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Electronic supplementary information for the manuscript:

Progressive Concentration Gradient Nickel-rich Oxide Cathode Material for High-Energy and Long-Life Lithium-ion Batteries

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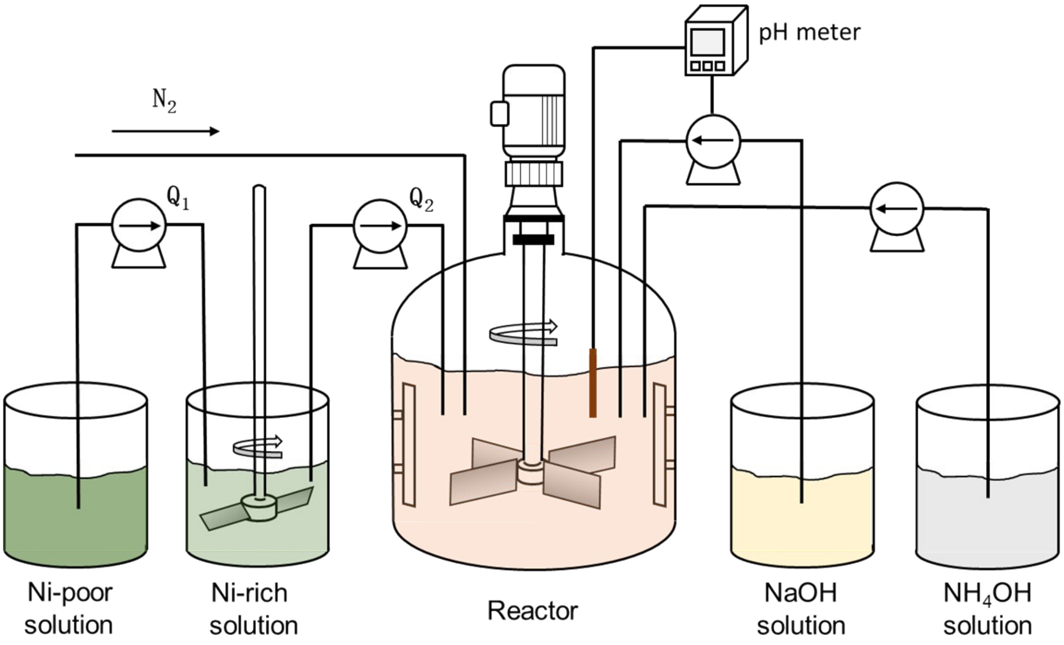

Fig. S1 Schematic illustration of the co-precipitation process.

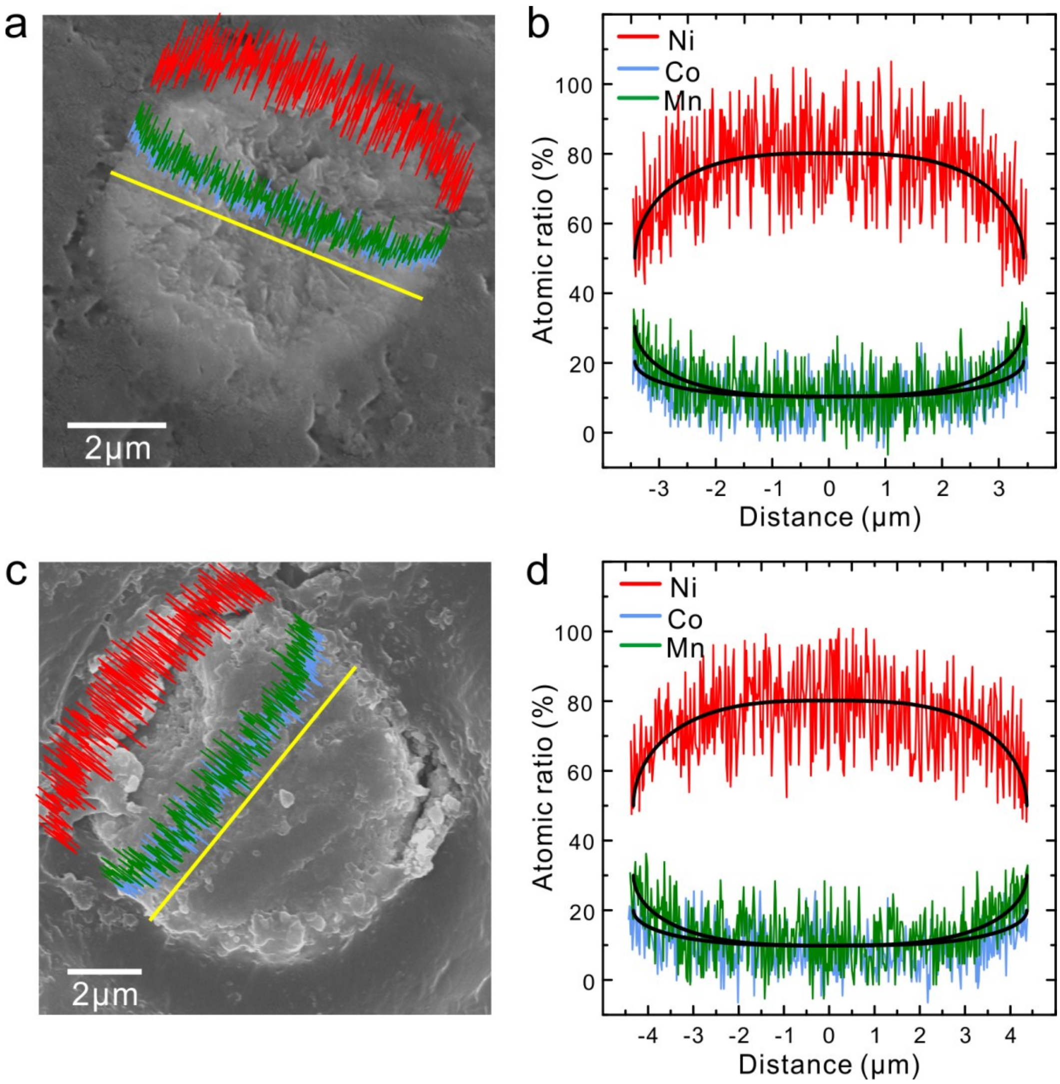

Fig. S2 EDS line scanning analysis across the precursor particle (a-b) and the PCG NCM particle (c-d), the yellow line represents the EDS scanning line.

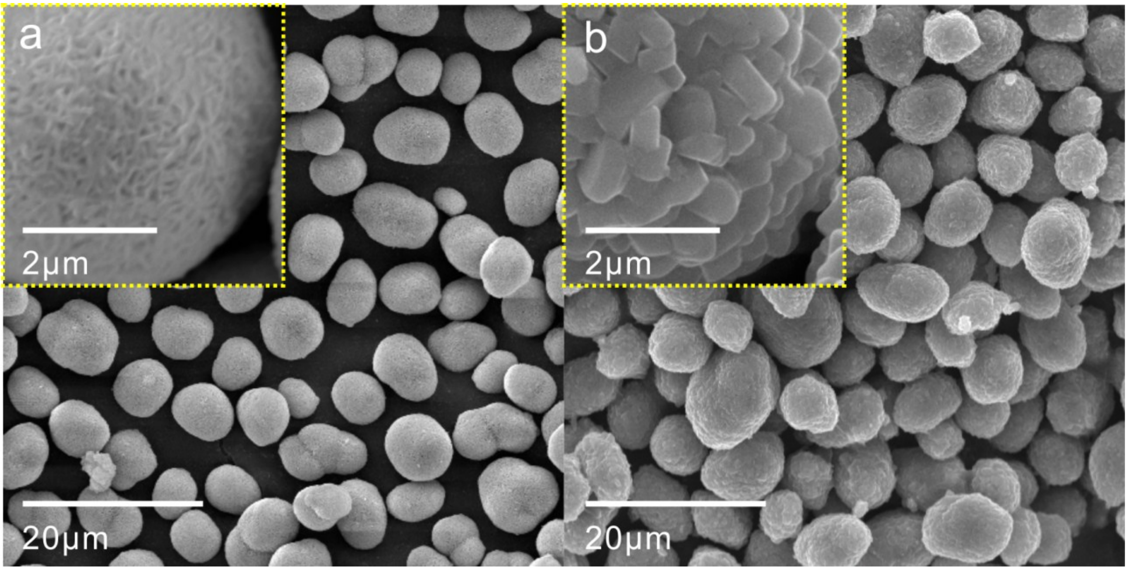

Fig. S3 SEM images of (a) precursor of NCM811 and (b) NCM811.

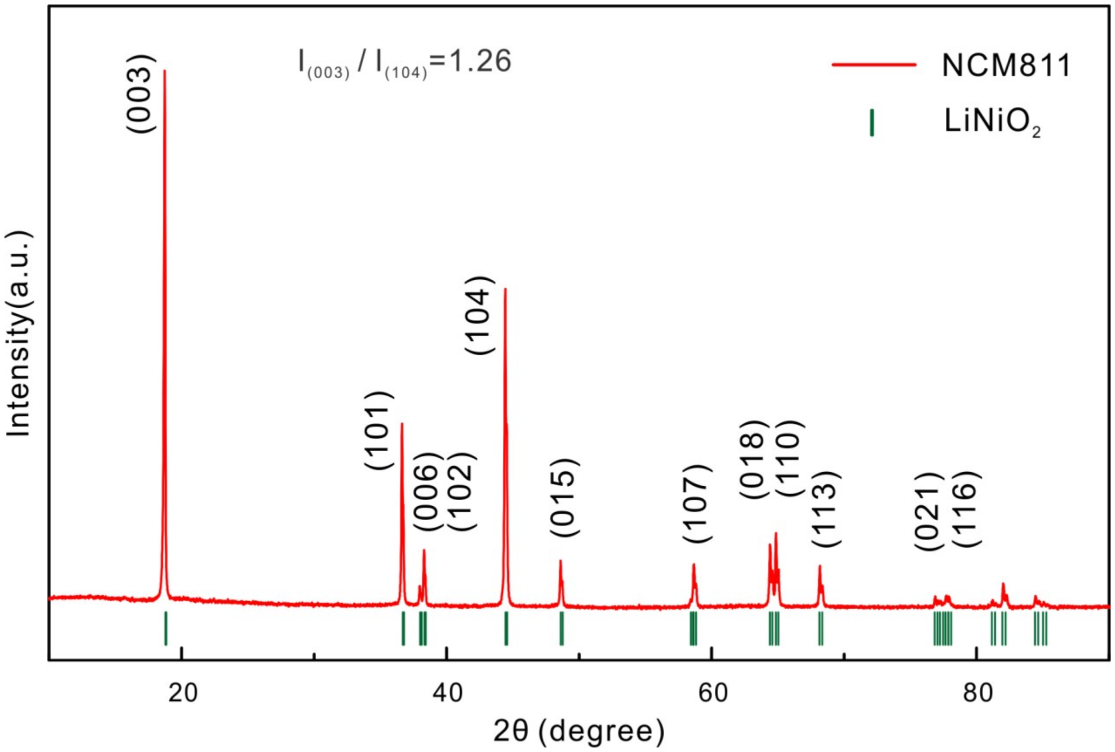

Fig. S4 Powder XRD pattern of NCM811.

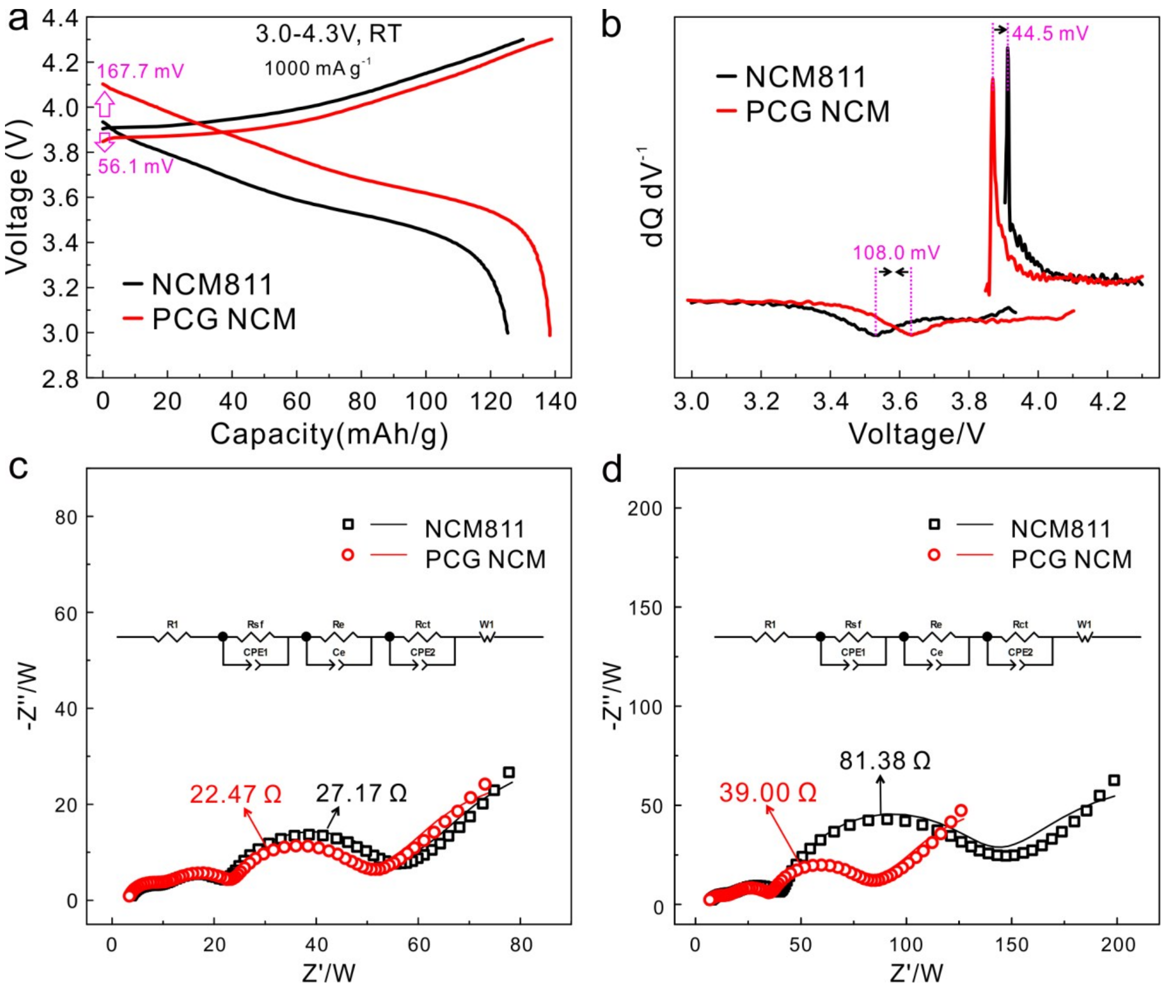

Fig. S5 (a) Charge-discharge curves and (b) the corresponding differential capacity curves of NCM811 and PCG NCM at 5 C rate; Electrochemical impedance spectra and their fitted results of PCG NCM and NCM811 cells (c) before and (d) after the rate capability test at charged state (4.3 V).

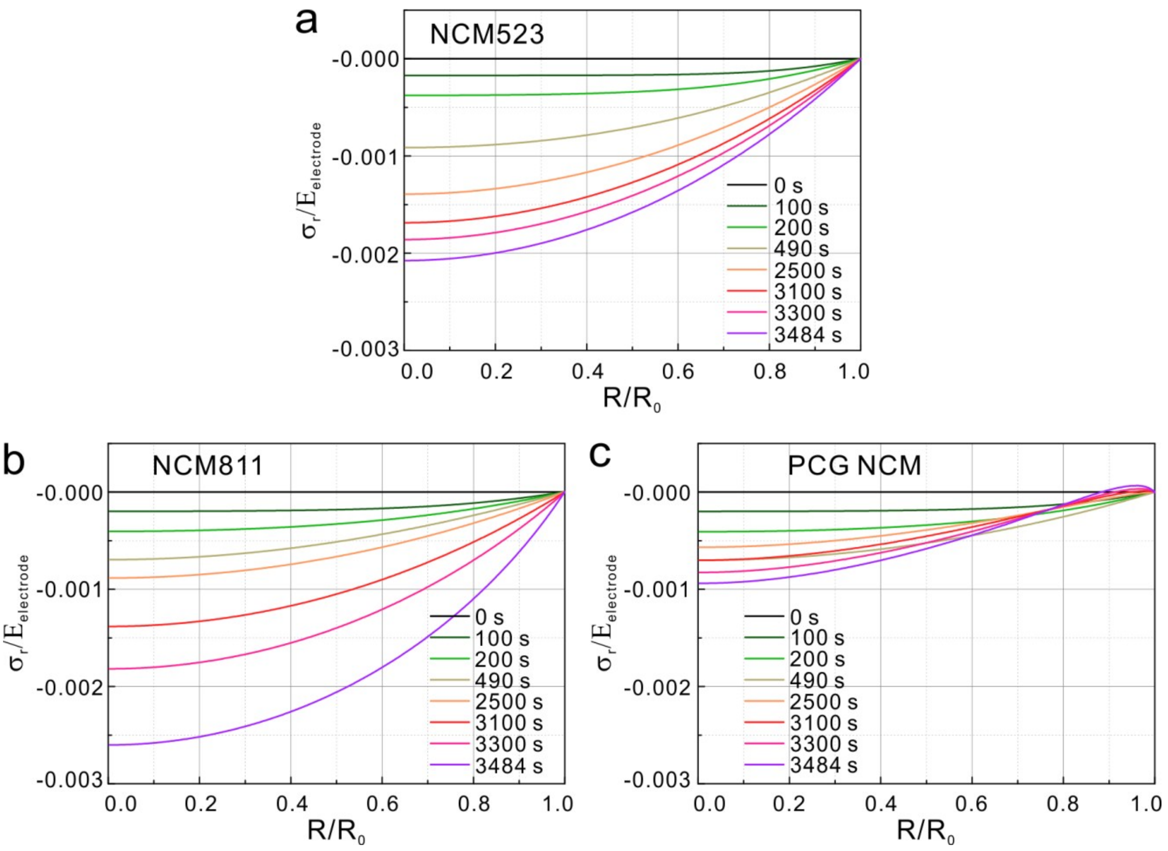

Fig. S6 Normalized radial stress versus relative location R/R_0 for different times: (a) NCM23, (b) NCM811 (c) PCG NCM. The radial stress is believed to have little effect on the nucleation and propagation of the cracks, as it is mainly compressive and decreases with the increment of radial position.

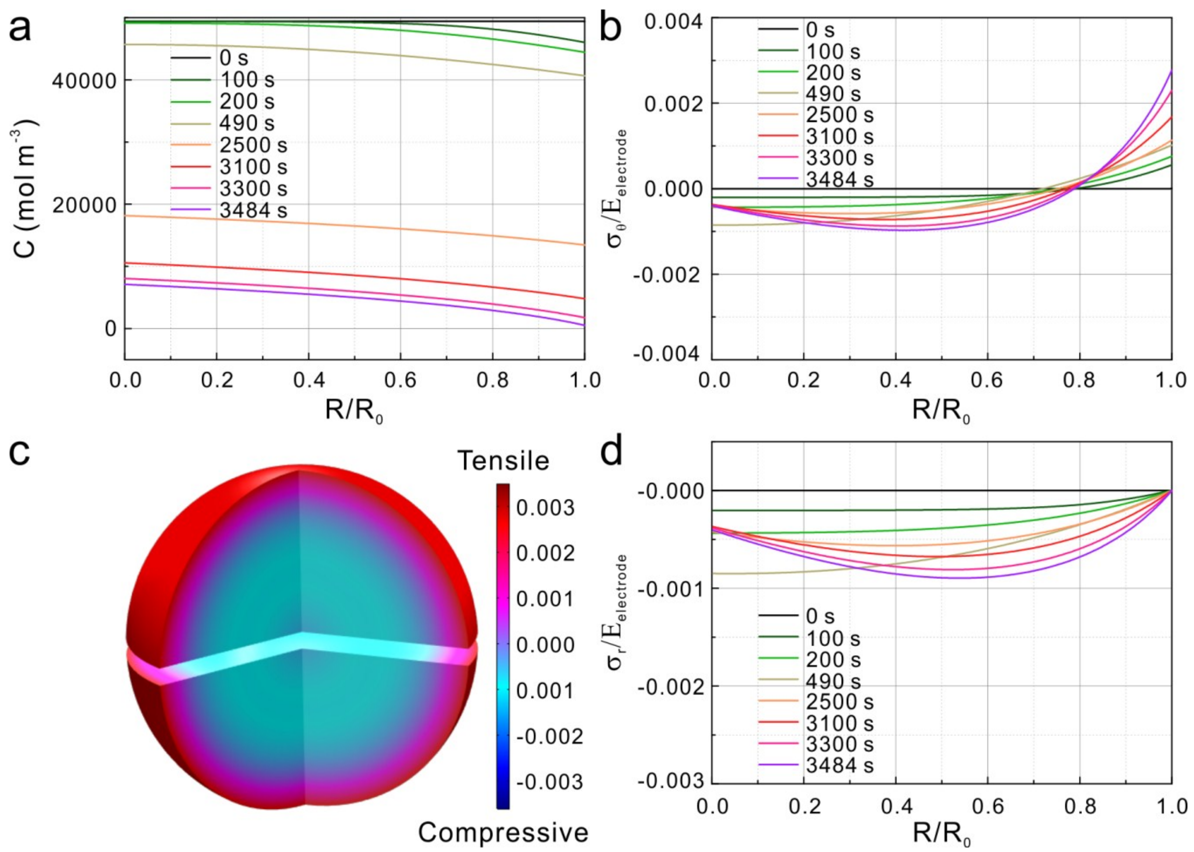

Fig. S7 Calculated results of conventional linear-change concentration gradient material: (a) Li$^+$ concentration and (b) normalized tangential stress versus the relative location R/R$_0$ for different times; (c) Nnormalized tangential stress distribution after fully charged in 1C rate. (d) Normalized radial stress versus the relative location R/R$_0$ for different times; Distribution of the internal stress inside the constant concentration gradient material is similar to that of NCM811 with only slight decrease of tensile tangential stress.

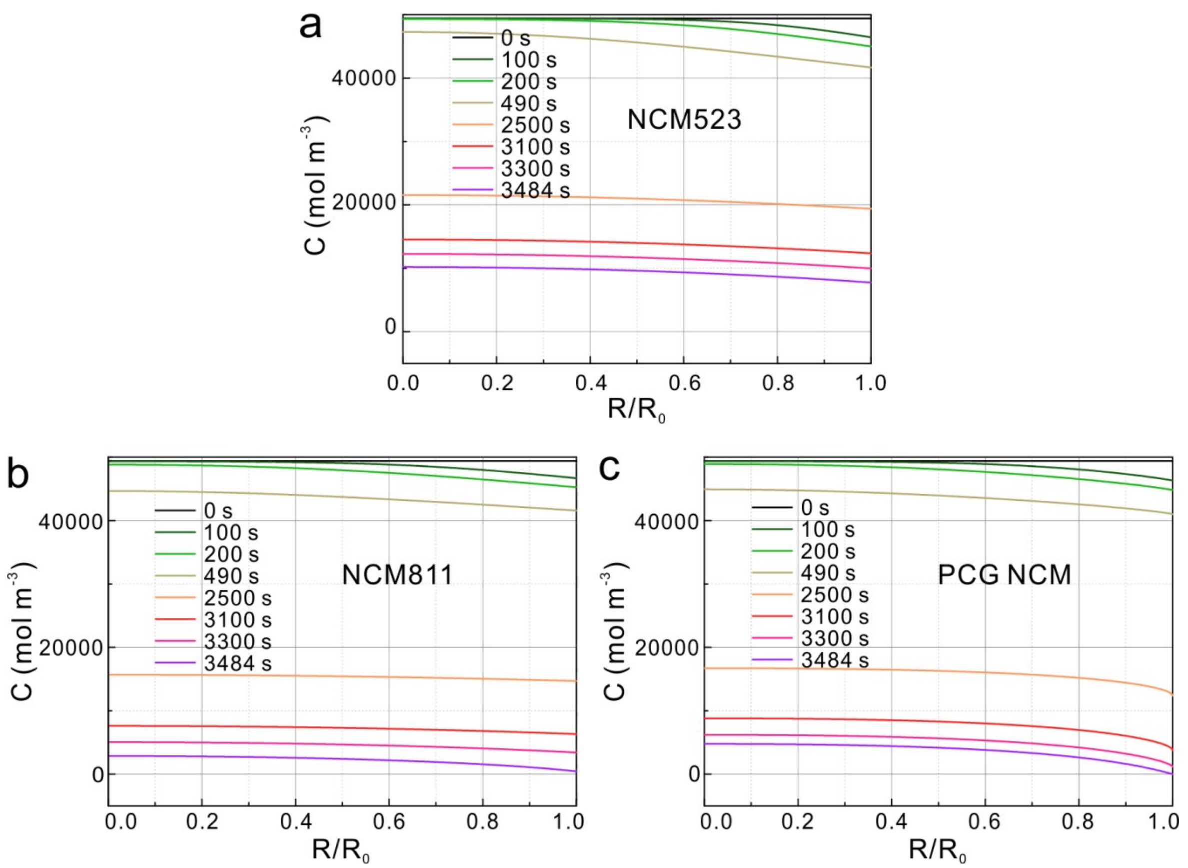

Fig. S8 Li$^+$ concentration versus the relative location R/R$_0$ for different values of time under galvanostatic condition: (a) NCM523, (b) NCM811 and (c) PCG NCM.

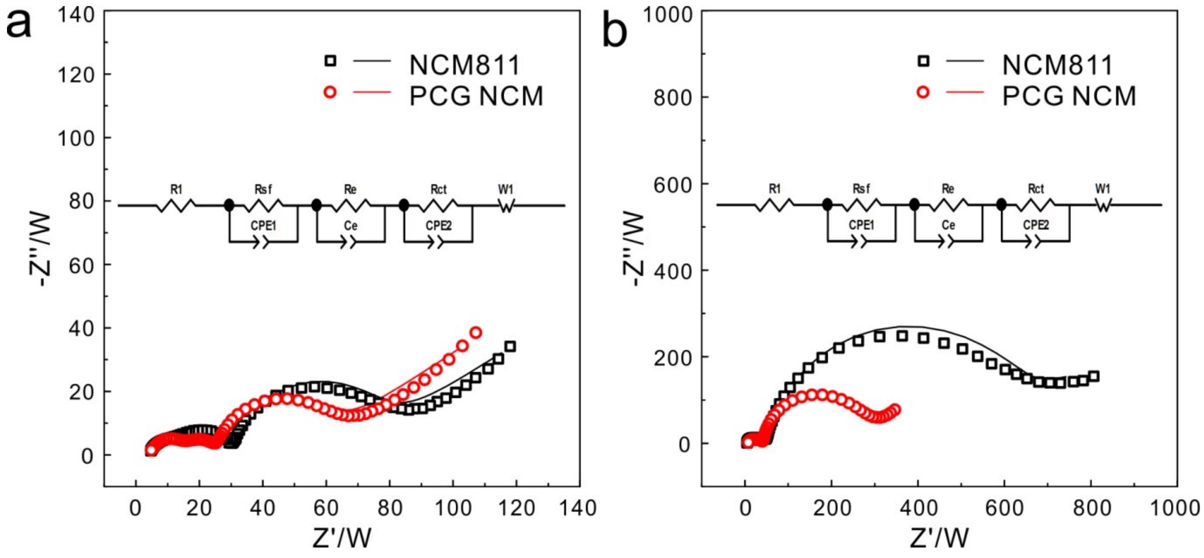

Fig. S9 Electrochemical impedance spectra and their fitted results of PCG NCM and NCM811 cells (a) before and (b) after 300 cycles at charged state (4.3 V). The equivalent circuit used for simulation is shown in the inset.

Table S1 Calculated impedance parameters before and after 300 cycles.

	1st cycle			**300th cycle**		
	R_{sf} (Ω)	**R_e** (Ω)	**R_{ct}** (Ω)	**R_{sf}** (Ω)	**R_e** (Ω)	**R_{ct}** (Ω)
NCM811	9.138	12.72	38.68	29.54	14.9	590.9
PCG NCM	10.64	6.754	28.74	25.82	6.824	224.7

DIS calculation:

Concentration gradient electrode

The diffusion induced stress (DIS) calculations were performed using the finite element method with a commercial package COMSOL Multiphysics. For a concentration gradient solid sphere of radius R, Young's modulus (E), partial molar volume (Ω) and diffusion coefficient (D) are functions of composition. E, Ω and D were assumed to change linearly with the content of Mn, Ni and Co, respectively. [1-3]

$$E(Mn) = a_1 * w(Mn) + b_1 \quad \text{(1-1a)}$$

$$\Omega(Ni) = a_2 * w(Ni) + b_2 \quad \text{(1-1b)} \qquad \text{(1-1)}$$

$$D(Co) = a_3 * w(Co) + b_3 \quad \text{(1-1c)}$$

Moreover, the partial molar volume is also influenced by the Li^+ concentration. [1] Thus, in the concentration gradient material, the partial molar volume is a function of both Ni and Li^+ content. Therefore, the partial molar volume can be expressed by the following equation

$$\Omega(Ni,C) = \Omega_0(Ni) + k(Ni) * C \tag{1-2}$$

where C is the molar concentration of Li^+, $k(Ni) = \frac{\Omega_F(Ni) - \Omega_0(Ni)}{C_{max}}$ is the lithiation induced swelling factor, Ω_0 is partial molar volume without Li^+, Ω_F is partial molar volume with Li^+ fully inserted, and C_{max} is the maximum Li^+ concentration when the material is fully inserted.

Mechanics Equations

Due to the symmetry of the spherical electrode, u(r) is used to indicate the radial displacement of the material. Under the assumption of small deformation, the radial strain ε_r and the tangential strain ε_θ can be expressed as

$$\varepsilon_r = \frac{\partial u}{\partial r}, \ \ \varepsilon_\theta = \frac{u}{r} \tag{1-3}$$

The diffusion induced stress caused by the insertion and extraction of Li$^+$ is formulated by the thermal analogy. [4, 5] The constitutive equations describing the stress and strain are given by

$$\varepsilon_r = \frac{1}{E}(\sigma_r - 2v\sigma_\theta) + \frac{1}{3}\Omega(C - C_0) \tag{1-4}$$

$$\varepsilon_\theta = \frac{1}{E}[(1-v)\sigma_\theta - v\sigma_r] + \frac{1}{3}\Omega(C - C_0) \tag{1-5}$$

where σ_r and σ_θ are the stress components along radial and tangential, respectively. v is Poisson's ratio and C_0 is the initial concentration of Li$^+$. The radial and tangential stress equations can be obtained by transforming equations (1-4) and (1-5)

$$\sigma_r = \lambda e + 2\mu\varepsilon_r - \frac{1}{3}(3\lambda + 2\mu)\Omega(C - C_0) \tag{1-6}$$

$$\sigma_\theta = \lambda e + 2\mu\varepsilon_\theta - \frac{1}{3}(3\lambda + 2\mu)\Omega(C - C_0) \tag{1-7}$$

where $e = \varepsilon_r + 2\varepsilon_\theta$ is the elastic volume strain, and λ and μ are Lamè constants denoted by Young's modulus E and Poisson's ratio v as

$$\lambda = \frac{vE}{(1+v)(1-2v)}, \ \mu = \frac{E}{2(1+v)}$$

In the absence of any body force, the equation for static mechanical equilibrium of a sphere is given by [4, 5]

$$\frac{d\sigma_r}{dr} + \frac{2}{r}(\sigma_r - \sigma_\theta) = 0 \tag{1-8}$$

The boundary conditions are:

$$\begin{gathered} \sigma_r|_{r=R} = 0 \\ \sigma_r|_{r=0} = finite \end{gathered} \tag{1-9}$$

Substituting equations (1-3), (1-6) and (1-7) into equation (1-8), we can obtain the Lamè equation in terms of the radial displacement

$$(\lambda+2\mu)\frac{d^2u}{dr^2}+\left(\frac{d\lambda}{dr}+2\frac{d\mu}{dr}+\frac{2\lambda+4\mu}{r}\right)\frac{du}{dr}+\left(\frac{2d\lambda}{rdr}-\frac{2\lambda+4\mu}{r^2}\right)u=\frac{1}{3}\frac{d}{dr}\Big[(3\lambda+2\mu)\Omega(\tag{1-10}$$

The boundary conditions are:

$$\begin{gathered}\sigma_r|_{r=R}=0\\ u(r)=0\end{gathered} \tag{1-11}$$

Diffusion equation

For the diffusion problem, the chemical potential is expressed by [6]

$$\mu_s=\mu_0+RT\ln C-\Omega\sigma_m+\Omega\Delta U_E \tag{1-12}$$

where μ_0 is the potential in a given standard state, and R is the universal gas constant. T is the temperature, $\sigma_m=\sigma_r+2\sigma_\theta$ is the hydrostatic pressure and $\Delta U_E=\frac{1}{2}\sigma_{ij}\varepsilon_{ij}$ is the strain energy density.

The gradient of the chemical potential drives the flux of Li^+, which is written by

$$J=-\frac{DC}{RT}\nabla\mu_s=-D\left(\nabla C-\frac{C}{RT}\nabla\left(\Omega\sigma_m-\Omega\Delta U_E\right)\right) \tag{1-13}$$

According to the mass conservation equation, we can obtain the following equation

$$\frac{\partial C}{\partial t}+\nabla J=0 \tag{1-14}$$

By substituting equations (1-13) into equation (1-14), the diffusion equation is obtained as:

$$\frac{\partial C}{\partial t}=\frac{2}{r}\left(D\frac{\partial C}{\partial r}-\frac{CD}{RT}\frac{\partial\left(\Omega\sigma_m-\Omega\Delta U_E\right)}{\partial r}\right)+\frac{\partial}{\partial r}\left(D\frac{\partial C}{\partial r}-\frac{CD}{RT}\frac{\partial\left(\Omega\sigma_m-\Omega\Delta U_E\right)}{\partial r}\right) \tag{1-15}$$

We assume that the initial stress of the spherical material is zero, and at this time Li^+ is fully inserted. Therefore, the initial condition is written as

$$C(r,0) = C_{max} \tag{1-16}$$

For galvanostatic charging, the particle is charged by prescribing a constant flux J_R on the surface of the particle. Namely,

$$J(R,t) = J_R \tag{1-17}$$

where J_R is in constant proportional to current density, and can be expressed through [7]

$$|J_R| = \frac{C_{max}c}{a_v(3600s)} \tag{1-18}$$

where a_v is specific surface area of the spherical particle, and c means C-rate.

The material properties used in the model are listed in Table S2.

Table S2 Material properties used in the model.

Parameters	**$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$**	**$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$**	**Units**
$\boldsymbol{E}$	175 (Ref. 2)	183 (Ref. 2)	GPa
$\boldsymbol{v}$	0.3 (Ref. 6)	0.3 (Ref. 6)	/
$\boldsymbol{C}_{\mathbf{max}}$	49398 (assumed)	49398 (assumed)	mol m^{-3}
$\boldsymbol{D}$	7.08×10^{-15} (Ref. 3)	3.8×10^{-15} (Ref. 3)	m^2 s^{-1}
$\boldsymbol{\Omega}_{\mathbf{0}}$	3.497×10^{-6} (assumed, Ref. 1)	2.7976×10^{-6} (assumed, Ref. 1)	m^3 mol^{-1}
$\boldsymbol{\Omega}_{\mathbf{F}}$	3.497×10^{-7} (assumed, Ref. 6)	3.497×10^{-7} (assumed, Ref. 6)	m^3 mol^{-1}
$\boldsymbol{k}$	-6.3712×10^{-11}	-4.9555×10^{-11}	m^6 mol^{-2}
$\boldsymbol{R}$	4×10^{-6}		m

Parameters of a_i and b_i used in the concentration gradient cathodes are listed in Table S3.

Table S3 Parameters of a_i and b_i used in the PCG-NCM cathode.

	a_1	**b_1**	**a_2**	**b_2**	**a_3**	**b_3**
Value	4×10^{10}	1.71×10^{11}	2.3313×10^{-6}	1.6319×10^{-6}	-3.28×10^{-14}	1.036×10^{-14}

In the NCM811 cathode, the contents of Ni , Mn and Co are constant from center to surface

$w_{NCM811}(Ni) = 0.8$

$w_{NCM811}(Mn) = 0.1$

$w_{NCM811}(Co) = 0.1$

For the constant concentration gradient cathode (CCG), the contents of Ni, Mn and Co are all functions of the radial coordinate r. The functional relationships can be described with linear functions

$$w_{CCG}(Ni) =- \frac{0.3}{R} \times r + 0.8$$

$w_{CCG}(Mn) = \frac{0.2}{R} \times r + 0.1$

$w_{CCG}(Co) = \frac{0.1}{R} \times r + 0.1$

The contents of Ni, Mn and Co in the PCG NCM material can be described as:

$$w_{PCG}(Ni) = 0.3 \times \left(1 - \left(\frac{r}{R}\right)^3\right)^{\frac{1}{2}} + 0.5$$

$w_{PCG}(Mn) =- 0.2 \times \left(1 - \left(\frac{r}{R}\right)^3\right)^{\frac{1}{2}} + 0.3$

$w_{PCG}(Co) =- 0.1 \times \left(1 - \left(\frac{r}{R}\right)^3\right)^{\frac{1}{2}} + 0.2$

It should be noted that many other factors related to the distribution of stresses are not considered in our present model, such as surface mechanism, [5] grain boundary, [8] dislocation [9] and so on. More sophisticated analysis will be concluded in future works.

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