



# Cathode materials with cross-stack structures for suppressing intergranular cracking and high-performance lithium-ion batteries

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## ABSTRACT

Full concentration-gradient  $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$  (FCG622) layered oxide cathodes, consisting of Ni-rich cores and concentration-gradient shells, were synthesized by heterogeneous co-precipitation method. The cross-stack structure of FCG622 appeared different from the polycrystalline aggregates of homogeneous  $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$  (H622). The FCG622 showed structural stability and excellent electrochemical performances when compared to H622. The cathode based on this material showed superior rate capability and high voltage performance. The results of charge and discharge testing illustrated that FCG622 could suppress the intergranular cracks delivering initial discharge capacity of  $185.2 \text{ mAh g}^{-1}$  at 1C in the voltage window of 2.8–4.4 V. The corresponding capacity retention after 300 cycles was estimated to 81.1% at 4.4 V. By comparison, the initial discharge capacity of H622 was estimated to only  $170.6 \text{ mAh g}^{-1}$  under the same conditions, with capacity retention of 68.5%. These results suggested that FCG622 had stable morphology, high capacity and superior voltage stability when compared to polycrystalline aggregates.

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## 1. Introduction

Lithium-ion batteries have widely been used as primary power sources in new energy vehicles, especially in plug-hybrid vehicles (PHEVs) and electric vehicles (EVs) [1–5]. High-capacity, superior voltage, and environmental friendly cathode materials are increasingly required for high-energy batteries [6,7]. Among studied cathode materials, Ni-rich layer oxide cathode materials have generally high specific capacity and reduced cost, making them promising cathode materials for high-energy density lithium-ion batteries [8–10]. However, these Ni-rich layer oxides often show poor cyclability due to the irreversible phase transition occurring at high voltages and unstable electrode/electrolyte interface during cycling [2]. Moreover,  $\text{Ni}^{4+}$  could easily reacts with the electrolyte, especially at high temperatures, accelerating the capacity fade and lead to poor thermal stability [11,12].

To alleviate these limitations, several methods have been employed, including ion doping [13], surface modification [14,15], and composite design fabrication [16]. Among these, the core-shell structure has been demonstrated as an effective method [17], because surface modification shell hinders the direct contact with the organic electrolyte and enhances cyclability of Ni-rich layered oxides [18]. Unfortunately, different volume expansions resulting from the interface between the core and shell during charge and discharge processes are harmful to rate capability and reversible capacity [19]. Therefore, novel strategies to enhance the performance of Ni-rich layer oxides are highly desirable. To eliminate the adverse effects of core-shell structures, previous efforts have investigated full concentration-gradient (FCG) materials, where concentrations of transition metals change gradually from the inner core to the outer layer [6,20]. In other words, the concentration of Ni decrease, and concentrations of both Mn [21] and Co content increase from the core to the surface. Hence, they can safely operate without risks of structural mismatch during long-term cycling, because they have no obvious interfacial gap throughout the gradient material [22].  $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$  is also reported with Li-ion diffusivity higher than that of  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$  ( $x + y + z = 1$ )

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materials, but its diffusion coefficient is the smaller and affected by temperature [23].

In this study, a novel method for fabricating cross-stack structure concentration-gradient materials with low cost, high capacity, long cycle life, and improved thermal stability for advanced lithium-ion batteries was proposed. This methodology should integrate the advantages of Ni-rich as an inner core and structural stability of the outer layer to obtain the materials with superior reversible capacities at high voltages combined with excellent cyclability. Spherical layered oxides  $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$ , involving  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$  cores and stable concentration-gradient outer shells, were prepared by heterogeneous co-precipitation method. The results indicated that the growth of FCG622 precursors was different from that of homogeneous precursors. The traditional homogeneous materials were piled by brick-shaped primary particles. But, concentration gradient materials were formed by origami-plane cross-stacked. Here, the FCG622 precursors were synthesized, and the growth mechanisms were described. The electrochemical performances of the resulting materials were studied at high voltages from 4.4 to 4.6 V. For comparison, the H622 electrochemical performances were also evaluated and the results were discussed.

## 2. Experimental

### 2.1. Material synthesis

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  were used as starting materials in the heterogeneous co-precipitation method to synthesize FCG622 and H622 precursors. The detailed synthetic procedures were described in previous reports for homogeneous  $(\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2})(\text{OH})_2$  [24]. Fig. 1 shows a schematic diagram of the continuously stirred tank reactor (CSTR) used for preparing the FCG622 precursor. Three aqueous solutions (A, B, and C) were prepared for concentration-gradient materials with a concentration of  $2.5 \text{ mol dm}^{-3}$ . The molar ratio of the inner core Ni-rich solution A was (Ni: Co: Mn = 8:1:1), that of the transition part of solution B was (Ni:Co:Mn = 4:1:1), and finally that of the outer-layer Ni-poor solution C was (Ni:Co:Mn = 1:2:2). During the reaction, solutions B and C were pumped into the solution A tank, respectively. Meanwhile, the mixed solution was fed into a continuously stirred tank reactor (CSTR) under a  $\text{N}_2$  atmosphere. The obtained precursors were filtered off, then washed and dried overnight at  $60^\circ\text{C}$ . The reaction time (24 h), temperature ( $50^\circ\text{C}$ ), stirring speed (800 rpm), pH (11.5–11) decreases with increasing

feeding time, amount of  $\text{NH}_4\text{OH}$  ( $0.5 \text{ mol dm}^{-3}$ ) and re-feeding time in the reactor were carefully controlled, respectively. During the reaction, the preparation conditions were controlled by changing the transition metal ratios. The obtained spherical precursor and 5% excess  $\text{LiOH} \cdot \text{H}_2\text{O}$  powders were mixed thoroughly. Next, they were heated to  $500^\circ\text{C}$  for 5 h in air then followed by heating to  $700^\circ\text{C}$ ,  $750^\circ\text{C}$ , and  $800^\circ\text{C}$  for 10 h under air atmosphere to obtain FCG622 powders. The mixture of the homogeneous  $(\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2})(\text{OH})_2$  was obtained by the same sintering method at  $500^\circ\text{C}$  for 5 h, and then heated in air at  $820^\circ\text{C}$  for 10 h.

### 2.2. Materials characterization

The chemical compositions of the resulting powders were evaluated by inductively coupled plasma test (ICP). The crystalline phases of the prepared materials were determined by X-ray diffraction in the  $2\theta$  ranges of  $10^\circ$ – $80^\circ$  (XRD, BrukerD2 Advance, Germany). Using the XRD data, lattice parameters were calculated using the least-squares method. The synthesis of microspheres powders was observed by scanning electron microscopy (Phenom ProX) coupled with energy dispersive spectroscopy (EDS). The cross-sections of the particles were obtained by mechanical crushing of the powders.

### 2.3. Electrochemical measurements

The electrochemical properties of synthesized materials were evaluated in CR2025 coin cells, assembled in the Ar-filled glovebox. The cathodes were fabricated by mixing the calcined powder (80 wt%), Ketjen Black (10 wt%), and polyvinylidene fluoride (PVDF) (10 wt%) in N-methyl-2-pyrrolidone (NMP). The obtained slurry was spread on aluminum foil and dried in vacuum oven at  $80^\circ\text{C}$  for 12 h. A circular positive electrode was punched out with a diameter of 10 mm, and then dried in vacuum oven at  $110^\circ\text{C}$  for more than 12 h. The electrolyte solution was composed of  $1 \text{ mol L}^{-1}$   $\text{LiPF}_6$  dissolved in a mixture of EC-DMC (1:1 by volume). The charge and discharge measurements were carried out using a LAND CT2001A system at the voltage range of 2.8–4.6 V at  $25^\circ\text{C}$ . The electrochemical workstation (Solartron1260/1470E) was employed to carry out the electrochemical impedance spectroscopy (EIS) tests on cells in fully charged states in the frequency range from 1000 kHz to 0.01 Hz and amplitude voltage of 5 mV.

## 3. Results and discussion

The chemical formula of the prepared concentration gradient material determined by ICP was  $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$ . Table 1 shows the chemical composition of the final sample, obtained by ICP. The measured composition was close to the designed target component. The ratio of Ni: Co: Mn was identified as 0.6: 0.2: 0.2, in accordance with the expected chemical formula.

The FCG622 precursors grown at different times during the co-precipitation reaction are shown in Fig. 2. To display the growth process, SEM was utilized to follow the growth of the particles at different feeding periods. The growth was explored by adjusting the experimental conditions during synthesis of FCG622 precursor, formed by origami-plane cross stacked. The structure was found to be similar to origami lanterns. During the first hour (Fig. 2a), hexagonal lamellae with roughly  $2 \mu\text{m}$  in diameters was formed, and then accumulated to form a core. This pre-morphology was consistent with commonly observed polycrystalline aggregates of H622. At nucleation stage, since the transition metal ratios of the elements and the reaction conditions were fixed, the primary particles would grow to reach certain sizes followed by the formation of dispersed deposits (Fig. 2b). The core was formed by

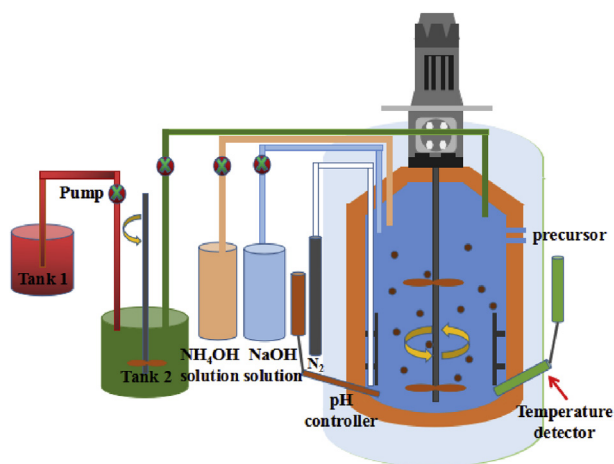


Fig. 1. Schematic diagram of the CSTR for preparing the FCG precursors.

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