A self-discharging reaction mediated by imide salt enables the prevention of explosive thermal runaway in high-Ni material/graphite full cells

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Figure S1. Structural characteristics of the delithiated NCM811 obtained from the charged full cell after 100 °C hold for 24 hrs. (a) Wide range of XRD results of NCM811 after heating with different electrolytes. (b) Comparison Ni oxidation state of NCM811 from the heated cell with EL1 and EL2. (EL1 = $0.9M \text{ LiPF}_6 + 0.9M \text{ LiFSI}$, EL2 = $1.8M \text{ LiPF}_6$)



Figure S2. Structural change of fully delithiated NCM811 accompanied by O₂ release during TGA measurement. Comparison of XRD results of fully delithiated NCM811 (EL3 case) after TGA measurement up to 350 °C with & without self-discharging reaction. [A polymer holder was used for XRD measurement with a small amount of powder obtained after TGA measurement. A diffracted polymer peak corresponds to 20 of 25~27°] (R: Rhombohedral phase, RS: Rocksalt phase)

The powder samples after 350 °C heating with TGA tests (showed in Figure 3) were obtained and XRD measurements were conducted with the powder samples. For the sample without a self-discharging reaction that is the same sample as the fully charged NCM811 without 100 °C hot box test for 24 hrs, the phase transition from the layered to rock-salt structure can be occurred resulting in the oxygen gas release. Therefore, the O₂ gas release can be the main cause of the weight loss about 14% in Figure 3(a). In contrast, for the sample with the self-discharging reaction that is the same sample as the fully charged NCM811 with 100 °C hot box test for 24hrs, the layered structure is maintained by suppressing the phase transformation behavior and the O₂ gas release. As a result, the weight loss, 4% in Figure 3(b) is much smaller than that in the sample without a self-discharging reaction. It indicates that the self-discharging reaction occurring at 100 °C hold test when the LiFSI salt exists substantially improve the phase stability of the delithiated NCM811 by suppressing the phase transformation to the rock-salt structure from the layered structure.



Figure S3. Electrochemical stability of the electrolytes with different salts. Linear scan voltammetry (LSV) results of Li / Pt cell with EL1~EL3 at (a) 25 °C and (b) 100 °C. At high voltage, the electrolytes oxidation occurs at the surface of Pt electrode. (EL1 = $0.9M \text{ LiPF}_6 + 0.9M \text{ LiFSI}$, EL2 = $1.8M \text{ LiPF}_6$, EL3 = 1.8M LiFSI).

Electrochemical stability of the electrolytes (EL1~3) can be compared by LSV tests by using Li/Pt coin cell. The amount of current generated when the specific voltage is applied to the Pt electrode, which has no electrochemical reactivity, indicates the electrochemical stability of the electrolyte.

At 25 °C, for all the three electrolytes, the decomposition of the electrolytes starts with just below 5.0 V. It means that the three electrolytes have excellent oxidative stabilities below 5.0 V at 25 °C.

At 100 °C, generated current density from the oxidative decomposition of the electrolytes was much lower in the electrolyte containing LiFSI salt. This indicates that the electrolytes containing LiFSI salt show much higher electrochemical stability at 100 °C than electrolyte containing only LiPF₆ salt. It means that the supply of Li ions and electrons due to the electrochemical decomposition of the electrolyte containing LiFSI salt is insufficient for showing the self-discharging reaction of the NCM811 described here.



XPS fitting results of NCM811 and graphite electrode : After 100 °C 24 hrs hold

	NCM811				Graphite			
Energy (eV)	170.4	169	165	163.5	170.1	169.4	165.1	163.8
Species	SO42-	SO22-	S	Li _x S	SO42-	SO22-	S	Li _x S
Area	4785	2023	2671	537	4717	4506	732	1650

Figure S4. Surface analysis of the charged NCM811 electrode materials with/without selfdischarging reaction. The charged NCM811 electrode material without heating did not have the self-discharging reaction but the electrode material with heating at 100 °C for 24 hrs did have. Comparison of XPS analysis of S-2p for NCM811 cathodes from the charged full cell with/without heating. And the XPS fitting results of S-2p for NCM811 cathode and graphite anode with heating (EL1 [0.9M LiPF₆ + 0.9M LiFSI] was used).



Figure S5. The effect of the lithiated graphite on the self-discharging reactions as Li ions source. XRD patterns of the fully charged NCM811 with/without the lithiated graphite anode during 100 °C hot box test for 24 hrs. For heating the charged NCM811 without the lithiated graphite, the charged NCM811 full cell was disassembled, and then the lithiated graphite electrode was removed. After the removing the lithiated graphite, the cell was reassembled with only the charged NCM811 and electrolyte without the lithiated graphite. After then, the reassembled NCM811-electrolyte cell was hold at 100 °C for 24 hrs.

Before 100°C heating

After 100°C heating



Figure S6. Additional surface analysis of the charged NCM811 electrode materials before/after heating at 100 °C for 24 hrs. Comparison of XPS analysis of the C1s, O1s, F1s and P2p for NCM811 cathodes from the charged full cell with/without heating. (EL1 [0.9M LiPF₆ + 0.9M LiFSI] and EL2 [only 1.8M LiPF₆] were used).

To understand the effects of electrolyte salt on the byproducts formed on the cathode surface, the byproducts formed on the cathode surface were measured by XPS measurements with respect to the C1s, O1s, F1s and P2p in the NCM811 electrodes before and after 100 °C heating for 24hrs with different electrolytes. XPS spectra of the NCM811 electrode reacted with EL1 (0.9M LiPF₆ + 0.9M LiFSI) and EL2 (Only 1.8M LiPF₆) were compared.

According to the XPS results of the C1s and O1s spectra of the charged NCM811 cathode reacted with EL1 and EL2, the organic materials such as ROCO₂Li and other carbonized species having chemical states of the C-O-C and C=O-C were formed on the surface of NCM811 for the both EL1 and EL2. After 100 °C heating for 24 hrs, larger amount of the organic materials exhibiting similar XPS spectra of C1s and O1s were generated on the surface of the NMC811. For the XPS results of the F1s and P2p spectra, the inorganic byproducts such as $Li_xPO_yF_z$ and Li_xPF_z were also formed on the surface of the charged NCM811 electrode and the amount of inorganic byproduct also increased during the 100 °C heating for both EL1 and EL2. Therefore, the XPS results show that the electrolyte decomposition was activated at the 100 °C for both EL1 and EL2, and the byproducts piled on the cathode surface before and after 100 °C heating contain similar chemical species related to the C, O, F and P regardless of the coupled electrolyte. It should be noted that the thermal driven self-discharge reaction of the NCM811 did not occur without LiFSI salt, the organic and inorganic species related to the C, O, F and P is not be a key chemical species of the self-discharge reaction.