Electronic supplementary information (ESI)

Nano-$(Cd_{1/3}Co_{1/3}Zn_{1/3})CO_3$: a new and high capacity anode material for Li-ion batteries

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Fig. S1-S7 and Table S1

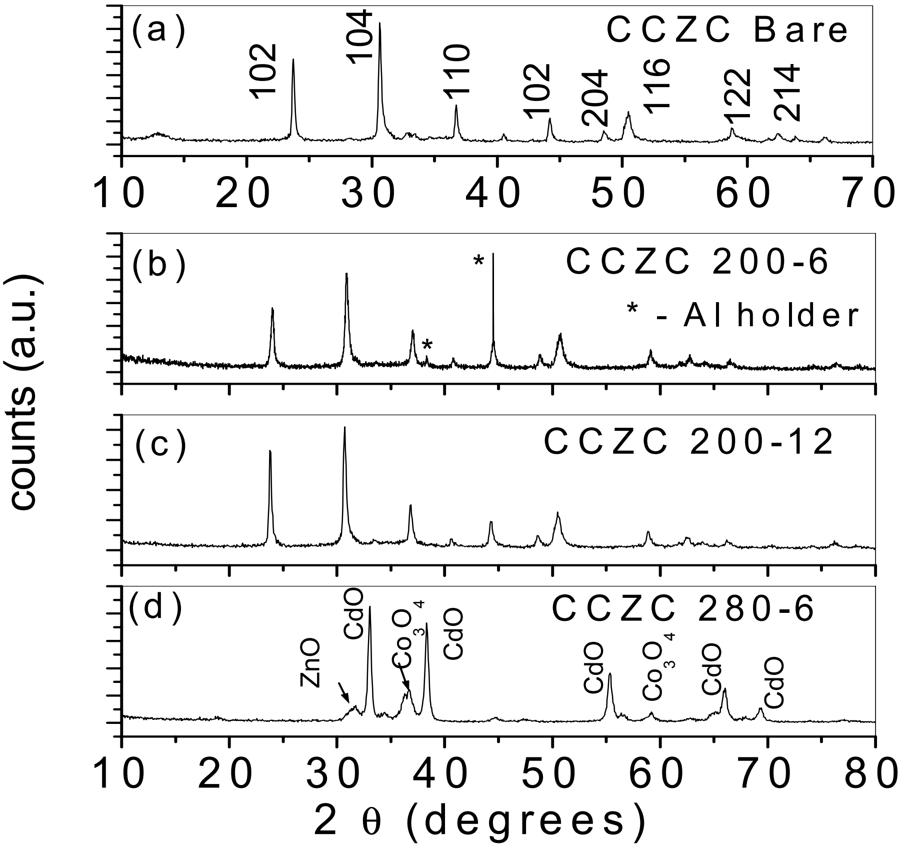


Fig. S1 XRD patterns of (a) bare $(Cd_{1/3}Co_{1/3}Zn_{1/3})CO_3$ (CCZC), (b) heat-treated CCZC at 200^{0}C for 6 h (CCZC 200-6), (c) heat-treated CCZC at 200°C for 12 h (CCZC 200-12) and (d) heat-treated CCZC at 280°C for 6 h (CCZC 280-6). Lines assigned to the metal oxides are indicated. Miller indices (hkl) of bare CCZC are shown. The peaks due to Al-sample holder in (b) are indicated. Cu-K_α radiation. As can be seen, the crystal structure is stable to the heat-treatment at 200°C. However, decomposition occurs up on heating CCZC to 280°C for 6 h, resulting in the formation of the metal oxides.

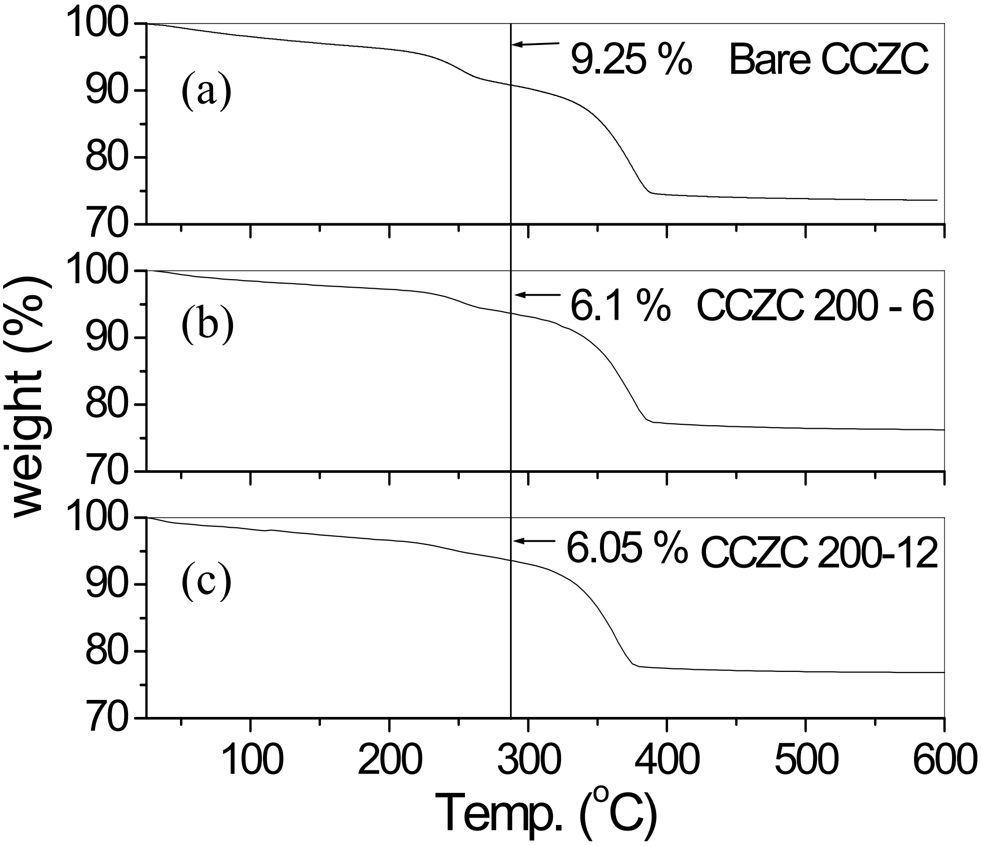
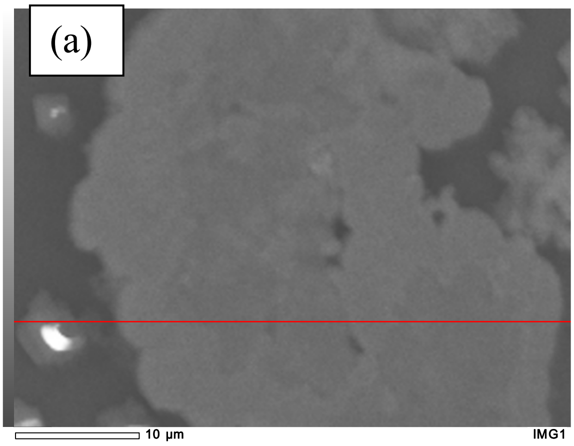


Fig. S2 Thermogravimetric analysis (TGA) curves at the heating rate of 5 °C min^{-1}, in nitrogen atmosphere. (a) Bare $(Cd_{1/3}Co_{1/3}Zn_{1/3})CO_3$ (CCZC), (b) heat-treated CCZC at 200°C for 6 h (CCZC 200-6) and (c) heat-treated CCZC at 200°C for 12 h (CCZC 200-12). Weight loss up to 280°C is 9.25% in (a) bare CCZC and ~ 6% in (b and c) heat-treated CCZCs.



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Resolution          : 512 x 384
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Instrument          : 6701F
Acc. Volt.          : 15 kV
Magnification       : x 2,700
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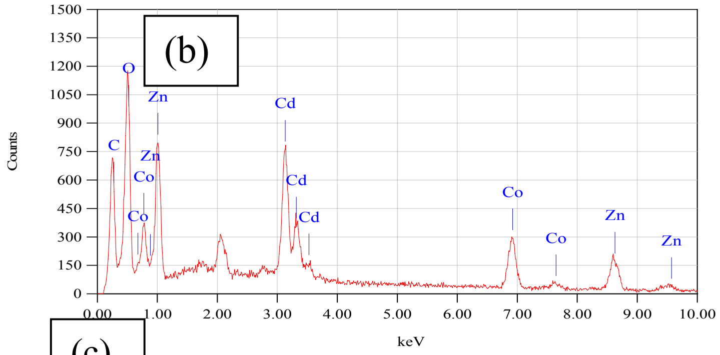

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Acquisition Parameter
Instrument     : 6701F
Acc. Voltage  : 15.0 kV
Probe Current: 2.56200 nA
PHA mode       : T3
Real Time      : 42.59 sec
Live Time      : 36.44 sec
Dead Time      : 12 %
Counting Rate: 2742 cps
Energy Range  :  0 - 20 keV
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(c)

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Thin Film Standardless  Standardless Quantitative Analysis
Fitting Coefficient : 0.3491
Element         (keV)   Mass%    Counts   Error%    Atom%
 C K            0.277   11.04   3151.36    0.00    37.50
 O K            0.525    7.93   5860.25    0.01    20.24
Co K            6.924   19.52   3892.49    0.03    13.51
Zn K            8.630   24.59   2638.33    0.06    15.35
Cd L   (Ref.)   3.133   36.92   7203.49    0.02    13.40
Total                  100.00                     100.00
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Fig. S3 (a) SEM picture of bare-$(Cd_{1/3}Co_{1/3}Zn_{1/3})CO_3$ (CCZC). Scale bar is 10 µm. The line indicates the selected part for EDAX analysis. (b) The EDAX spectrum. The peaks due to elements, Cd, Co, Zn, C and O are shown. (c) Quantitative analysis data, as atom % values are shown. The chemical formula, derived from the atom% values and normalized to cadmium content, is $(Cd_{0.33}Co_{0.33}Zn_{0.38})(CO_3)_{0.9}$. This matches very well with the chemical analysis data, except for the oxygen content. The reason for the discrepancy in the latter value is not clear at present.

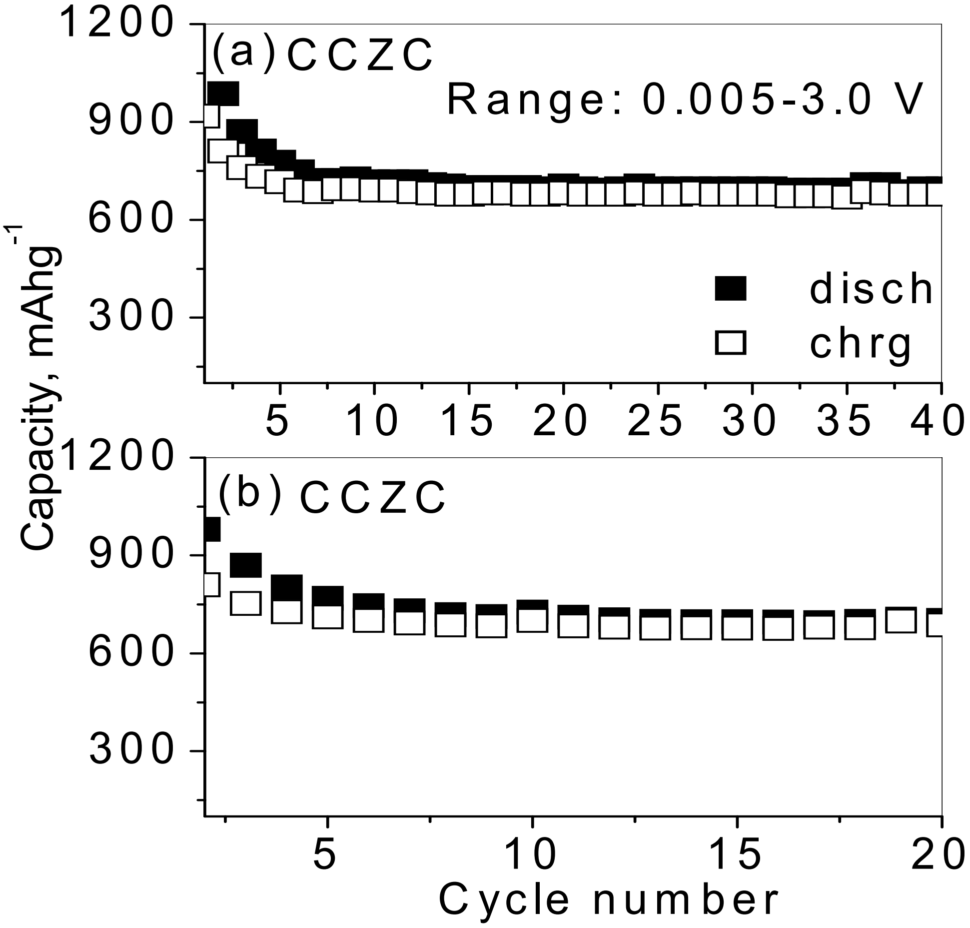

Fig. S4 Capacity vs. cycle number plots for the duplicate cells of bare-$(Cd_{1/3}Co_{1/3}Zn_{1/3})CO_3$ (CCZC) cycled in the voltage range of 0.005-3.0 V at 0.09 C (1C = 680 mAg^{-1}).(a) Up to 40 cycles and (b) up to 20 cycles. The plots overlap very well with the plot in Fig. 3c thereby showing excellent reproducibility of the data in CCZC-Li system.

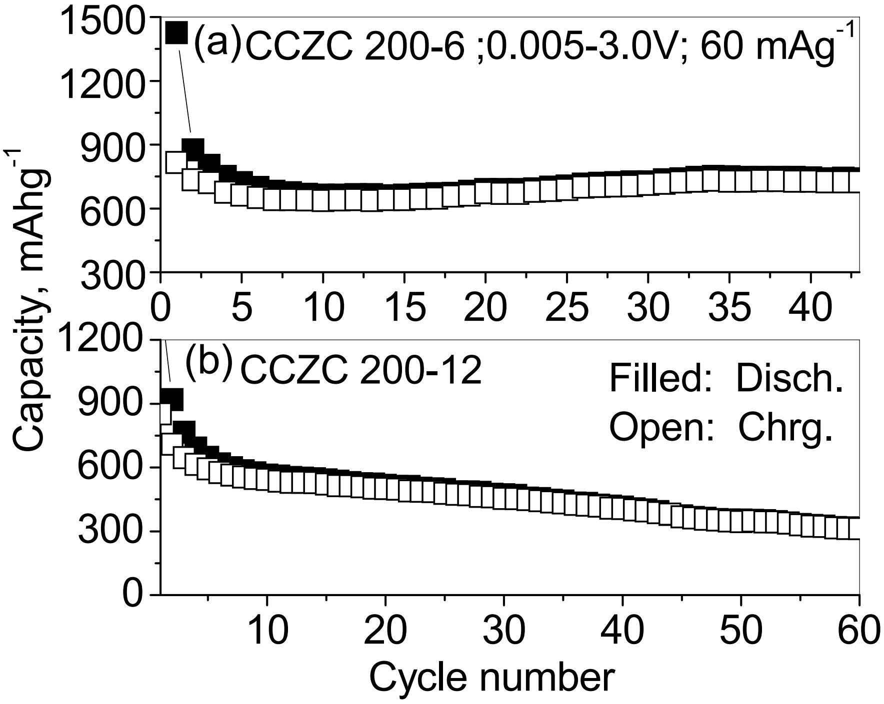

Fig. S5 Capacity vs. cycle number plot of 200°C-heat treated $(Cd_{1/3}Co_{1/3}Zn_{1/3})CO_3$ (CCZC) in the voltage range, 0.005-3.0V vs. Li at the current rate, 60 mAg^{-1} (0.09C). (a) CCZC 200-6 up to 45 cycles. As can be seen, the reversible capacity stabilizes to 720 (±10) mAhg^{-1} at the 45th cycle. (b) CCZC 200-12 up to 60 cycles. As can be seen, there is a continuous capacity-fading, at the rate of 5 mAhg^{-1} per cycle, in the range, 5-60 cycles. Filled and open symbols represent discharge and charge capacities, respectively.

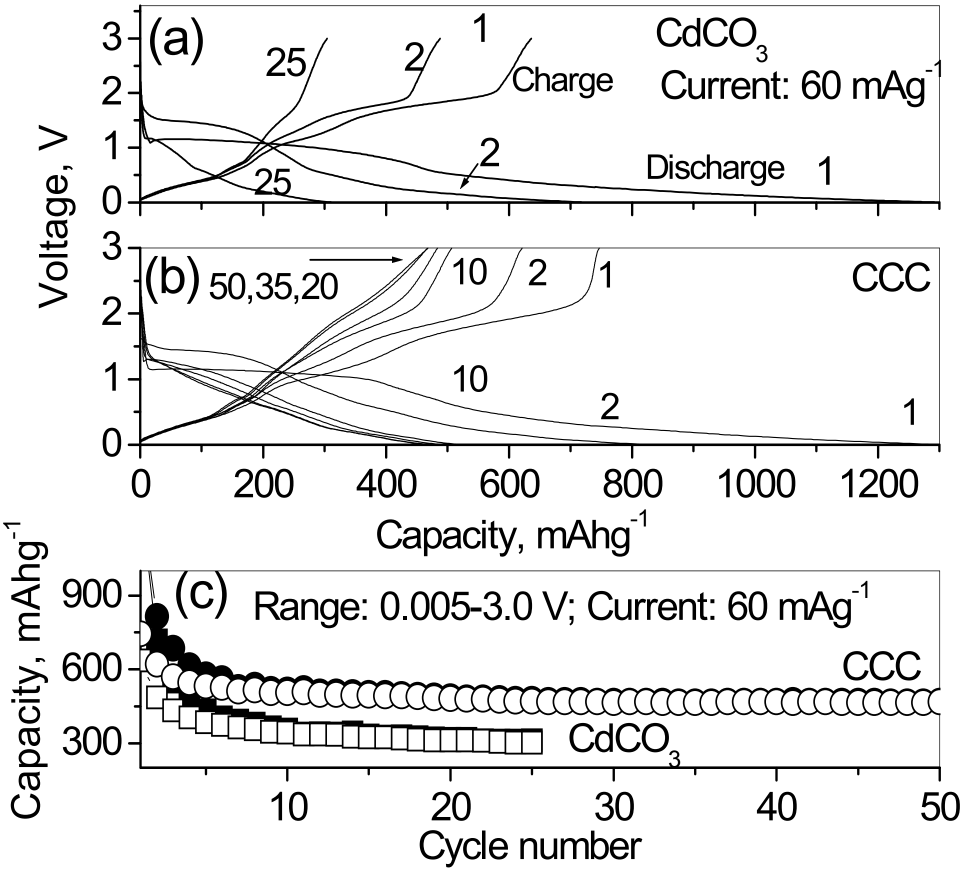

Fig. S6 The voltage vs. capacity profiles of (a) $CdCO_3$ and (b) $(Cd_{0.75}Co_{0.25})CO_3$ (CCC) in the voltage window, 0.005-3.0V vs. Li at the current rate of 60 mAg^{-1} at room temperature. Only selected cycles are shown for clarity. The numbers refer to the cycle number. (c) The capacity vs. cycle number plots. The capacity at the end of 25th cycle for $CdCO_3$ is 300 (±10) $mAhg^{-1}$ (1.9 moles of Li) whereas for CCC the value at the 50th cycle is 475(±10) $mAhg^{-1}$ (3.0 moles of Li). Thus, the presence of cobalt in the lattice has a beneficial effect on the Li-cyclability of $CdCO_3$. The filled and open symbols represent discharge and charge capacities, respectively.

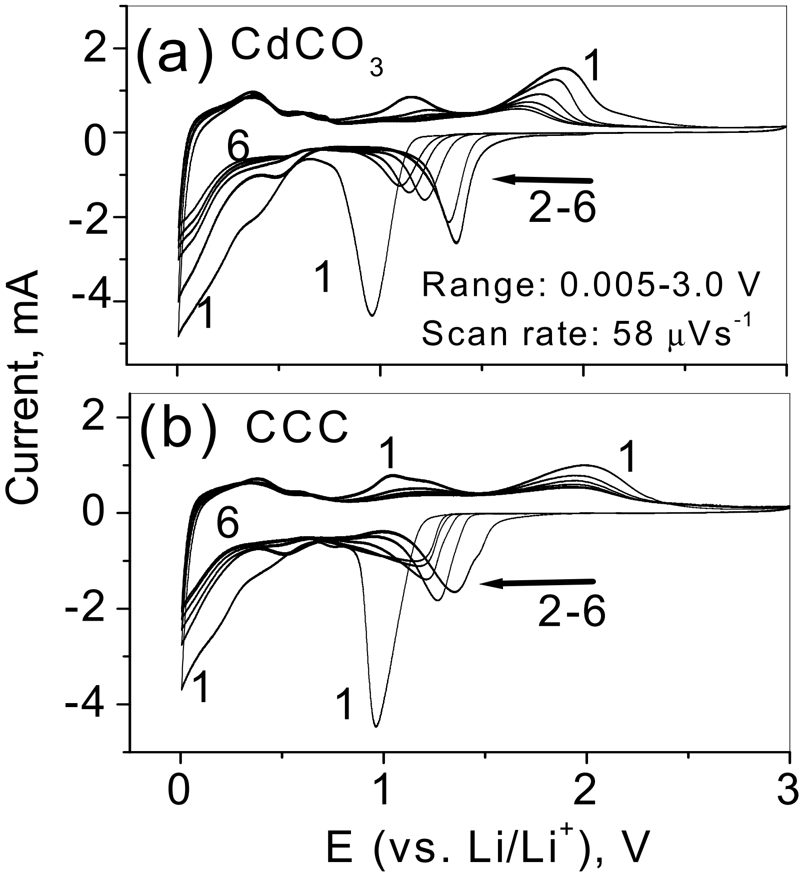

Fig. S7 Cyclic voltammograms (CVs) in the potential window, 0.005 -3.0 V vs. Li at the slow scan rate of 58 μVs^{-1}. Li metal was the counter and reference electrode: (a) $CdCO_3$ and (b) $(Cd_{0.75}Co_{0.25})CO_3$ (CCC). The numbers indicate the cycle number. As can be seen, the CVs of $CdCO_3$ and CCC bear very good qualitative, and to some extent quantitative resemblance to the CVs of CCZC (Fig. 6).

Table S1: Change in Gibbs free energy of formation (ΔG_f) as per the forward reaction of Eqns. (5) or (1). The electromotive force (E, Volts) values are calculated using Nernst's equation ($\Delta G = - n.E.F$) where F is the Faraday constant and n = 2, the number of electrons involved in the reactions of Eqn. (1).

Reaction	ΔG_f (reactant) (MCO_3)[a] (kJ mol^{-1})	ΔG_f (product) (kJ mol^{-1})		ΔG (kJ mol^{-1})	emf (E) value (Volt)
		MO	CO_2		
$MCO_3 \rightarrow MO + CO_2$ --- (5)	-671 (M = Cd) -731 (M = Zn) -657 (M = Co) -689 (M=1/3(Cd+Zn+Co))[b]	-229 (CdO) -307 (ZnO) -214 (CoO) -253 (1/3(Cd+Zn+Co)O)[b]	-394	+ 48 + 30 + 49 + 42	- - - -
$MCO_3 + Li \leftrightarrow M + Li_2CO_3$ --- (1)	---	-1132 (Li_2CO_3)	---	-461 -401 -475 -443	2.38 2.07 2.46 2.30

[a] By convention, ΔG_f of elements (Li and M) in their standard states is zero.

[b] Calculated from the respective values of MX (X= CO_3 or O), assuming solid solution formation (ideal mixing), according to the Eqn.[35]

$$\Delta G_f (MX) = 1/3\ \Delta G_f (CdX + CoX + ZnX) + RT (\ln (1/3))$$

where R, is gas constant and T = 298 K.

As is clear, Eqn. (5) is not spontaneous, whereas Eqn. (1) is spontaneous. See text.