Nanostructured high-energy cathode materials for advanced lithium batteries

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Nickel-rich layered lithium transition-metal oxides, LiNi1−xMxO2 (M = transition metal), have been under intense investigation as high-energy cathode materials for rechargeable lithium batteries because of their high specific capacity and relatively low cost1–3. However, the commercial deployment of nickel-rich oxides has been severely hindered by their intrinsic poor thermal stability at the fully charged state and insufficient cycle life, especially at elevated temperatures4–6. Here, we report a nickel-rich lithium transition-metal oxide with a very high capacity (215 mA h g−1), where the nickel concentration decreases linearly whereas the manganese concentration increases linearly from the centre to the outer layer of each particle. Using this nano-functional full-gradient approach, we are able to harness the high energy density of the nickel-rich core and the high thermal stability and long life of the manganese-rich outer layers. Moreover, the micrometre-size secondary particles of this cathode material are composed of aligned needle-like nanosize primary particles, resulting in a high rate capability. The experimental results suggest that this nano-functional full-gradient cathode material is promising for applications that require high energy, long calendar life and excellent abuse tolerance such as electric vehicles.

In the past decade, major efforts have been devoted to searching for high-capacity cathode materials based on LiNi1−xMxO2, mostly on account of their very high practical capacities (220–230 mA h g−1) at high voltages (4.4–4.6 V). However, at such high operating voltages, these materials react aggressively with the electrolyte owing to the instability of tetravalent nickel in the charged state, leading to very poor cycle and calendar life. Therefore, these materials operate reversibly only at a potential range below 4 V, resulting in low capacities of 150 mA h g−1. To improve the stability of these materials, several researchers have investigated the effect of Mn substitution on cycle and calendar life. The introduction of Mn to the transition-metal layer can help stabilize the transition-metal oxide framework, because part of the Mn does not change valence state during charge and discharge7–9. Recently, we reported several approaches to improve both the life and safety of nickel-rich cathode materials for potential use in plug-in hybrid electric vehicles10. For instance, a core–shell approach11 resulted in a nickel-rich LiNi0.8Co0.1Mn0.1O2 core that delivered high capacity at high voltage, and a manganese-rich LiNi0.3Mn0.7O2 shell that stabilized the surface of the material. However, owing to the structural mismatch and the difference in volume change between the core and the shell, a large void forms at the core/shell interface after long-term cycling, leading to a sudden drop in capacity12,13. We also demonstrated that this structural mismatch could be mitigated by nano-engineering of the core–shell material, where the shell exhibits a concentration gradient14–16. However, because of the short shell thickness, the manganese concentration at the outer layer of the particle is low; therefore, its effectiveness in stabilizing the surface of the material is weak, especially during high-temperature cycling (55 °C).

The nickel-rich lithium transition-metal oxide investigated here has a nominal composition of LiNi0.75Co0.15Mn0.15O2, and the concentration gradient of transition metals shown in Fig. 1; the concentration of nickel decreases gradually from the centre towards the outer layer of the particle, whereas the concentration of manganese increases gradually so that the manganese-rich and nickel-poor outer layer can stabilize the material, especially during high-voltage cycling. The full concentration gradient (FCG) cathode material was prepared by a newly developed co-precipitation method involving the precipitation of transition-metal hydroxides from the precursor solutions, where the concentration ratio of Ni/Mn/Co changes continuously with the reaction time (see Methods).

Figure 2 shows scanning electron microscopy (SEM) images and the elemental distribution of Ni, Co and Mn within a single particle of both the precursor ((Ni0.75Co0.15Mn0.15)(OH))2 and the final lithiated product (LiNi0.75Co0.15Mn0.15O2) having a concentration gradient. The atomic ratio between Ni, Co and Mn was determined by integrated two-dimensional (2D) electron probe micro-analysis (EPMA). Figure 2 clearly demonstrates that the atomic percentage of Co remained constant at about 10% in both the precursor and the lithiated particles as originally designed, whereas the concentration of Ni decreased and Mn increased continuously from the centre towards the outer layer of the particle. Note that the slopes representing the metal (Ni and Mn) concentration change of the precursor are greater than those of the lithiated material because of the directional migration of the metal elements during the high-temperature calcination to increase the entropy.

Hard X-ray nanotomography was used to determine the 3D distribution of Ni in a single lithiated particle. Similar to medical computerized tomography, this technique uses X-rays to obtain a 3D structure at up to 20 nm resolution. Figure 3a shows the 3D volume rendering of a particle acquired with the technique. The data are imaged with the particle’s volume partially removed to reveal the central cross-section. With this 3D image, we are able to illustrate the concentration profiles of Ni at any given plane (see Fig. 3b for a view of a plane going through the centre of the particle). Figure 3a,b shows that the structure of the centre, with a diameter of

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Ni-rich composition: high capacity

Surface
Mn-rich composition: high thermal stability

Inside
Ni-rich composition: high capacity

Full gradient composition
Gradual Ni decrease and Mn increase from inner part to outer part of a particle

Figure 1 | Schematic diagram of the FCG lithium transition-metal oxide particle with the nickel concentration decreasing from the centre towards the outer layer and the concentration of manganese increasing accordingly. A SEM image of a typical particle is shown in Fig. 2b.

Figure 2 | SEM and EPMA results. a,b, SEM mapping photograph of Ni, Co and Mn within a single particle for the precursor (a) and for the lithiated material (b). c,d, EPMA line scan of the integrated atomic ratio of transition metals as a function of the distance from the particle centre to the surface for the precursor (c) and the lithiated material (d). The Ni-rich particle centre and Mn-rich outer surface are clearly seen from the SEM mapping images. The Ni concentration decreased linearly towards the particle surface for both the precursor and the lithiated particle whereas the Mn concentration increased, and the Co concentration remained constant.

about 2 µm, was markedly different from that of the outer layer. The central core is mainly composed of bright islands with numerous voids represented by the dark background. This structure could result from the different formation kinetics of the transition-metal hydroxide seed at the beginning of the co-precipitation process, during which the seed developed along with many stacking voids.

After the initial formation process, the growth of the particles reached a relatively steady state, and a denser layer developed above the loosely stacked core. Figure 3b also confirms the results of EPMA (see Fig. 2b). A striking feature in Fig. 3b is that the bright area with high nickel content tends to form needle-shaped spikes pointing from the centre towards the edge; this feature was
clearly captured in the transmission electron microscopy image as highly aligned large-aspect-ratio nanorods (Fig. 3c). We believe that this nano-pattern was the result of the directional transition-metal migration during the high-temperature calcination that led to the reduction in the slope of the concentration gradient (Fig. 2c versus d). Owing to the pre-conditioned concentration gradient in the particles of the precursor, the crystal growth during the high-temperature calcination was energetically preferred to forming a highly percolated nanorod network, which minimizes the diffusion length\textsuperscript{17} between the centre and the edge for transition-metal ions. In the particle centre, the migration of the transition metal had to rely on the limited contact of loosely packed primary particles, and the development of an aligned nanorod network was limited, as shown in Fig. 3d.

A potential benefit of forming such a percolated aligned nanorod network is that it also provides a shorter pathway for lithium-ion diffusion during normal charge/discharge cycling at ambient temperatures, leading to a better rate capability. Figure 4a shows the rate capability of the FCG material along with the inner composition (IC, LiNi\textsubscript{0.46}Co\textsubscript{0.19}Mn\textsubscript{0.35}O\textsubscript{2}) and outer composition (OC, LiNi\textsubscript{0.70}Co\textsubscript{0.10}Mn\textsubscript{0.20}O\textsubscript{2}) materials, both of which were synthesized by the conventional constant concentration approach. When discharged at the C/5 rate, the IC material delivered a reversible capacity of 210.5 mAh g\textsuperscript{-1}; the OC material, 188.7 mAh g\textsuperscript{-1}; and the FCG material, 197.4 mAh g\textsuperscript{-1}; these results are as expected because the IC material has the highest nickel content and the OC material has the lowest nickel content. However, when discharged at the 5C rate, the FCG material delivered the highest reversible capacity. As a cross-validation, the diffusion coefficient of lithium ions in the three materials was measured by the galvanostatic intermittent titration technique\textsuperscript{18}. The results showed that the FCG material has, in general, the highest lithium-ion diffusion coefficient (Supplementary Fig. S1). Meanwhile, the electronic conductivity was measured to be the highest for the IC material, 1.67 × 10\textsuperscript{-4} S cm\textsuperscript{-1}, followed by the FCG material, 3.10 × 10\textsuperscript{-5} S cm\textsuperscript{-1}, and the OC material, 7.30 × 10\textsuperscript{-6} S cm\textsuperscript{-1}. Therefore, we believe that the high rate capability of the FCG material has no strong correlation with the electronic conductivity, but mostly originated from the special percolated aligned nanorod network that shortened the diffusion pathway of lithium ions in the particle.

Figure 4b shows the initial charge and discharge curve of coin-type half-cells based on IC, FCG and OC materials. Both the IC material (highest nickel content) and the FCG material delivered a higher capacity of 220.7 and 215.4 mAh g\textsuperscript{-1}, respectively, whereas the OC material (lowest nickel content) showed a lower capacity of 202 mAh g\textsuperscript{-1}. Note that the Coulombic efficiency of the FCG was higher (94.8%) when compared with both the IC and OC electrodes (91%) owing to a well-developed aligned nanorod network in the FCG material that facilitates Li\textsuperscript{+} diffusion, and thus high lithium utilization.

Another important observation is that the reversible capacity of the IC material decreased markedly with cycling (Fig. 4c). This rapid
capacity fade was mainly caused by the direct exposure of a high content of Ni(IV)-based compound to non-aqueous electrolyte at a high potential; this exposure led to the chemical decomposition of both the surface of the electrode material and the electrolyte. In contrast, the OC material had a higher manganese content and a lower oxidizing capability towards non-aqueous electrolyte. Therefore, this material had a lower reversible capacity, but a much better capacity retention. Figure 4c shows that the FCG material had combined advantages of a high capacity from the high nickel content in the bulk and a high electrochemical stability from the high manganese content on the surface. More detailed investigation by varying the upper cutoff voltage of the test cells consistently led to the same conclusion (Supplementary Fig. S2).

We assembled a pouch cell using the FCG material as the cathode and mesocarbon microbeads (MCMB, graphite) as the anode. This cell was cycled between 3.0 and 4.2 V with a constant current of 1C (33 mA). The full-cell showed an outstanding capacity retention after 1,000 cycles both at room and high temperature (Fig. 4d). We also fabricated pouch-type full-cells; the cells were cycled to 4.3, 4.4 and 4.5 V at 1C rate. In all cases, the cells exhibited excellent cycling performance (Supplementary Fig. S3). The capacity of the cells increased with cutoff voltage owing to the higher lithium utilization at high voltage. The cell cycled to 4.5 V showed very minor capacity fade at 55°C possibly caused by a limited reactivity between the charged cathode and the electrolyte.

To investigate the safety of the FCG approach, we developed an in situ high-energy X-ray diffraction (HEXRD) technique\(^\text{9,20}\) and used it to study the thermal decomposition of delithiated cathode materials in the presence of the electrolyte. The delithiated cathode material was recovered from the charged cell at 4.3 V and mixed with an equivalent amount of non-aqueous electrolyte, and the mixture was placed in a stainless-steel high-pressure vessel for differential scanning calorimetry (DSC). The sample was then heated from room temperature to 375°C with a heating rate of 10°C min\(^{-1}\). During the thermal ramping, a high-energy X-ray beam (\(\sim\)0.1 Å), which is able to penetrate through a 4-mm-thick stainless-steel block, was deployed to continuously monitor the structural change of the delithiated material. High-quality X-ray diffraction data were collected at an interval of 20 s per spectrum (see Supplementary Fig. S4 for the full index of the layered material).

Figure 5a,b shows zoomed (2.4°–2.80°) contour plots of the in situ HEXRD profiles of delithiated IC and FCG materials during thermal ramping. In these profiles, red represents a high intensity; blue, a low intensity. The complete spectra of the in situ data can be seen in Supplementary Figs S5 and S6. Three diffraction peaks can be seen in Fig. 5a,b; the left one starting at 2.57° is the (101) peak for layered transition-metal oxides, and the right weak one starting at 2.68° is the (012) peak for layered oxides. The one in the middle (starting at 2.62°) is the diffraction peak from the DSC vessel and can be used as a semi-reference. Figure 5a shows that the delithiated IC material (\(\text{Li}_{1-x}\text{Ni}_{x}\text{Mn}_{2/3}\text{Co}_{2/3}\text{O}_2\)) starts converting to a new phase at around 100°C; the (101) and (012) peaks shift towards a smaller angle (more details can be seen in Supplementary Fig. S5).

Figure 5b shows that the low-temperature phase transformation occurred at about 140°C for the FCG material.

Figure 5c shows the DSC profiles of delithiated cathodes in the presence of non-aqueous electrolyte. No heat flow was detected with DSC within the temperature range between 100°C and 150°C for both samples. Thus, this phase transformation is not related to the safety of the cathode materials, but can cause the degradation of the electrochemical performance of high-nickel-content cathode materials. It was previously reported that \(\text{Li}_{x}\text{Ni}_{2/3}\text{Co}_{1/3}\)O\(_2\) markedly loses its reversible capacity when aged at 90°C (ref. 21). Therefore, we believe that the better capacity retention of the FCG material (as shown in Fig. 4b) can be attributed to the suppressed kinetics of detrimental phase transformation at temperatures around 100°C. The in situ HEXRD data also showed that the newly formed phase started to disappear at about 200°C for the delithiated IC material,

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**Figure 4 | Charge-discharge characteristics of IC, OC and FCG materials.** **a.** Comparison of rate capabilities of the FCG with the IC and OC materials (upper cutoff voltage of 4.3 V versus Li\(^+\)/Li\(^-\)). **b.** Initial charge-discharge curves. **c.** Cycling performance of half-cells using the FCG, IC and OC materials cycled between 2.7 and 4.5 V versus Li\(^+\)/Li using a constant current of C/5 (about 44 mA g\(^{-1}\)). **d.** Discharge capacity of MCMB/FCG cathode full-cells at room and high temperature. The electrolyte used was 1.2 LiPF\(_6\) in EC/EMC (3.7 by volume) with 1 wt% vinylene carbonate as an electrolyte additive. The cells were characterized between 3.0 and 4.2 V with a constant current of 1C.
For the DSC experiments, the cells containing the cathode materials were to 0.70:0.10:0.20 molar ratio for 250 °C and Li(Ni0.80Co0.10Mn0.10)O2. To synthesize spherical constant-concentration layered oxide cathodes, NiSO4 · 6H2O, CoSO4 · 7H2O and MnSO4 · 5H2O (0.86:0.10:0.04, molar ratio for Li(Ni0.80Co0.10Mn0.10)O2 and 0.70:0.10:0.20 molar ratio for Li(Ni0.75Co0.10Mn0.15)O2) were used as the starting materials for the co-precipitation process52. The obtained spherical precursors were mixed with LiOH · H2O (Li/(Ni + Co + Mn) = 1 molar ratio) and calcined at 750 °C for 20 h in air.

**Methods**

**Synthesis of Li(Ni0.80Co0.10Mn0.10)O2 and Li(Ni0.75Co0.10Mn0.15)O2.** To synthesize spherical constant-concentration layered oxide cathodes, NiSO4 · 6H2O, CoSO4 · 7H2O and MnSO4 · 5H2O (0.86:0.10:0.04, molar ratio for Li(Ni0.80Co0.10Mn0.10)O2 and 0.70:0.10:0.20 molar ratio for Li(Ni0.75Co0.10Mn0.15)O2) were used as the starting materials for the co-precipitation process. During the reaction, a manganese-rich aqueous solution (Ni/Co/Mn, 0.64:10:26 molar ratio) was continuously pumped into the stock solution tank containing the starting nickel-rich solution, after which the homogenously mixed solution was continuously fed into a continuously stirred tank reactor. The obtained FCG hydroxide was mixed with LiOH · H2O (Li/(Ni + Co + Mn), 1 molar ratio) and calcined at 750 °C for 20 h in air.

**Morphology characterization.** The morphology of the prepared powders was characterized by SEM (S4800, HITACHI) and transmission electron microscopy (2010, JEOL). Element mapping was carried out with an electron-probe micro-analyser (JXA-8100, JEOL).

**Chemical composition characterization.** The chemical composition of the resulting powders was analysed by atomic absorption spectroscopy (Vario 6, Analyticjena).

**Hard X-ray 3D nanotomography.** This analysis was carried out at the beamline 32-ID of the Advanced Photon Source, Argonne National Laboratory. The instrument uses a Fresnel zone plate lens to magnify X-ray images to achieve up to 20 nm resolution. The X-ray energy can be continuously tuned between 8 and 30 keV with 0.01% energy resolution. A spherical particle with a diameter of about 6 μm was selected and mounted on the tip of a sharp sample pin. A series of 2D X-ray images was collected while the particle was rotated by 180°. A differential absorption contrast technique was used to map the Ni concentration in three dimensions. Two data sets were acquired, above the Ni K-edge (8,350 eV) and below the edge (8,320 eV). These data sets were reconstructed by computed tomography techniques to produce the 3D volume data53, and the image intensity changes within each voxel can be used to calculate the Ni concentration.

**Electrochemical test.** For fabrication of the cathodes, the prepared powders were mixed with carbon black and polyvinylidene fluoride (80:10:10) in N-methylpyrrolidinone. The obtained slurry was coated onto Al foil and roll-pressed. The electrodes were dried overnight at 120 °C in a vacuum before use. Preliminary cell tests were done with a 2032 coin-type cell using Li metal as the anode. The cycle-life tests were performed in a laminated-type full-cell wrapped with an Al foil. MCMB graphite (Osaka Gas) was used as the anode. The electrolyte solution was 1.2 M LiPF6 in ethylene carbonate-ethyl methyl carbonate (3/1 in volume, PANAX ETC). The cells were cycled between 3 and 4.2 V at a very low rate of 0.1 C (0.33–16.5 mA) during the initial formation process. The cells were charged and discharged between 3.0 and 4.2 V by applying a constant 1 C current (1 C corresponds to 33 mA) at 25 °C.

**Electric conductivity measurement.** The d.c. electrical conductivity was measured by a direct volt–ampere method (CMT-SR1000, AIT), in which disc samples were contacted with a four-point probe.

**DSC.** For the DSC experiments, the cells containing the cathode materials were constant-voltage charged to 4.3 V versus Li, and disassembled in an Ar-filled dry box. A 30-μl high-pressure stainless-steel DSC vessel with a gold-plated copper seal was used to host 3–5 mg samples, including solids and electrolyte. The measurements were carried out in a Pyris 1 differential scanning calorimeter (Perkin Elmer) using a scanning rate of 1 °C min⁻¹.

**In situ HEXRD.** The experimental set-up for the in situ experiment was similar to that reported in previous publications²⁹,³⁰. The experiment was carried out at beamline 11-ID-C of the Advanced Photon Source, Argonne National Laboratory; and the DSC data indicated a significant exothermal reaction at about 210 °C (Fig. 5c). The corresponding phase transformation for the FCG material was much slower: the new phase disappeared at about 250 °C, and the DSC data showed an exothermal reaction starting at about 250 °C (Fig. 5c). Thus, the FCG material shows better safety characteristics than the IC material by shifting its exothermal reaction to a higher temperature.

We have developed a high-performance cathode material composed of lithium transition-metal oxide with FCG within each particle. The structure takes advantage of the high capacity from nickel-rich materials, the high thermal stability of manganese-rich materials and the high rate capability of highly percolated and aligned nanorod morphology. This newly developed material can deliver a specific capacity of up to 215 mA h g⁻¹ with outstanding cycling stability in a full-cell configuration, maintaining 90% capacity retention after 1,000 cycles. This material based on the full gradient approach can lead to the rational design and development of a wide range of functional cathodes with better rate capability, higher energy density and better safety characteristics.

**Figure 5 | Contour plots of in situ HEXRD profile.** a, Delithiated IC material. b, Delithiated FCG material during thermal ramping from room temperature to 375 °C with a scanning rate of 10 °C min⁻¹. c, DSC profiles of the delithiated FCG material, the delithiated IC and the delithiated OC (Li0.80Ni0.70Co0.10Mn0.10O2) with a scanning rate of 1 °C min⁻¹. The cells were constant-voltage charged to 4.3 V versus Li⁺/Li before disassembling.
the X-ray wavelength was 0.10798 Å. A DSC sample contained in a high-pressure stainless-steel vessel was placed vertically in a programmable thermal stage, and the sample was heated up to 350 °C with a constant heating rate of 10 °C per minute. During the course of thermal ramping, high-energy X-rays penetrated through the sample horizontally, and a Perkin Elmer area detector was used to collect the X-ray diffraction patterns in the transmission geometry with a spectrum data collection rate of one pattern every 20 s. The collected 2D patterns were then integrated into conventional 1D data (intensity versus 2θ) using the fit2d program.35

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Author contributions

Additional information
Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to Y.-K.S. or K.A.

Competing financial interests
The authors declare no competing financial interests.