Supplementary information

Rational design of dual-ion doped cobalt-free Li-rich cathode for enhanced cycle stability of lithium-ion pouch cell batteries.

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Experimental section

Materials

Nickel acetate tetrahydrate (>99%), manganese acetate tetrahydrate (>99%), lithium acetate dihydrate (reagent grade), citric acid (>99%), N-Methyl-2-pyrrolidone (NMP, >99%), Lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate, 1.0 M LiPF6 in EC/DMC=50/50 (v/v), ammonium hydroxide solution 28% NH_3 in H_2O were obtained from Sigma–Aldrich. Additional materials, including conducting carbon (CC,Super C65), polyvinylidene fluoride (PVDF) as the binder, Al foil (cathode current collector), Cu foil (anode current collector), and tabs (Al and Ni), were obtained from MTI (USA). Trilayered (PP/PE/PP) 25 μm thick separator (Celgard 2325) was obtained from Celgard. Pure lithium foil (100 μm) as counter electrode for coin cell was purchased from Nanochemazone.
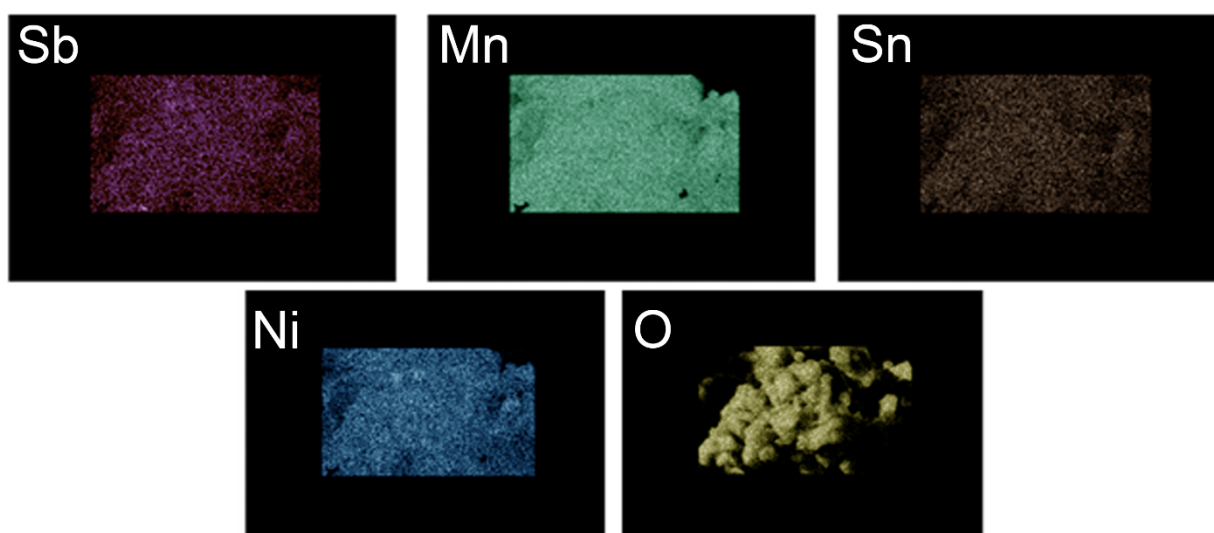

Figure S1. SEM images and EDS mapping of D-LR for Mn, Ni, O, Sb and Sn metals.
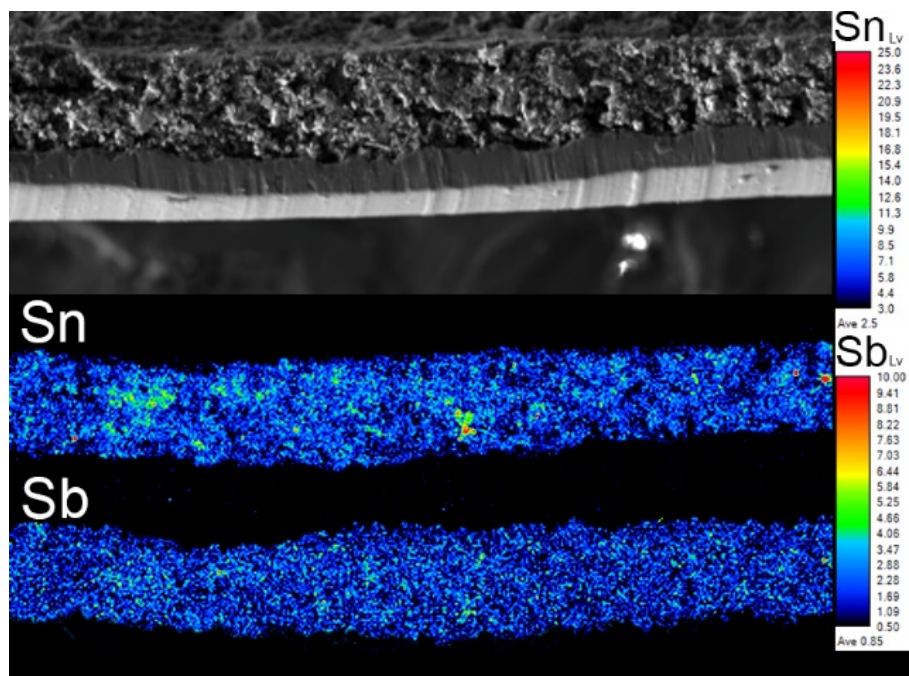
Figure S2. Field-emission electron probe microanalysis (EPMA) of the cross-section of the electrode.

Equations for thickness for TM slab and Li inter-slab

Equations for thickness of the TM slab ($S(MO_2)$) and the Lithium inter-slab ($I(LiO_2)$) calculation

$$S(MO_2) = 2\left[\left(\frac{1}{3}\right) - Z_{ox}\right] \times c \text{ ------ } (Equation\ S1)$$

$$I(LiO_2) = \frac{c}{3} - S(MO_2) \text{ ------ } (Equation\ S2)$$

The Randles–Sevcik equation for Li diffusion calculations

The cyclic voltammetry peak height, ip, is directly proportional to the electrolyte concentration, C, as described by the simplified Randles-Sevcik equation. In this equation, n is the number of electrons appearing in the half-reaction for the redox couple, A is the electrode area (cm^2), D is the analytes diffusion coefficient ($cm^2\ s^{-1}$) and v is the rate at which the potential is swept ($V\ s^{-1}$). v was measured over a range of scan rates from 0.2 to 1 mV / s.

$$Ip = 2.69\ x\ 10^5\ x\ n^{3/2}\ x\ A^{\frac{1}{2}}\ x\ D^{\frac{1}{2}}\ x\ C\ x\ v^{1/2} \text{ --- } - (Equation\ S3)$$

Equation	y = a + b*x
Plot	I
Weight	No Weighting
Intercept	0.4855 ± 0.13225
Slope	-3.88178 ± 0.17073
Residual Sum of Squares	0.01657
Pearson's r	-0.99711
R-Square (COD)	0.99423
Adj. R-Square	0.99231

Equation	y = a + b*x
Plot	D
Weight	No Weighting
Intercept	-1.33043 ± 0.15517
Slope	-2.1499 ± 0.23392
Residual Sum of Squares	0.06567
Pearson's r	-0.9827
R-Square (COD)	0.9657
Adj. R-Square	0.95427
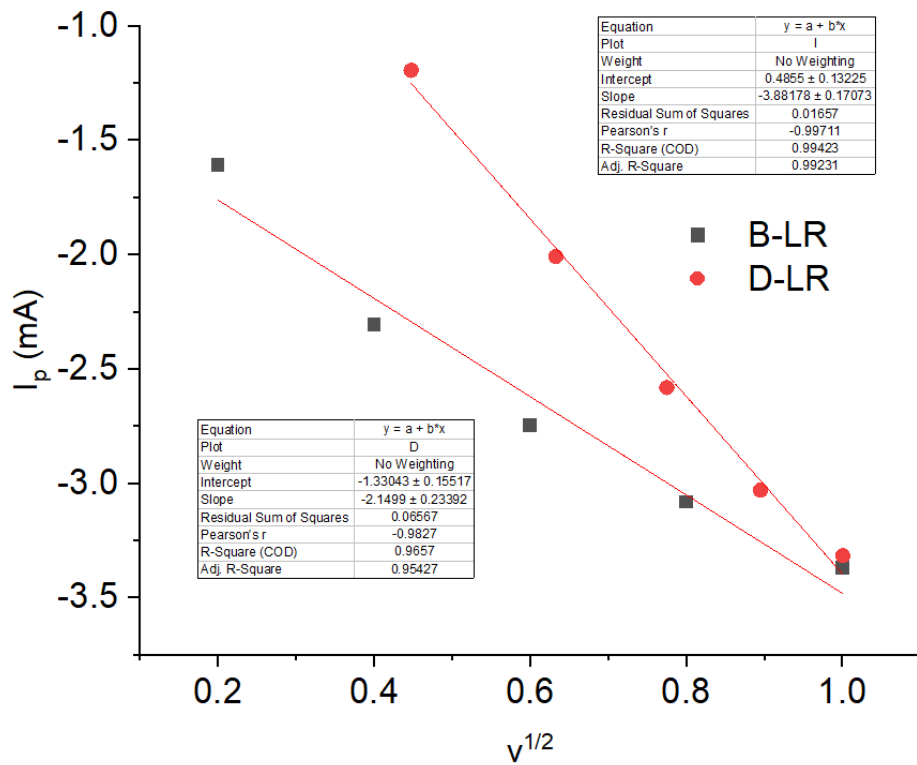
Figure S3. The Randles–Sevcik plots of L-RH and D-RH for total cathodic charge vs scan rate

Equation	$y = a + b \cdot x$
Plot	B
Weight	No Weighting
Intercept	-0.91742 ± 0.03882
Slope	6.7032 ± 0.05012
Residual Sum of Squares	0.00143
Pearson's r	0.99992
R-Square (COD)	0.99983
Adj. R-Square	0.99978

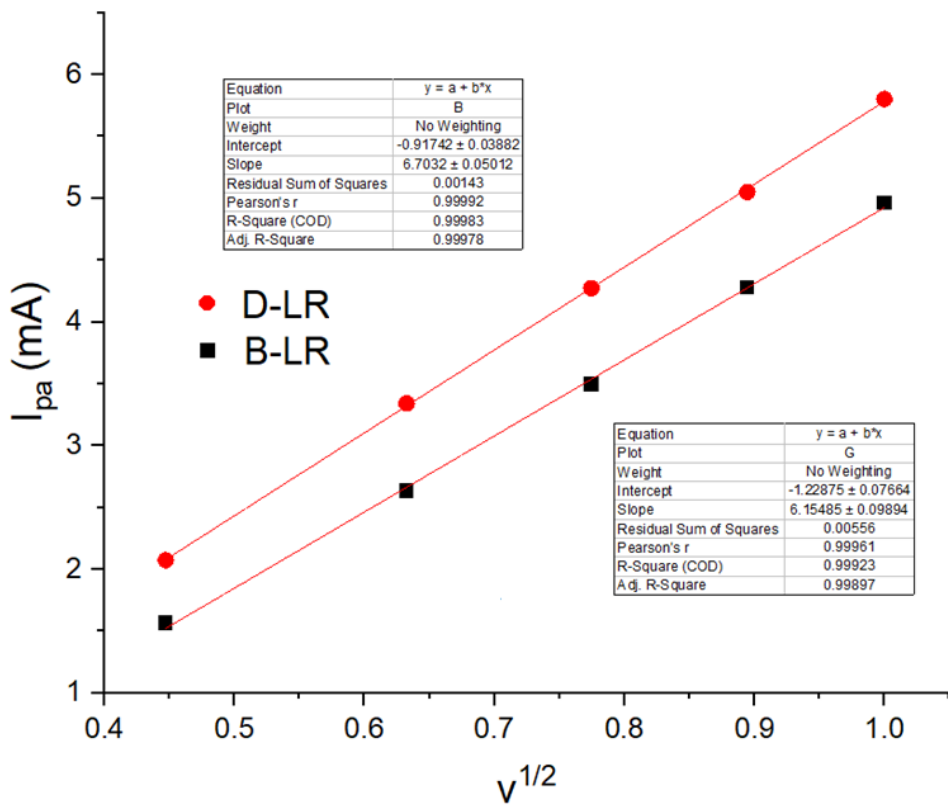| Equation	$y = a + b \cdot x$
Plot	G
Weight	No Weighting
Intercept	-1.22875 ± 0.07664
Slope	6.15485 ± 0.09894
Residual Sum of Squares	0.00556
Pearson's r	0.99961
R-Square (COD)	0.99923
Adj. R-Square	0.99897

● D-LR
■ B-LR

Figure S4. The Randles–Sevcik plots of L-RH and D-RH for total anodic charge vs scan rate

Figure S5. Visual inspection of cathode electrode after 250 cycles