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Surface Analyses on a Cycled $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ Cathode by X-Ray Photoelectron Spectroscopy

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$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) has been attracting attention as a high-nickel cathode material for lithium-ion rechargeable batteries. This study evaluates the influence of the electrode surface film on battery performance of NMC811 and demonstrates the heterogeneous distribution of the formed film by using X-ray photoelectron spectroscopy.

NMC811 was purchased from Toshima Manufacturing Co., Ltd. Test cells were fabricated using NMC811 as the cathode active material, mixed with polyvinylidene difluoride (PVDF) and acetylene black (AB), 1 M $LiPF_6$ dissolved in EC/EMC (volume ratio of 3:7) as the electrolyte solution, and Li foil as the counter electrode. Constant current charge-discharge measurements were carried out at a 0.1C rate up to 50 cycles. The cells were then disassembled in a glove box. The XPS measurements were performed for the disassembled electrodes using PHI Quantes (ULVAC-PHI) with an Al K_α radiation (SR center, SA-1). The pass energy was set to 26 eV. Dual-beam charge neutralization was applied to suppress sample charging. Binding energies were calibrated for the C 1*s* signal from AB at 284.6 eV.

Fig. 1 shows the F 1s core-level XPS spectra of the electrode samples. In the pristine sample, two signals at 685 and 688 eV are attributed to LiF and PVDF, respectively. PVDF is predominantly present on the electrode of the pristine sample. In the 1st charged sample at 0.1C, a new signal originating from $Li_xPF_yO_z$ (i.e., a decomposition product of $LiPF_6$) appeared around 686 eV, while the intensity of the PVDF signal relatively decreased. This indicates that $LiPF_6$ in the electrolyte was decomposed during charging. The $Li_xPF_yO_z$ signal was further increased in relative intensity during the subsequent discharging. The LiF signal was observed in the discharged electrode after 50 cycles. This indicates that $LiPF_6$ decomposition accelerates with increasing number of cycles, and LiF is significantly deposited on the cathode surface. In addition, the spectral intensity relative to the PVDF signal varied depending on the sampling position, suggesting that the surface film components (LiF and $Li_xPF_yO_z$) may be unevenly deposited on the electrode. The battery degradation of NMC811 appears to correlate with the formation of thicker surface films.

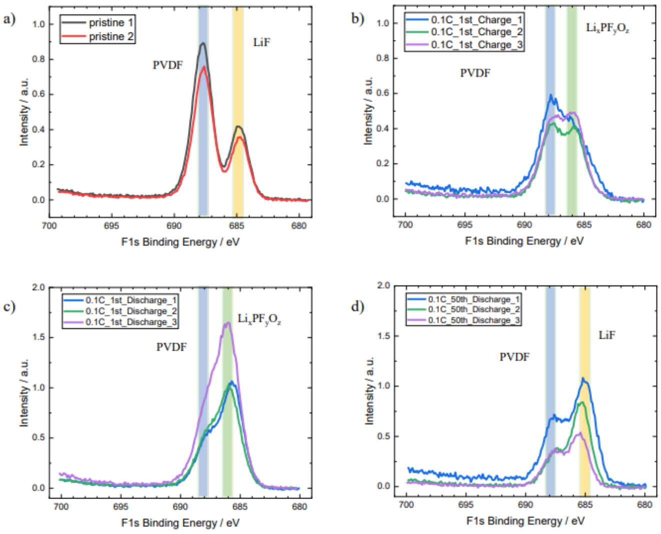

Fig. 1 F 1s core-level XPS spectra for (a) pristine electrode and the disassembled electrodes at (b) 1st charge, (c) 1st discharge, and (d) 50th discharge, respectively. Several sampling points were shown.