**Supporting information**

**TABLE SI**. Models of the NCR and CGR cathode (100% SOC) used in the sequential refinement.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| NCR Li(Ni0.6Co0.3Al0.1)O2 (*Rm*)  Lattice parameters\*  *a* = 2.8115(3) Å  *c* = 14.146 (5)Å | | | | | | |
| Atom | Site | *x* | *y* | *z* | Uiso (Å2) | Occupancy |
| Li1 | 3*b* | 0 | 0 | ½ | 0.2~ | 1~ |
| Ni | 3*a* | 0 | 0 | 0 | 0.2~ | 0.6(1)^ |
| Co | 3*a* | 0 | 0 | 0 | 0.2~ | 0.3(1)^ |
| Al | 3*a* | 0 | 0 | 0 | 0.2~ | 0.1~ |
| O1 | 6*c* | 0 | 0 | 0.250(1)\* | 0.2~ | 1~ |

~ Fixed. ^ Value initially refined and then but fixed in the sequential refinement. \*starting value, refined sequentially

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| CGR Li(Ni1/3Mn1/3Co1/3)O2 (*Rm*)  Lattice parameters\*  *a* = 2.8115(7) Å  *c* = 14.472(7) Å | | | | | | |
| Atom | Site | *x* | *y* | *z* | Uiso (Å2) | Occupancy |
| Li1 | 3*b* | 0 | 0 | ½ | 0.2~ | 1~ |
| Ni | 3*a* | 0 | 0 | 0 | 0.2~ | 1/3~ |
| Mn | 3*a* | 0 | 0 | 0 | 0.2~ | 1/3~ |
| Co | 3*a* | 0 | 0 | 0 | 0.2~ | 1/3~ |
| O1 | 6*c* | 0 | 0 | 0.2614(1)\* | 0.2~ | 1~ |

~ Fixed. \*starting value, refined sequentially.



**Figure S1**. Schematic diagram illustrating the *operando* NPD experiment. (1) incident neutron beam, (2) battery on the sample stage, (3) transmitted neutron beam, (4) beam stop, (5) diffracted beams, and (6) 120-degree area detector.



Figure S2. Contour plots of *operando* NPD data of (a) NCR- and (b) CGR-containing batteries.



Figure S3. Refinement profiles for NPD data of NCR- and CGR-containing batteries at fully charged and discharged states. Range of refinement figures of merit for the entire dataset include the weighted profile R-factor (Rwp) = 15.2-26.6 for the NCR battery and Rwp = 12.2-18.8 for the CGR battery.