



ELECTROCHEMISTRY LABORATORY

On the LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ system upon (de)litiathion: surface and bulk characterizations during the first three cycles

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LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (NCA)

- Promising 4 V electrode material
- High practical specific charge, ~200 mAh/g
- Co doping: maintains the layered structure
- Al doping: improves thermal stability

Motivation:

1st charge

x=0.8

x=0.70

x=0.11

x=0.03

x=0.8

=0.72

=0.5

8.2 8.4

2nd charge

9.0 9.2

9.0 9.2

 $\begin{array}{c} 17.0 \\ 2\Theta \ [^{\circ}\] \ (\lambda = 0.7089 \ \text{\AA}) \end{array}$

8.8

Detailed understanding of:

- Activation mechanism
- · (de)lithiation reaction mechanism for first three cycles



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Surface reaction characterization: XRD, DEMS & EIS

 $Li(Ni,Co,Al)O_2 + x/2 CO_2 + x/4 O_2 = Li_{1-x}(Ni,Co,Al)O_2 + x/2 Li_2CO_3$

- Decomposition of the $\rm Li_2CO_3$ film during oxidation $\rightarrow \rm CO_2$ evolution
- Li_2CO_3 phase re-formed during reduction \rightarrow consumption of CO_2



EIS

<u>After 1st cycle</u>: resistance decreases during delithiation (4.3V) and increases upon lithiation (3.0V) → dissolution and re-formation of the insulating Li_2CO_3 surface film

Kinetic limitations due to resistance to Li⁺ ion transfer through the surface films → CV peaks shift in the order of tens of mV



.8 0.6 0.4 0.2 0.0 0.2 0.4 0.6 Li content [x in $Li_{1-x}Ni_{0.80}Co_{0.15}Al_{0.05}O_2$]

30

0.8

Bulk characterization: reaction mechanism by in situ XRD & electrochemical exp.

Operando synchrotron XRD **Electrochemical experiments** ш ₹ 14.4 Potential 250 eter 4.5 14.2 On discharge R2 R1 R1 R2 [mAh/g] Daran 14.0 200 4.0 ≤ 13.8 S. attice Charge 150 Li⁺/Li 13.6 3.5 1st Charge: 13.4 100 R2 2nd Charge: Specific 13.: 0.2 0.4 0.6 0.8 1.0 0.0 50 Li content [x in Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O₂] 0 1st charge: ò 10 15 20 25 · Stage I+II: two-phase/solid solution 165 30.0 Cvcle 17.0 17.5 2Θ [°] (λ = 0.7089 Å) 20 0 29.5 RI R2 Discharge 4.2 Charge 4.0 1,1/Li Stage III: R2 solid solution S 3.8 (contraction of the c axis) ≥ 3.6 2nd & 3rd charges: Potential · Mainly solid solution 3.4 3.2 Shift of E_{start} to lower

potentials in CV: composition &

reaction mechanism changes

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