Electronic Supplementary Information

Operando Observation of the Structural Evolution and Kinetics of Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2 at Elevated Temperature

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Experimental section

Materials: NCM622 were purchased from Guangdong Minor Technology Co., Ltd..

Electrode preparation: The electrodes were prepared by thoroughly mixing 60 wt.% active material, 30 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride. The slurries made into pieces with 6 mm diameters. All electrodes were stored in an Ar-filled glove-box before use (Lab Star, Mbraun, Germany, H_2O < 0.5 ppm, O_2 < 0.5 ppm).

Electrochemical testing: For electrochemical characterization, 2016-type coin cells were assembled with NCM cathodes, 0.5 mm thick Li foils with 15 mm in diameter as the anodes, and polypropylene membranes (20 mm in diameter, Celgard 2600, USA) as the separators, the electrolyte of 1M LiPF_6 in ethylene carbonate and ethyl-methyl carbonate (EC : EMC = 1:1 wt./wt.). Galvanostatic discharge–charge cycling at 0.2C (C: C-rate) was carried out in a battery cycler (Landt CT2001, China) at 25 °C or 55 °C.

In situ XRD setup: The in situ experiments were carried out in a homemade in situ XRD cell, which was assembled with the same configuration as the standard coin cells except that the bottom of the cell was replaced by a Be window to allow the penetration of X-ray onto the cathode. The diffraction experiment was conducted in a Bruker X-ray diffractometer (Bruker D8 Advanced, Germany) equipped with a Cu tube operated at 40 kV and 40 mA. The electrochemical data was recorded by Landt, and the testing temperature can be controlled by a small oven (room temperature to 55 °C). The cells were cycled at ~ 0.3 C (1C is defined as ~ 180 mA/g for NCM622). XRD patterns were refined using the Rietveld method, as implemented in the program TOPAS.
Fig. S1 Rietveld crystal structure of Li[Li_{0.6}Co_{0.2}Mn_{0.2}]O_2 (NCM622).

Fig. S2 SEM images of NCM622.

Fig. S3 Voltage profiles of NCM622 for the first cycle at 25 °C (A) and 55 °C (B) at 0.3 C.
Fig. S4 CV curves of first and second cycles at 25 °C (A) and 55 °C (B) (0.03 mV/s, 3.0-4.2 V).

Table S1. The calculated intercept and slope at 25 and 55 °C from anodic and cathodic peaks.

<table>
<thead>
<tr>
<th></th>
<th>25 °C cathodic</th>
<th>25 °C anodic</th>
<th>55 °C cathodic</th>
<th>55 °C anodic</th>
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<tr>
<td>intercept</td>
<td>-0.0976</td>
<td>-0.0821</td>
<td>-0.0965</td>
<td>-0.0321</td>
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<td>slope</td>
<td>0.8029</td>
<td>0.5281</td>
<td>0.8209</td>
<td>0.5070</td>
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Fig. S5 Refined XRD patterns of NCM622 after charge and discharge process at 55 °C.