Supplementary information

Nanoindentation measurements of anisotropic mechanical properties of single crystalline NMC cathodes for Li-ion batteries

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Algorithm: Calculation of the components of elasticity tensor $\mathbb{C}$

Input: Initial guess of elasticity tensor ($\mathbb{C}$) components in laboratory reference basis, indentation modulus (obtained from nano-indentation), and the Euler angles (obtained from EBSD) for each of the N indented grains.

for i = 1 **to** N **do**
    while $E_{\mathrm{r}} < \text{tolerance}$ **do**
        Update values of elasticity tensor components based on lattice constraints
        Transform elasticity tensor $\mathbb{C}$ into $\mathbb{C}^r$ using the rotation matrix $\mathcal{R}$
        for $\theta = 0$ **to** 2π **do**
            Calculate the **m**, **n** unit vectors using (3) and (4)
            Calculate the integrand of **B** matrix using (2)
        end
        Compute integral of **B(t)** using (1)
        Calculate $h(\theta)$ using (5)
        Minimize the product $\underline{\alpha}(e,\varphi)E(e)$ using (6) and (7)
        Compute $M_{\mathrm{cal}}(\varphi_1, \Phi, \varphi_2)$ using (8)
        Calculate E_{r} using (9)
    end
end

Output: Components of elasticity tensor $\mathbb{C}$ at each experimental indentation site

Euler angles (φ_1, Φ and φ_2) are used to calculate the rotation matrix:

$$\mathcal{R} = \begin{bmatrix} \cos\varphi_1\cos\varphi_2 - \sin\varphi_1\cos\Phi\sin\varphi_2 & \sin\varphi_1\cos\varphi_2 + \cos\varphi_1\cos\Phi\sin\varphi_2 & \sin\Phi\sin\varphi_2 \\ -\cos\varphi_1\sin\varphi_2 - \sin\varphi_1\cos\Phi\cos\varphi_2 & -\sin\varphi_1\sin\varphi_2 + \cos\varphi_1\cos\Phi\cos\varphi_2 & \sin\Phi\cos\varphi_2 \\ \sin\varphi_1\sin\Phi & -\cos\varphi_1\sin\Phi & \cos\Phi \end{bmatrix}$$

Table S1. Algorithm used for the numerical calculation of stiffness constants. At each indented grain (108 in total), the Euler angle obtained from EBSD analysis is used to evaluate M_{cal}. The values of the 6 stiffness constants (C_{11}, C_{12}, C_{13}, C_{14}, C_{33}, C_{44}) are modified iteratively to reduce the error between M_{cal} (calculated indentation modulus) and M_{exp} (experimental indentation modulus obtained from nanoindentation) at each indentation site. The tolerance is set as 0.1%.

Effective elastic/indentation modulus, M_{exp}	$\dfrac{1-\upsilon^2}{\dfrac{2\beta}{S}\sqrt{\dfrac{A_{\mathrm{c}}}{\pi}}-\dfrac{1-\upsilon_i^2}{E_i}}$
Hardness, H	$\dfrac{F}{A_{\mathrm{c}}}$
Crack length, c	$\sqrt{2}h_{\mathrm{m}}+\left(Q\dfrac{E'}{H}-\sqrt{2}\right)h_{\mathrm{x}}$
Fracture toughness, K_{c}	$\alpha\left(\dfrac{M_{\mathrm{exp}}}{H}\right)^{1/2}\dfrac{F}{c^{\frac{3}{2}}}$

Table S2. Expressions to calculate the effective indentation modulus, hardness, and fracture toughness from the load-displacement curves. β is a geometric factor (1.034 for the Berkovich tip), A_{c} is the calibrated contact area using a standard fused silica sample, S is the dynamic stiffness, υ is the Poisson's ratio of NMC, E_i is the elastic modulus of the diamond indenter (1141 GPa) and υ_i the Poisson's ratio of the indenter (0.07), F is the measured load, h_{m} is the total measured tip displacement, h_{x} is the tip displacement during the pop-in event, Q is the geometric constant (4.55 for the cube corner tip), E' is the plane strain modulus (M_{exp} from Figure 6a is used for the respective NMC compositions to calculate the fracture toughness), α is another empirical constant (0.036 for the cube corner tip). The fracture toughness is calculated based on the assumption of penny-shaped radial cracks.

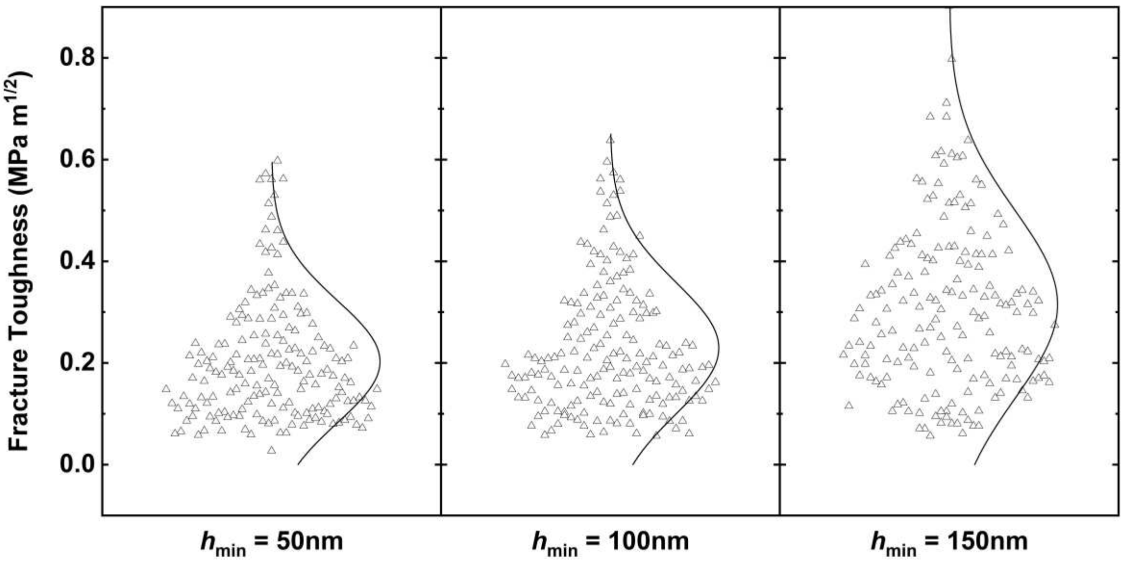

Figure S1. Sensitivity of the $h_{\min}$ value on the fracture toughness measurements ($N = 174$) for NMC622 single crystals. $h_{\min}$ defines the indentation depth before which no radial cracking is assumed to have taken place. While $h_{\min} = 50$ nm discards too many tests (due to fewer pop-in events), $h_{\min} = 150$ nm or higher values exhibit more spread of the fracture toughness values.

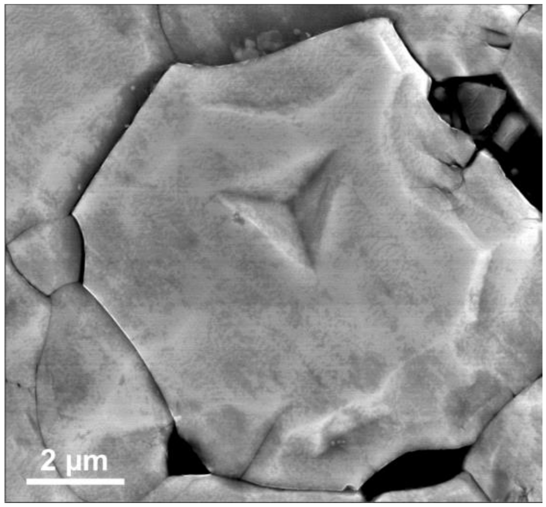

Figure S2. An SEM image of the Berkovich indenter impression on the sintered NMC grain.

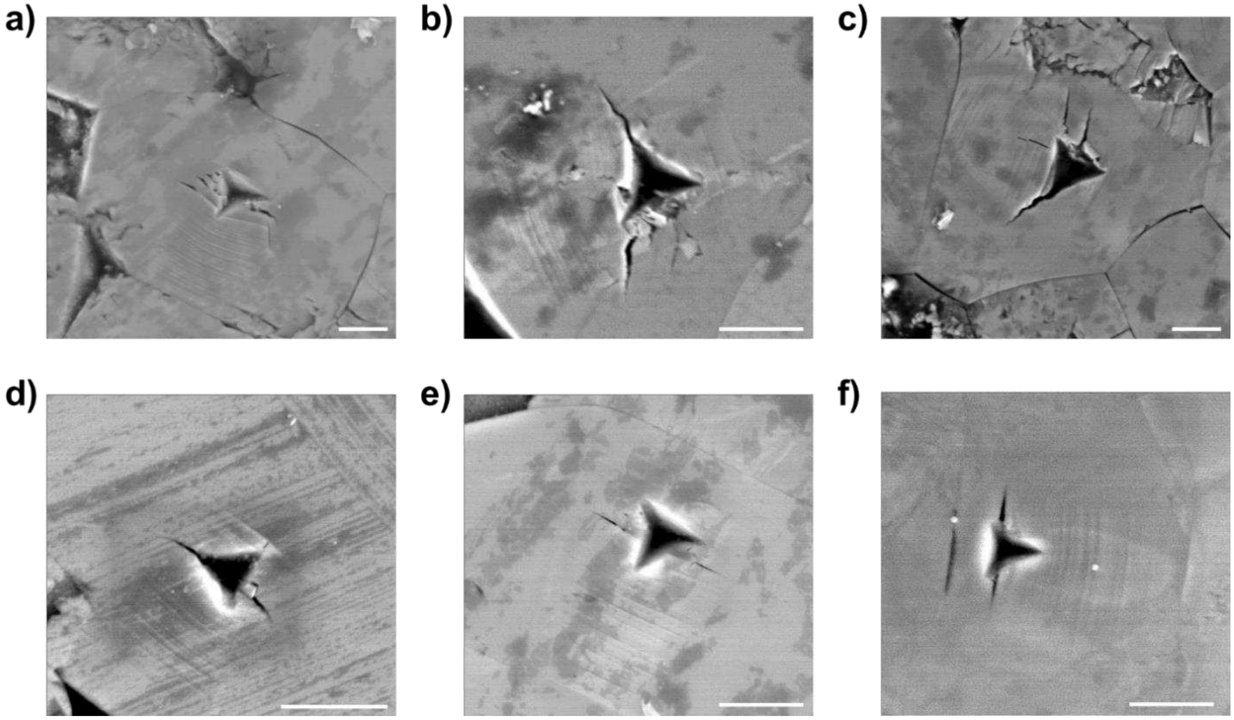

Figure S3. Shear bands around the cube corner tip induced fracture in the NMC grains. The white scale bar is 2µm.

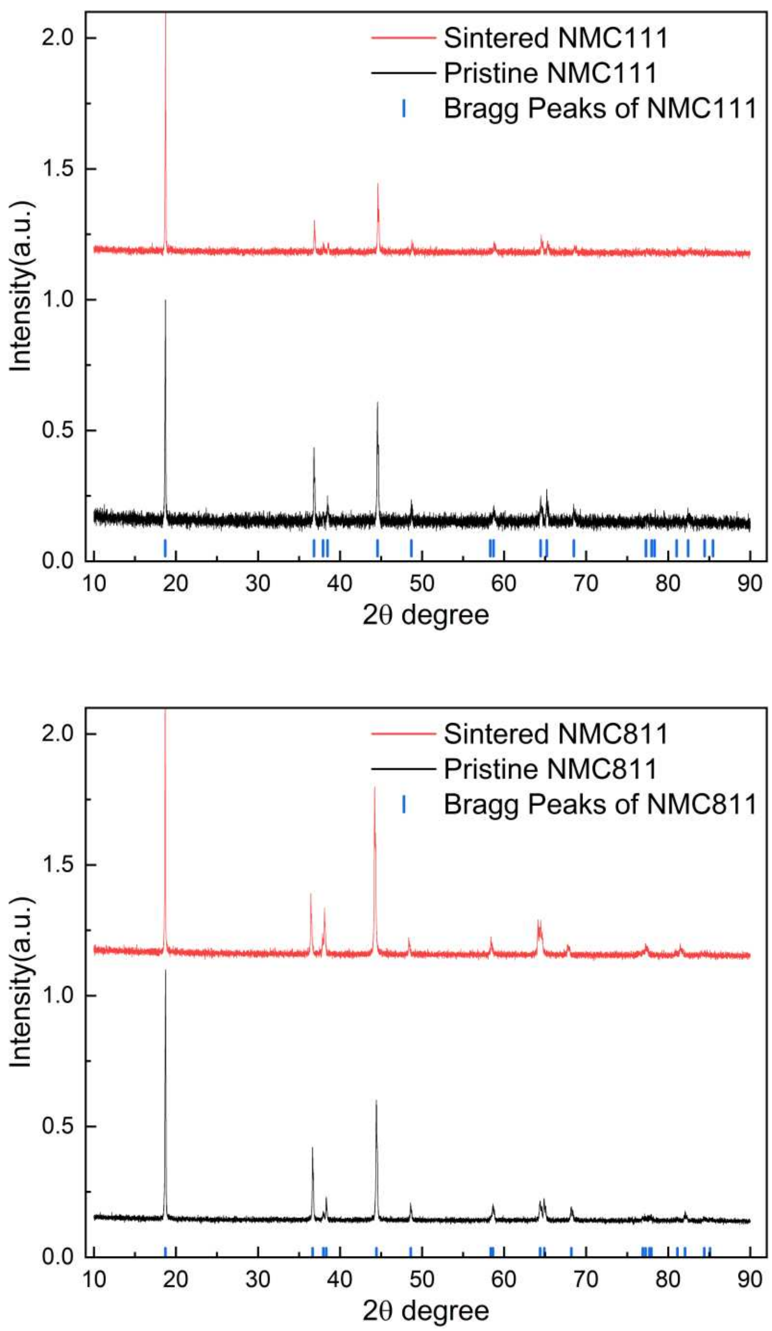

Figure S4. XRD profiles for the sintered NMC111 and NMC811 pellets.