

Supplementary figures and tables

Fig. S1 Laser Scattering of Li-rich NMC

Particle size distribution analysis by HORIBA (LA 950) laser scattering
particle size distribution analyzer
Material: Li-rich NMC

Median Size : 11.55661(μm)
Mean Size : 11.94824(μm)
Std.Dev. : 3.8740(μm)
Variance : 15.008(μm^2)
Chi Square : 1.738760
S.P.Area : 5601.7(cm^2/cm^3)
CV : 32.4228(%)
Span : OFF
Diameter on Cumulative % : (1)10.00 (%) - 7.2715(μm)
: (2)50.00 (%) - 11.5566(μm)
: (3)90.00 (%) - 17.0642(μm)

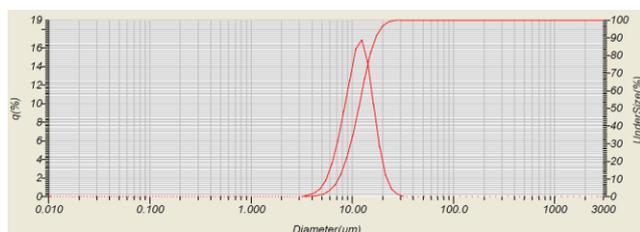


Fig. S2 a. XPS spectra for O1s measured from pristine Li-rich NMC
pristine powders [From Reference 15]

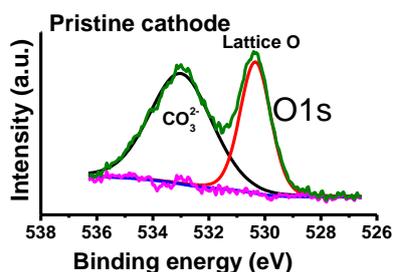


Fig. S2b. XPS spectra for C1s, Mn2p, Ni2p, and Co2p measured from 1hr
LiPON coated Li-rich NMC pristine powders

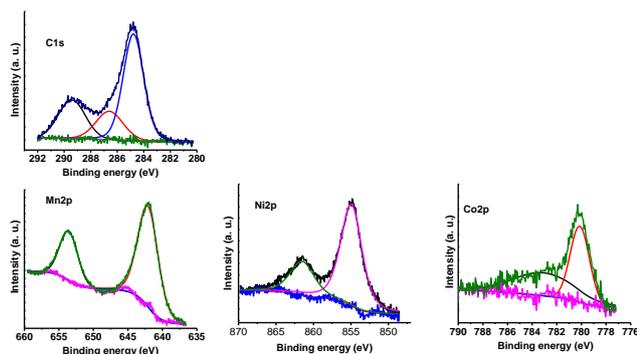


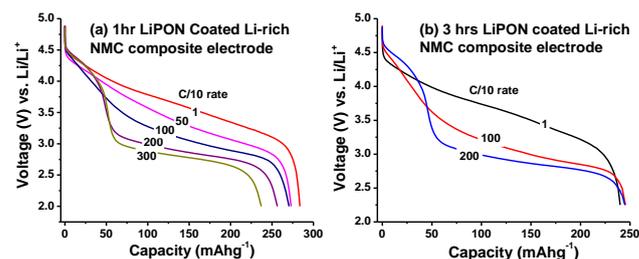
Table S1 First cycle irreversible capacity loss (ICL) as a function of
depth of charge (SOC)

| Positive active material $\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2$ | Applied voltage vs. Li/Li^+ | % of 1 st cycle irreversible capacity loss (ICL) | Discharge capacity (mAh/g) |
|--|--|---|-------------------------------|
| Conventional Li-rich NMC | 4.6 V | 15 | 210 |
| 1hr LiPON coated Li-rich NMC | | 13-14 | 225 (240 after 8 cycles) |
| Conventional Li-rich NMC | 4.8 V | 21 | 235 (250 after 8 cycles) |
| 1hr LiPON coated Li-rich NMC | | 13-15 | 250 (~270 after 10 cycles) |
| Conventional Li-rich NMC | 4.9 V | 18-19 | 275 |
| 1hr LiPON coated Li-rich NMC LiPON coated onto Li-rich NMC electrode surface | | 14 15 | 283 245-255 |

Table S2 Impedance parameters obtained by fitting of Nyquist plots
presented in Fig 9 with and without LiPON coated Li-rich NMC samples
at open circuit voltage, 4.5V and 4.9V during 1st charge.

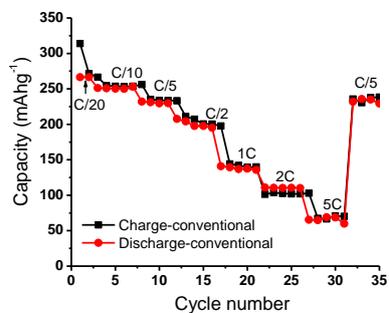
| Impedance Parameters | 1hr LiPON coated on to Li-rich NMC | 3hrs LiPON coated on to Li-rich NMC | Conventional Li-rich NMC |
|--|---------------------------------------|--|-----------------------------|
| Ohmic resistance at OCV (R_{Ω}/Ω) | 10.94 | 13.52 | 11.6 |
| Surface layer resistance at OCV (R_s/Ω) | 36 | 35.5 | 49 |
| Charge transfer resistance at OCV (R_{ct}/Ω) | 284 | 413 | 3139 |
| Ohmic resistance at 4.5 V (R_{Ω}/Ω) | 11 | 11.1 | 11.5 |
| Surface layer resistance at 4.5V (R_s/Ω) | 42 | 45 | 98 |
| Charge transfer resistance at 4.5V (R_{ct}/Ω) | 63 | 200 | 720 |
| Ohmic resistance at 4.9 V (R_{Ω}/Ω) | 11.75 | 12.58 | 11.1 |
| Surface layer resistance at 4.9 V (R_s/Ω) | 29 | 54 | 80 |
| Charge transfer resistance at 4.9 V (R_{ct}/Ω) | 104 | 447 | 982 |

Figure S3. Cycling behavior at C/10 rates of charge-discharge for the (a)
1hr and (b) 3 hrs LiPON coated Li-rich NMC composite electrodes (as
indicated) in the potential range 2.0 – 4.9 V, in EC-DMC 1:1/LiPF₆ 1.2 M
solutions at 25°C. The cycling protocol was similar to that of Figure 4.



The discharge profiles both for the 1 hr and 3 hrs LiPON coated Li-rich
NMC composite electrodes move to lower voltage plateaus showing
significant loss of energy. The rapid drop in the discharge voltage profiles
during cycling is related to the gradual change to a spinel-like structure.

Fig. S4 Charge-discharge cycling data's of conventional Li-rich NMC composite electrodes at various rates followed by C/5 rate for 35 cycles in EC-DMC 1:2/LiPF₆ 1.2 M solutions



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Fig. S5a Charge-discharge cycling data's of 3 hrs LiPON coated Li-rich NMC composite electrodes at various rates followed by C/10 rate for 225 cycles in EC-DMC 1:2/LiPF₆ 1.2 M solutions (at 25 °C).

Fig. S5b The voltage profiles at various rates corresponding to Fig. S5a.

10 Cycling protocol was constant current – constant voltage step at 4.9 V vs. Li/Li⁺ until the current reach value of C/50. The lower cut off potential was 2.0 V vs. Li/Li⁺.

