Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary data

High Rate Capabilities Induced by Multi-phasic Nanodomains in Iron-substituted Calcium Cobaltite Electrodes

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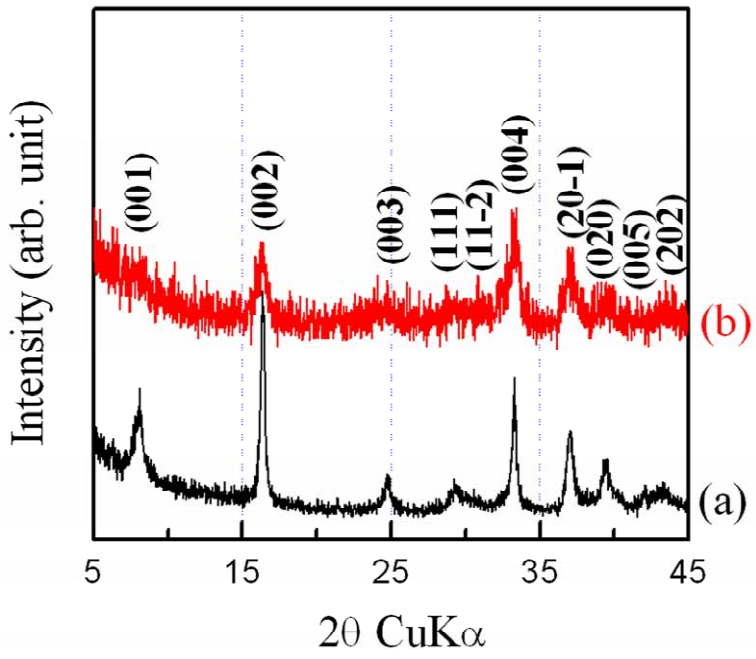

Figure S1. XRD patterns of the (a) $Ca_3Co_4O_9$ and (b) $Ca_3Co_3FeO_9$ nanoplates.

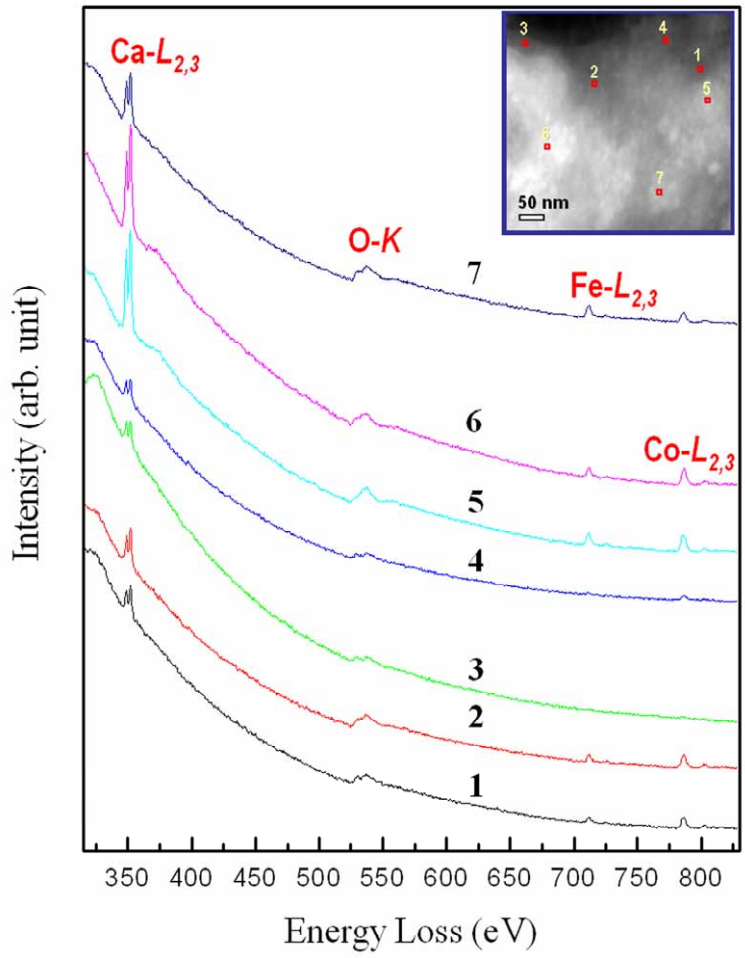

Figure S2. EELS spectra acquired at each position depicted in the inset HAADF image of fully lithiated $Ca_3Co_3FeO_9$.

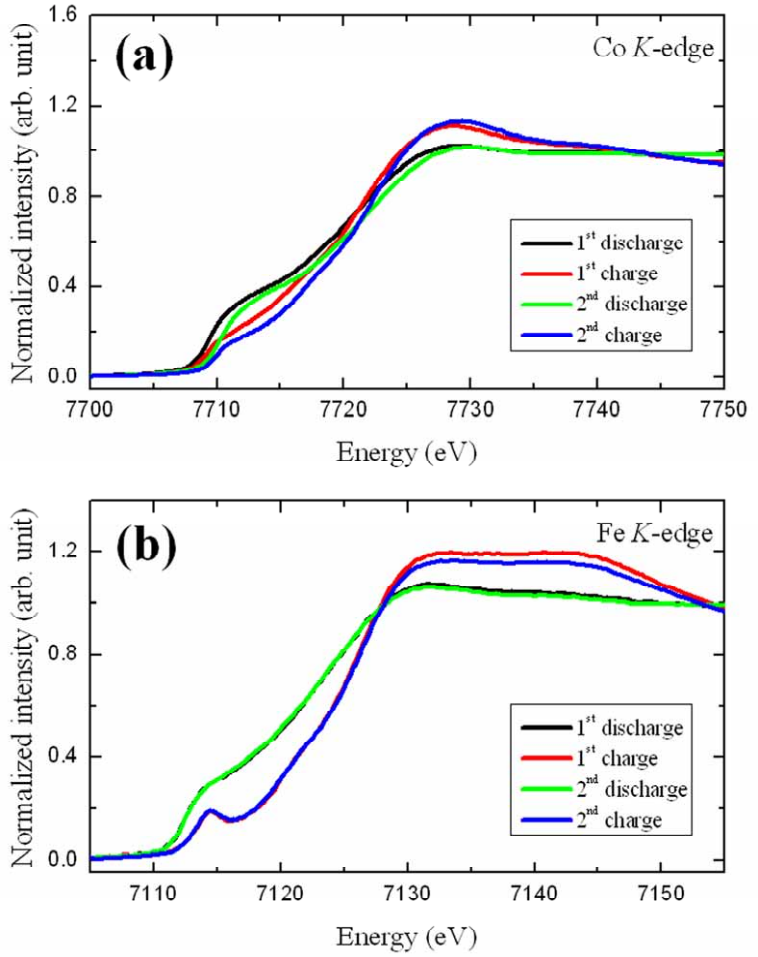

Figure S3. Normalized (a) Co and (b) Fe K-edge XANES spectra for the $Ca_3Co_3FeO_9$ at the charged and discharged states taken after first 2 cycles.

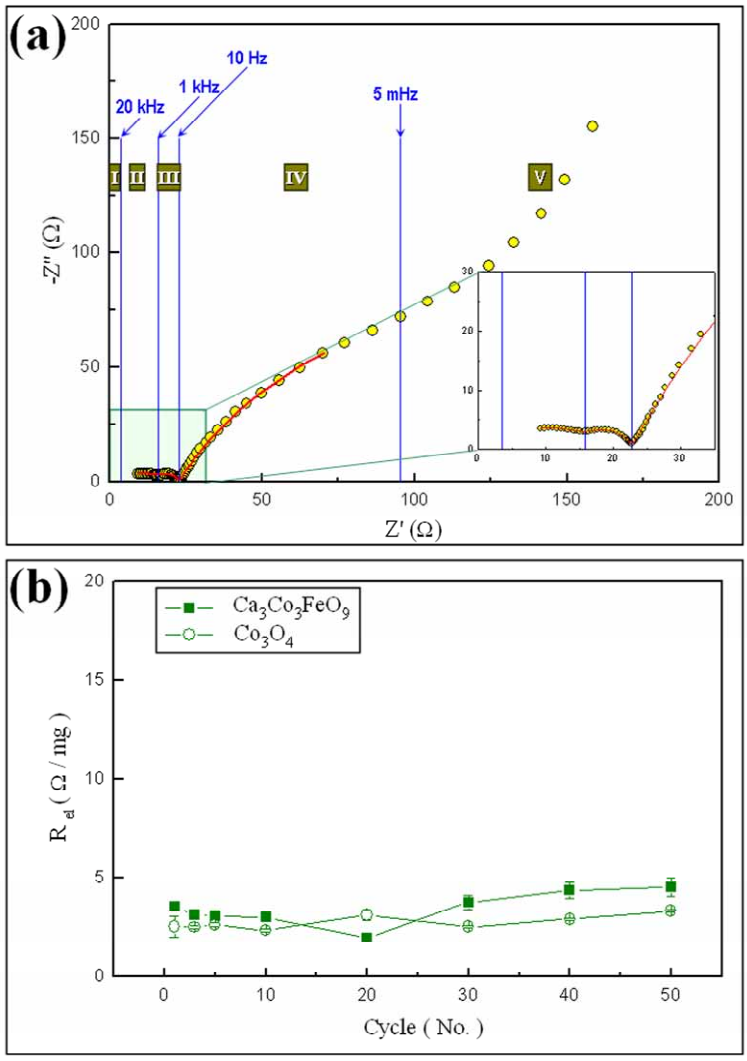

Figure S4. (a) Impedance spectrum of the $Ca_3Co_3FeO_9$/Li half cell at the discharged state taken after 20 cycles at a C/5 rate. The inset shows a magnified view of high frequency region. (b) Variation of the R_{el} versus the cycle number for the $Ca_3Co_3FeO_9$ and Co_3O_4 cycled at a rate of 1C.

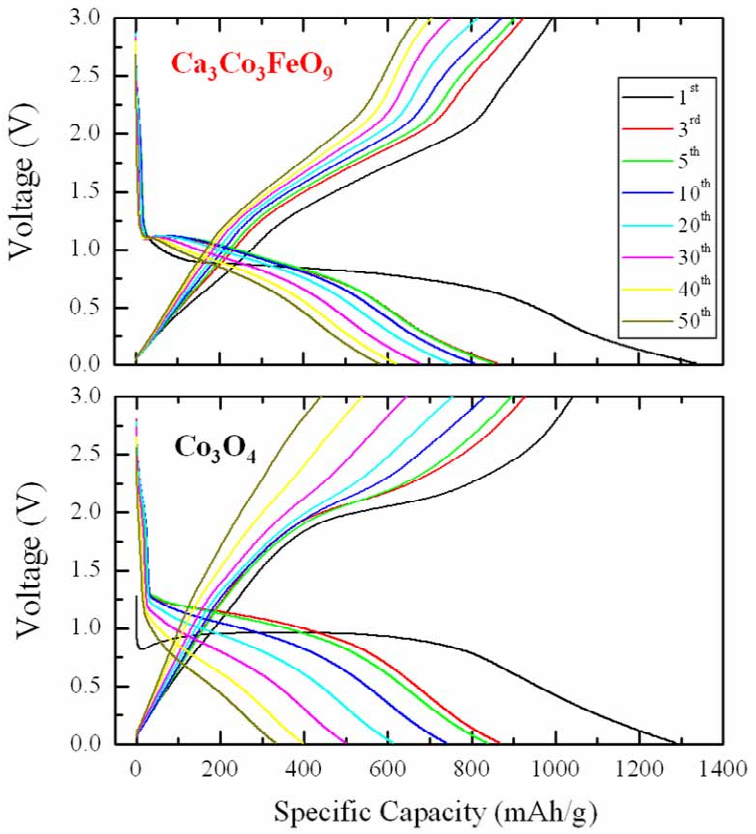

Figure S5. Charging-discharging curves for the $Ca_3Co_3FeO_9$/Li and Co_3O_4/Li half cells cycled between 3.0 and 0.01 V at a rate of 1C during the impedance measurements.

Table S1. Each volume of all components for the calculation of volume change in $Ca_3Co_3FeO_9$ electrodes.

	ρ, Density (g/cm^3)	**MW, Molecular weight (g/mol)**	**V, Molar volume (cm^3/mol)**
$Ca_3Co_3FeO_9$	4.68	496.869	106.1686
Co	8.789	58.93	6.7053
Fe	7.875	55.845	7.0914
Li_2O	2.026	29.881	14.7488
CaO	3.346	56.077	16.7594
CoO	6.433	74.93	11.6478
Fe_3O_4	5.202	231.531	44.5081

$V = MW/\rho$

(1) Volume change during 1st discharge based on reaction, **$Ca_3Co_3FeO_9 + 12Li \rightarrow 3Co + Fe + 6Li_2O + 3CaO$**

$\Delta V\ (\%) = [3V(Co) + V(Fe) + 6V(Li_2O) + 3V(CaO) - V(Ca_3Co_3FeO_9)] / V(Ca_3Co_3FeO_9) \times 100 =$ **56.32 %**

(2) Volume change during 1st charge and subsequent cycles based on reaction, **$3Co + Fe + 6Li_2O + 3CaO \leftrightarrow 3(CoO + 2Li) + 1/3(Fe_3O_4 + 8Li) + 5/3Li_2O + 3CaO$**

$\Delta V\ (\%) = [3V(Co) + V(Fe) + 6V(Li_2O) + 3V(CaO) - 3V(CoO) - 1/3V(Fe_3O_4) - 5/3V(Li_2O) - 3V(CaO)] / [3V(Co) + V(Fe) + 6V(Li_2O) + 3V(CaO)] \times 100 =$ **24.91%**