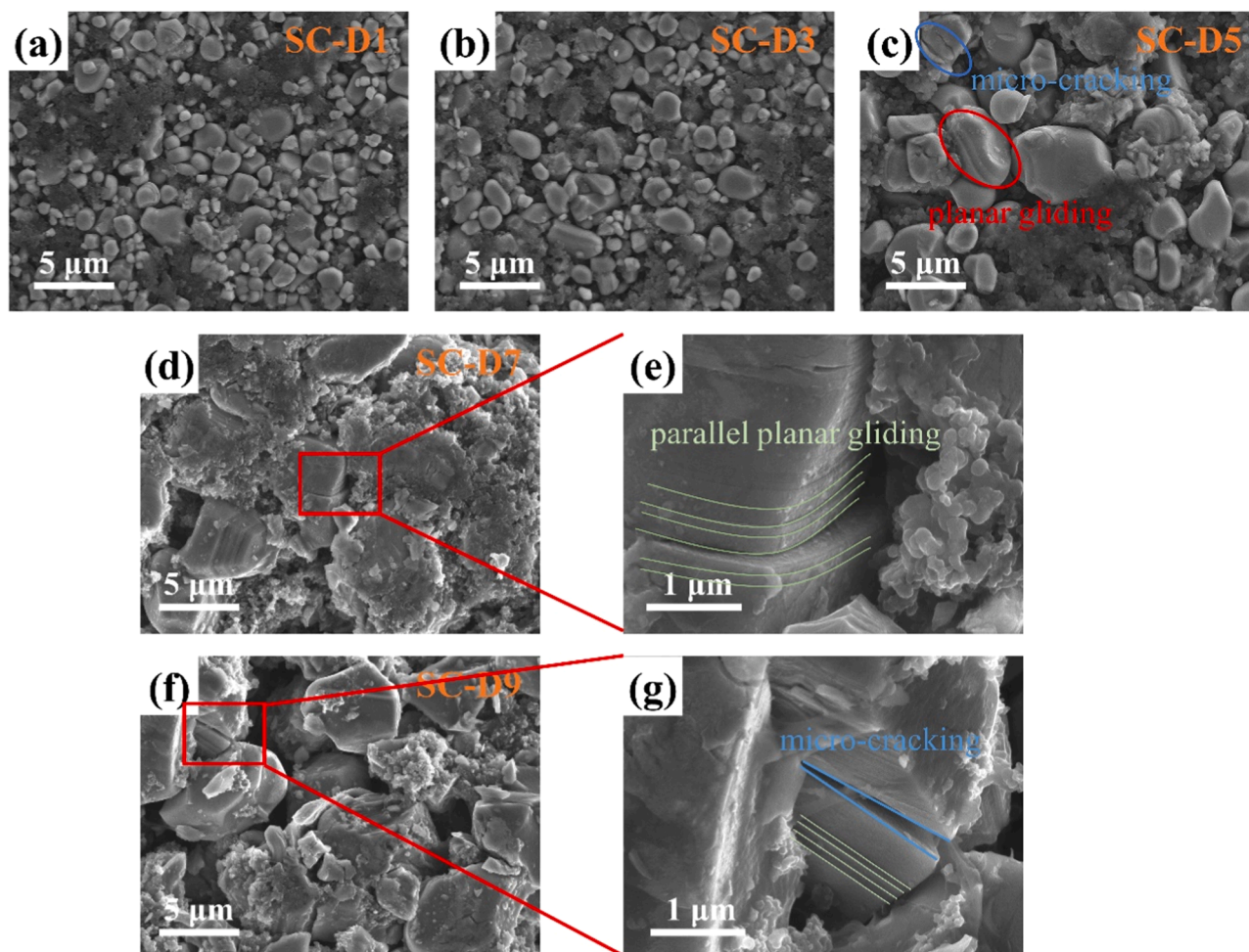


Fig. 7. SEM image of electrodes after 100 cycles between 2.8 and 4.5 V: (a) SC-D1; (b) SC-D3; (c) SC-D5; (d) and (e) SC-D7; (f) and (g) SC-D9.

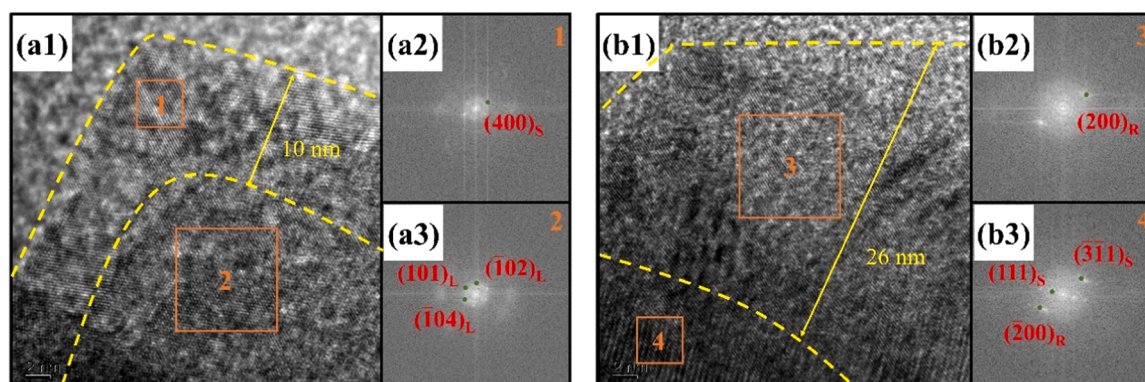


Fig. 8. The HRTEM and FFT images of electrodes after 100 cycles between 2.8 and 4.5 V for (a) SC-D3 and (b) SC-D9.

reaction, leading to poor electrochemical performance.

4. Conclusion

In conclusion, single crystalline cathode materials $\text{LiNi}_{0.65}\text{Co}_{0.07}\text{Mn}_{0.28}\text{O}_2$ with different grain size have been successfully prepared via controlling the key experimental parameters. The physical property and electrochemical performance of the as-synthesized samples were tested, and the effect of grain size on them was evaluated. The result indicates that with the growing grain size, the tap density and compact density increase while the specific surface area decreases. However, larger grain size leads to reduced initial coulombic efficiency, discharge capacity and capacity retention. The SC-D3 sample achieves initial discharge capacities of 180 and 200 mAh g^{-1} with capacity retentions of 92% and 83% after 100 cycles at the cut-off voltage of 4.3 V and 4.5 V, respectively. However, the capacity retention between 2.8 and 4.5 V for SC-D9 is only 40%. By disassembling the cycled cells, it is found that single crystalline material with excessively large grain size underwent severe planar gliding and cracking cycled at high cut-off voltage, which will result in fracture of particles and irreversible phase transition, leading to inferior electrochemical stability. Therefore, based on the above-mentioned result, in order to achieve desirable physical property and electrochemical performance, the grain size of single crystalline material should be controlled at between 3 and 5 μm .

CRediT authorship contribution statement

Luyu Li: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization. **Guorong Hu:** Conceptualization, Methodology, Resources, Supervision, Project administration. **Yanbing Cao:** Validation, Funding acquisition, Methodology, Data curation. **Dongjie Gong:** Resources. **Quanjun Fu:** Resources. **Zhongdong Peng:** Funding acquisition, Resources, Project administration, Data curation. **Ke Du:** Conceptualization, Methodology, Validation, Resources, Supervision, Project administration, Writing – review & editing, Data curation, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.electacta.2022.141386](https://doi.org/10.1016/j.electacta.2022.141386).

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