Long-Term Chemothermal Stability of Delithiated NCA in Polymer Solid-State Batteries

Supporting Information

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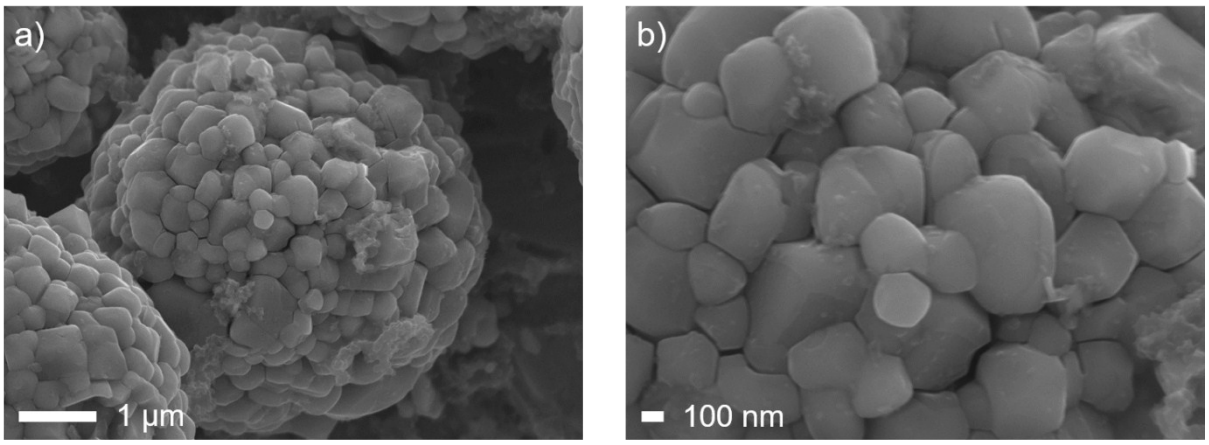

Figure S1. (a) SEM image of a typical secondary NCA particle. (b) Higher magnification of the surface showing primary particle grains of about 500 nm diameter.

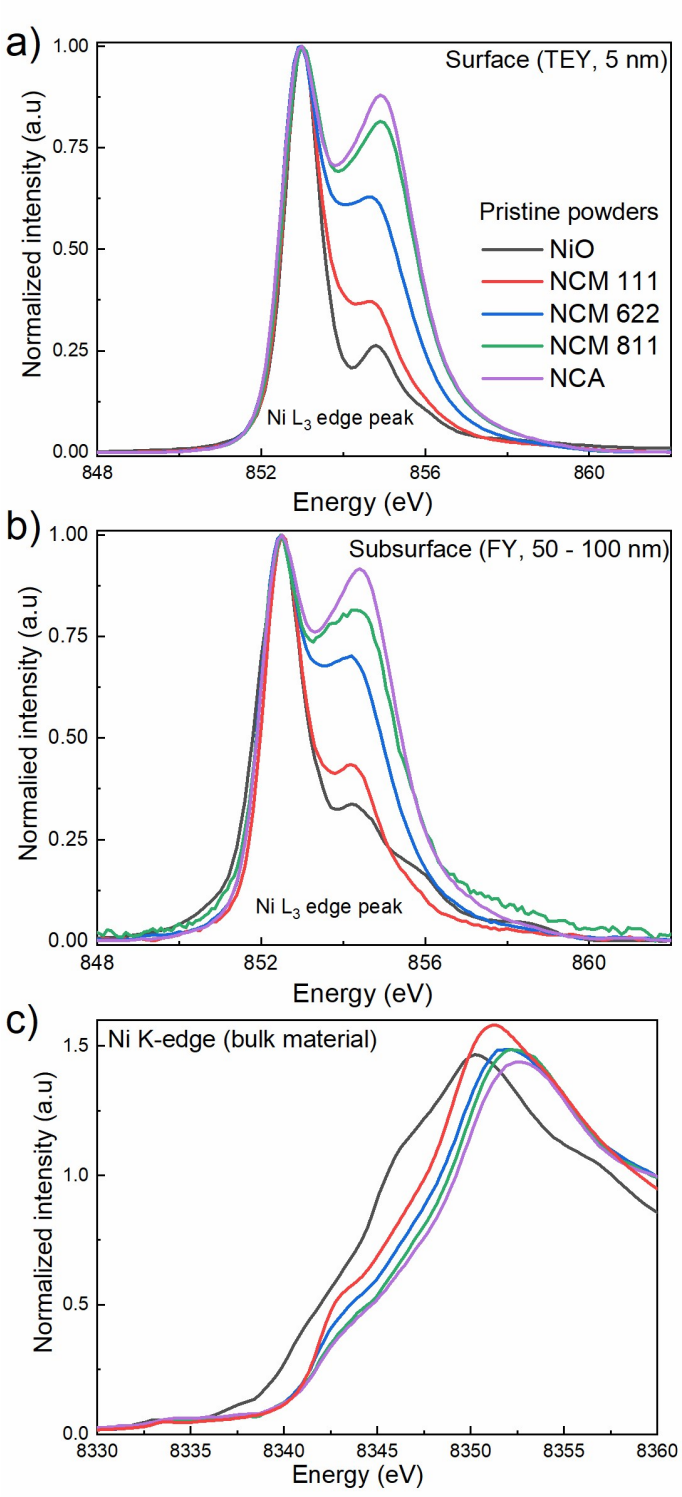

Figure S2. (a) and (b) Superimposed spectra of pristine nickel-rich oxides and nickel oxide (NiO) for TEY and FY mode, respectively. $L_{3,\,high}/L_{3,\,low}$ peak ratios are proportional to average oxidation states of nickel. (c) Nickel K-edge XANES spectra of pristine nickel-rich oxides and nickel NiO. With increasing oxidation state of nickel, a shift towards higher energy values is observed.

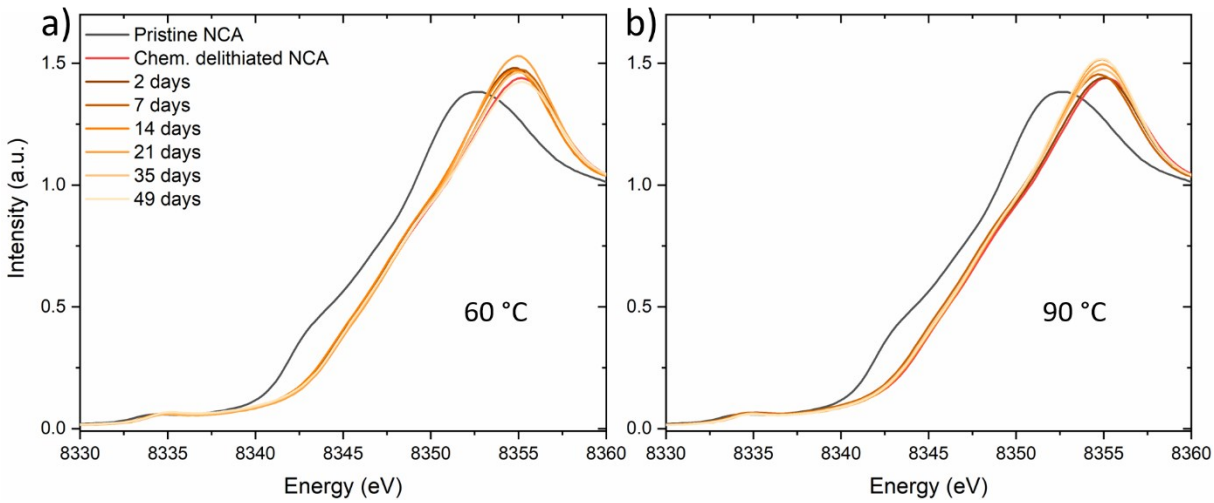

Figure S3. (a) Nickel K-edge XANES spectra for pristine NCA, $Li_{0.3}$NCA, and $Li_{0.3}$NCA stored at 60 °C for various lengths of time. (b) Nickel K-edge XANES spectra for pristine NCA, $Li_{0.3}$NCA, and $Li_{0.3}$NCA stored at 90 °C for various lengths of time.

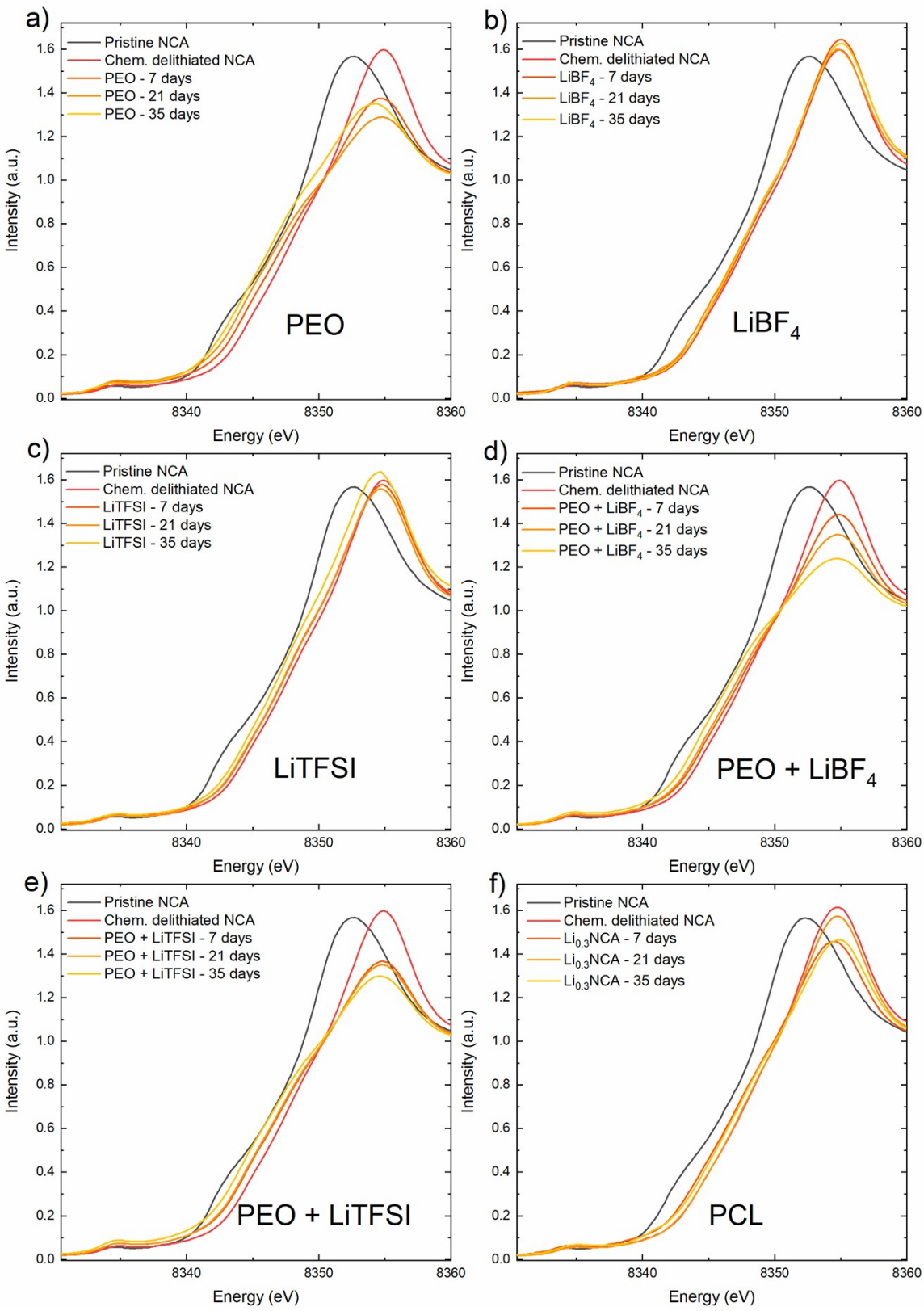

Figure S4. Nickel K-edge spectra for $Li_{0.3}NCA$ in combination with (a) PEO, (b) $LiBF_4$, (c) LiTFSI, (d) PEO + $LiBF_4$, (e) PEO + LiTFSI, and (f) PCL stored at 80 °C for 7 days, 21 days and 35 days.

Nickel oxide	Calculated nickel valence (in fully lithiated state)
NiO	+2
NMC111	+2
NMC532	+2 2/5
NMC622	+2 2/3
NMC811	+2 7/8
NCA	+3

Table S1. Calculated nickel valence for different nickelates in the fully lithiated state, under the assumption, that cobalt is 3+ and manganese is 4+.

Combination	TEY derived apparent oxidation state after 35 days	TEY derived degree of aging after 35 days	FY derived apparent oxidation state after 35 days	FY derived degree of aging after 35 days	Bulk apparent oxidation state after 35 days	Bulk degree of aging after 35 days
$Li_{0.3}$NCA only	3.38+	46%	3.39+	44%	3.67+	5%
+ PEO	2.41+	184%	2.70+	143%	3.14+	80%
+ PCL	3.18+	75%	3.29+	58%	3.34+	52%
+ $LiBF_4$	3.49+	30%	3.55+	21%	3.68+	3%
+ LiTFSI	2.54+	165%	3.03+	96%	3.52+	25%
+ PEO + $LiBF_4$	3.24+	66%	3.29+	59%	3.30+	56%
+ PCL + $LiBF_4$	3.46+	35%	3.52+	26%	3.57+	19%
+ PEO + LiTFSI	2.86+	120%	3.13+	81%	3.21+	69%
$Li_{0.3}$NMC811 + PCL	2.44+	180%	3.02+	98%	3.02+	98%
$Li_{0.3}$NMC811 + $LiBF_4$	3.26+	62%	3.40+	43%	3.63+	10%
$Li_{0.3}$NMC811 + PCL + $LiBF_4$	3.35+	50%	3.34+	51%	3.67+	4%
$Li_{0.3}$NMC622 + PCL	3.40+	43%	3.25+	64%	3.48+	31%
$Li_{0.3}$NMC622 + $LiBF_4$	3.55+	21%	3.58+	17%	3.67+	4%
$Li_{0.3}$NMC622 + PCL + $LiBF_4$	3.50+	28%	3.34+	51%	3.59+	16%

Table S2. Apparent oxidation state and degree of aging in percent after storing samples for 35 days at 80 °C. Apparent oxidation state and degree of aging is shown for surface (TEY), subsurface (FY), and bulk.