Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Hierarchically Nanoporous $La_{1.7}Ca_{0.3}CuO_{4-\delta}$ and $La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$ ($0.25 \leq x \leq 0.75$) as Potential Cathode Materials for IT-SOFCs

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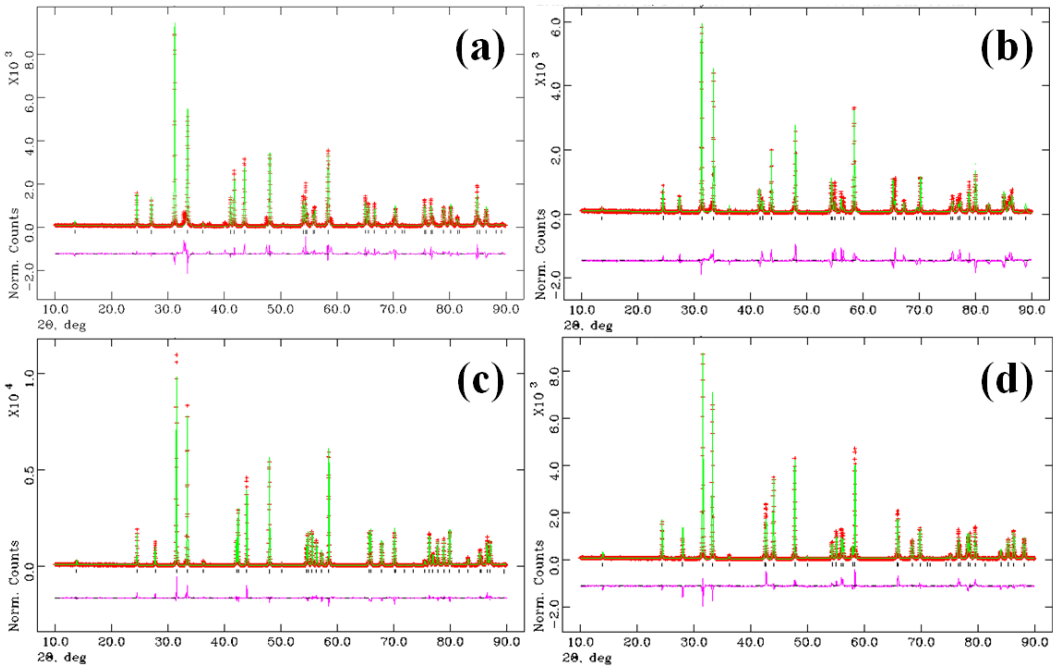

Figure S1. Observed (points) and calculated (full curve) XRD patterns using I4/mmm model for $La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$: (a) $La_{1.7}Ca_{0.3}CuO_{4-\delta}$, (b) $La_{1.7}Ca_{0.3}Ni_{0.25}Cu_{0.75}O_{4-\delta}$, (c) $La_{1.7}Ca_{0.3}Ni_{0.5}Cu_{0.5}O_{4-\delta}$, (d) $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$.

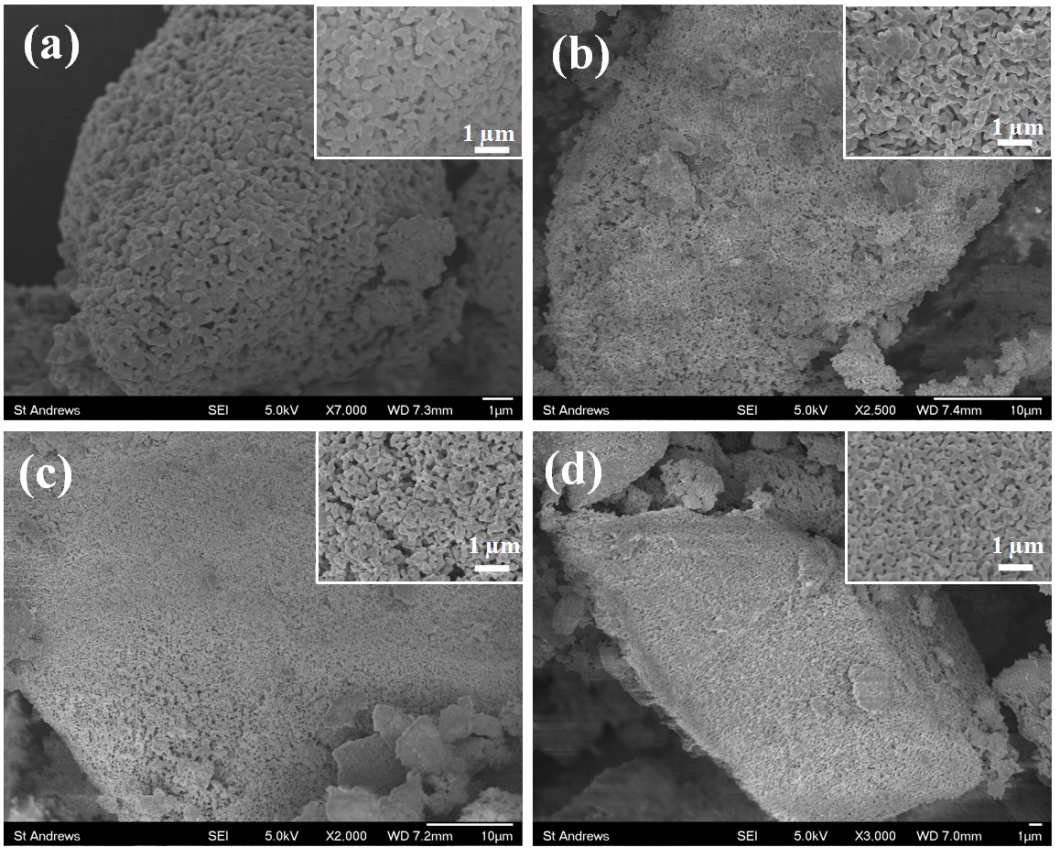

Figure S2. FESEM images of $La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$ after calcination at 900 °C for 2 h: (a) $La_{1.7}Ca_{0.3}CuO_{4-\delta}$, (b) $La_{1.7}Ca_{0.3}Ni_{0.25}Cu_{0.75}O_{4-\delta}$, (c) $La_{1.7}Ca_{0.3}Ni_{0.5}Cu_{0.5}O_{4-\delta}$, (d) $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$. Inset are their SEM images with higher magnification.

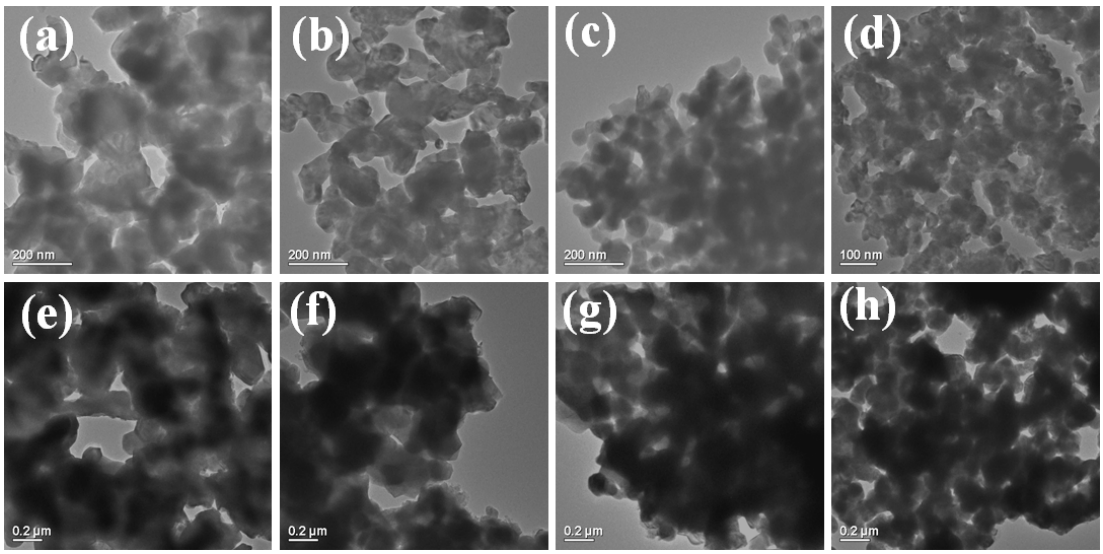

Figure S3. TEM images of $La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$ after calcination at 750 °C (a-d) and 900 °C (e-h) for 2 h: (a, e) $La_{1.7}Ca_{0.3}CuO_{4-\delta}$, (b, f) $La_{1.7}Ca_{0.3}Ni_{0.25}Cu_{0.75}O_{4-\delta}$, (c, g) $La_{1.7}Ca_{0.3}Ni_{0.5}Cu_{0.5}O_{4-\delta}$, (d, h) $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$.

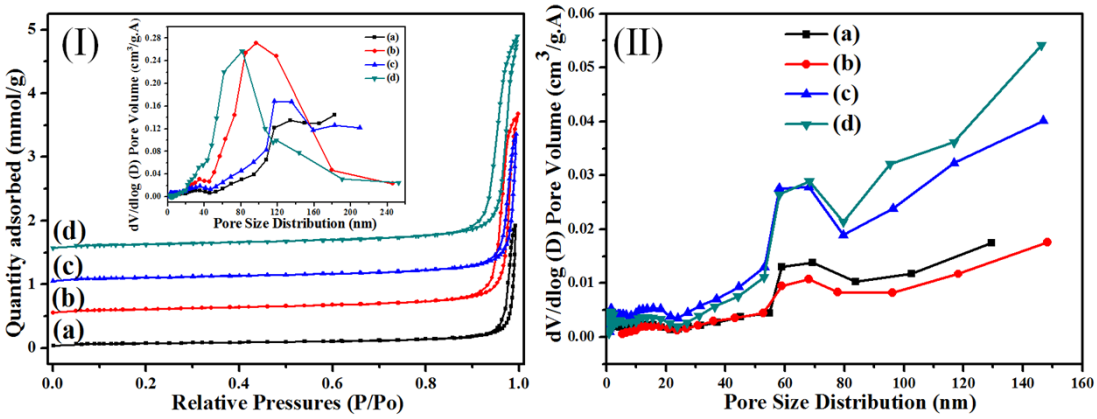

Figure S4. (I) N_2 adsorption/desorption isothermal curves of $La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$ samples after calcination at 750 °C and (II) pore size distribution curves after calcination at 900 °C for 2 h: (a) $La_{1.7}Ca_{0.3}CuO_{4-\delta}$, (b) $La_{1.7}Ca_{0.3}Ni_{0.25}Cu_{0.75}O_{4-\delta}$, (c) $La_{1.7}Ca_{0.3}Ni_{0.5}Cu_{0.5}O_{4-\delta}$, (d) $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$. Inset of (I) is the pore size distribution curves for $La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$ obtained at 750 °C for 2 h.

Table S1. Textural properties of perovskites obtained at 750 °C and 900 °C for 2 h

Temperature	Sample	BET ($m^2\ g^{-1}$)	Pore Volume ($cm^3\ g^{-1}$)	Average pore size (nm)
750 °C	$La_{1.7}Ca_{0.3}CuO_{4-\delta}$	5.49	0.050	49.37
	$La_{1.7}Ca_{0.3}Ni_{0.25}Cu_{0.75}O_{4-\delta}$	8.65	0.105	55.92
	$La_{1.7}Ca_{0.3}Ni_{0.5}Cu_{0.5}O_{4-\delta}$	8.32	0.071	40.41
	$La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$	10.07	0.113	53.20
900 °C	$La_{1.7}Ca_{0.3}CuO_{4-\delta}$	2.23	0.010	7.85
	$La_{1.7}Ca_{0.3}Ni_{0.25}Cu_{0.75}O_{4-\delta}$	1.23	0.008	45.35
	$La_{1.7}Ca_{0.3}Ni_{0.5}Cu_{0.5}O_{4-\delta}$	4.42	0.024	12.11
	$La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$	3.06	0.024	13.92

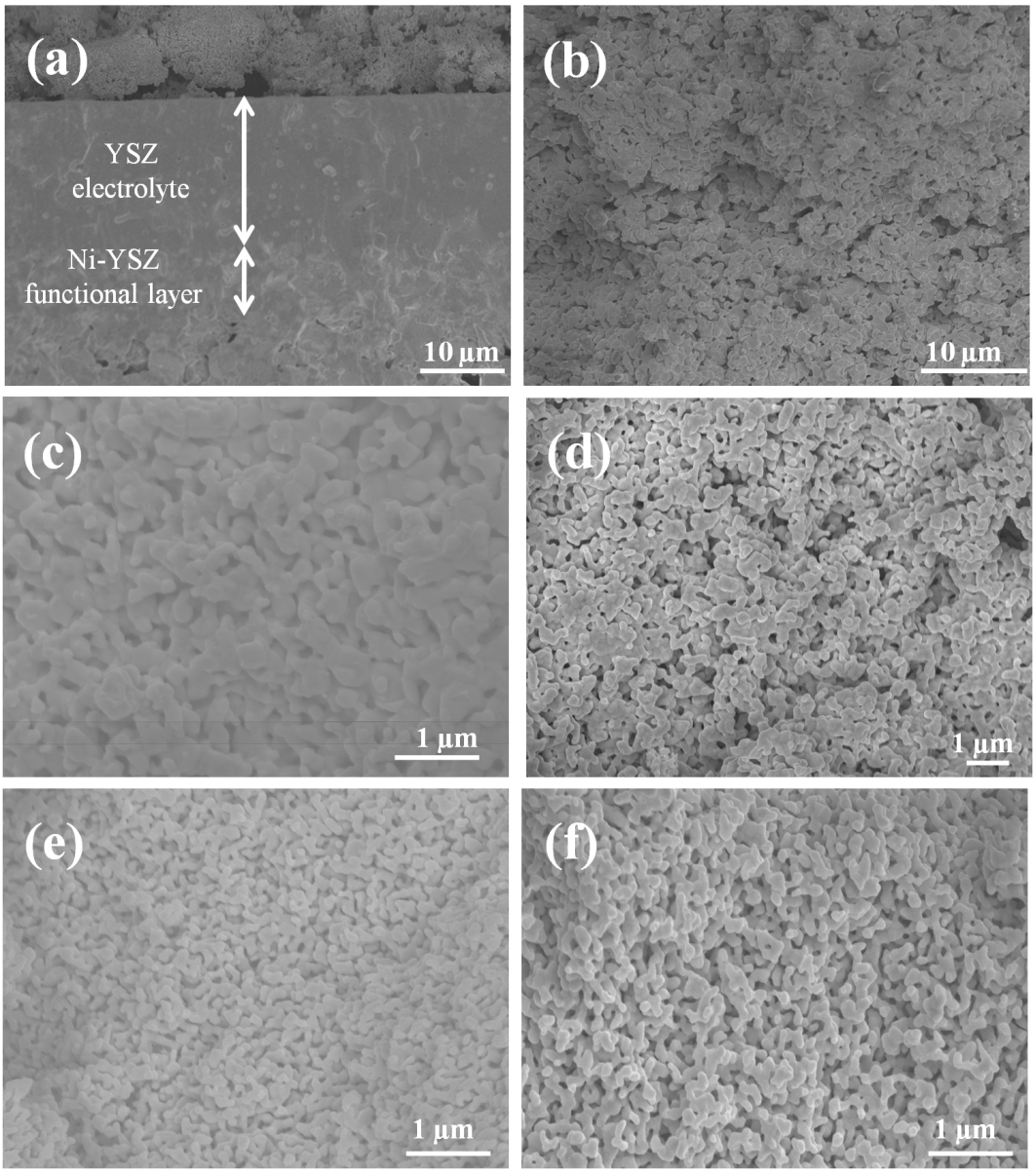

Figure S5. SEM images of Ni-YSZ|YSZ|$La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$ single cell cross section: (a) $La_{1.7}Ca_{0.3}CuO_{4-\delta}$-YSZ, (b) Ni-YSZ anode, (c) $La_{1.7}Ca_{0.3}CuO_{4-\delta}$, (d) $La_{1.7}Ca_{0.3}Ni_{0.25}Cu_{0.75}O_{4-\delta}$, (e) $La_{1.7}Ca_{0.3}Ni_{0.5}Cu_{0.5}O_{4-\delta}$, (f) $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$.

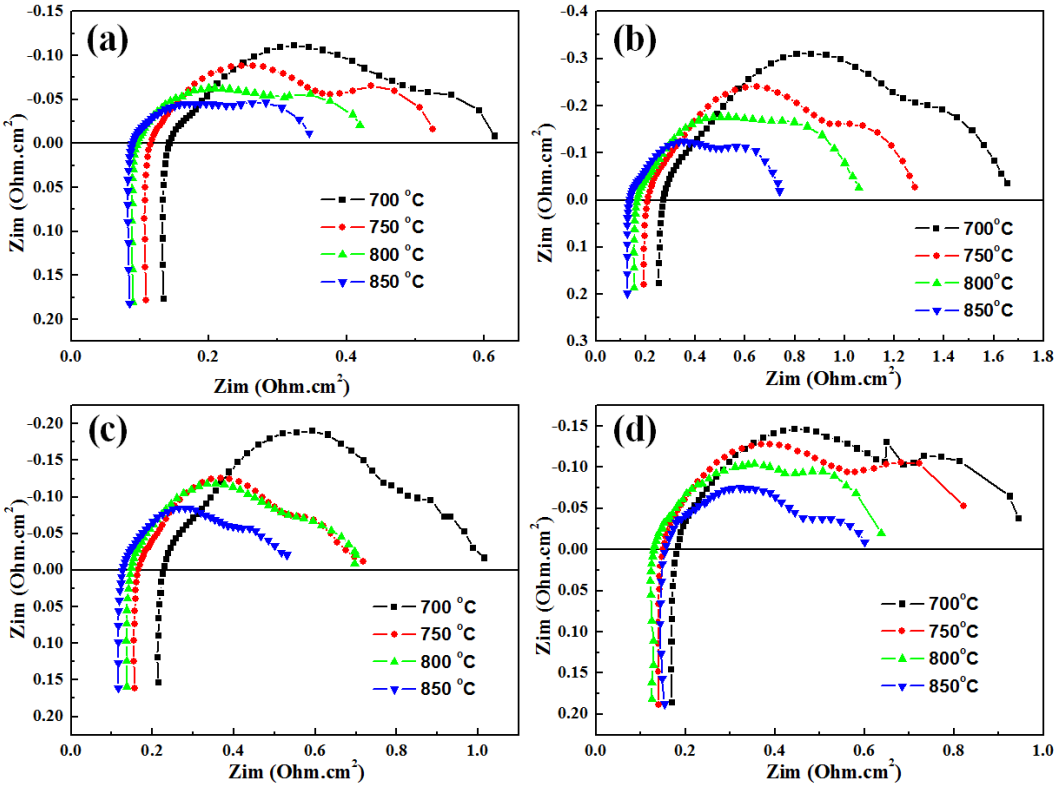

Figure S6. Impedance spectra of single cell Ni-YSZ|YSZ|$La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$: (a) $La_{1.7}Ca_{0.3}CuO_{4-\delta}$; (b) $La_{1.7}Ca_{0.3}Ni_{0.25}Cu_{0.75}O_{4-\delta}$; (c) $La_{1.7}Ca_{0.3}Ni_{0.5}Cu_{0.5}O_{4-\delta}$; (d) $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$.

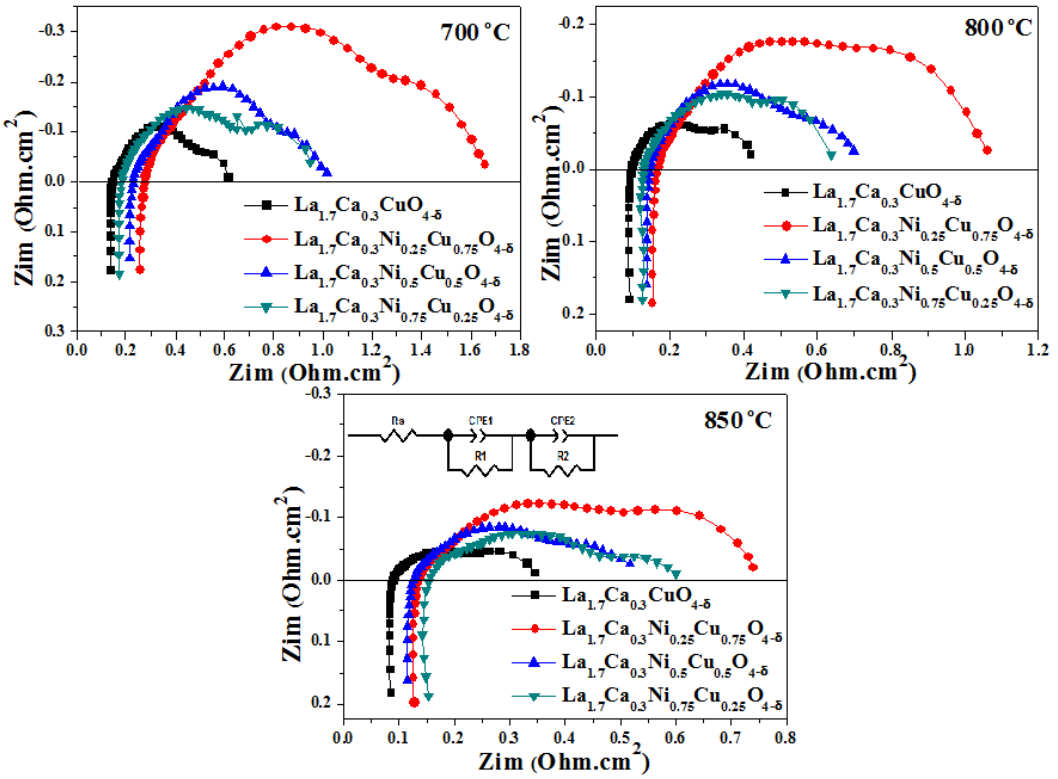

Figure S7. Impedance spectra of single cell Ni-YSZ|YSZ|$La_{1.7}Ca_{0.3}Ni_xCu_{1-x}O_{4-\delta}$ with different cathode materials at operating temperatures.

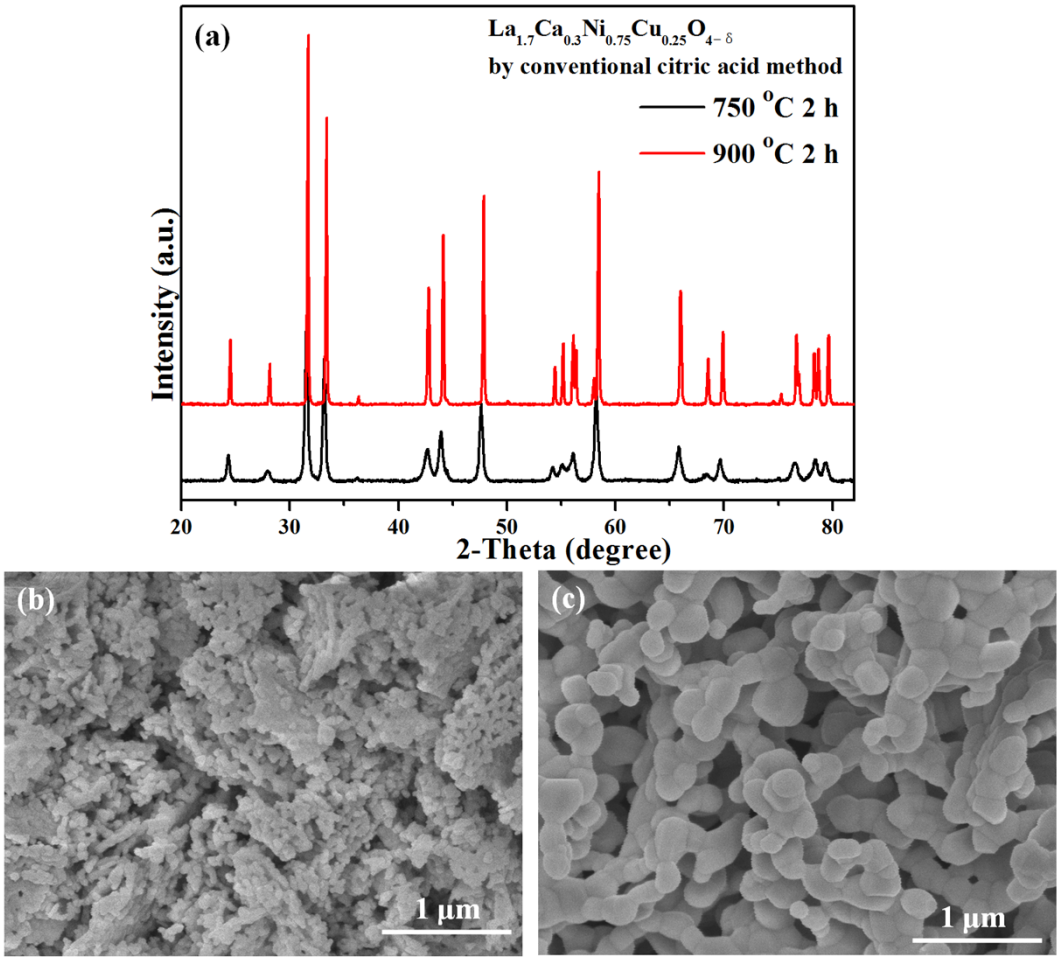

Figure S8. XRD patterns (a) and SEM images of $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$ by conventional citric acid method after calcination at 750 °C (b) and 900 °C (c) for 2 h.

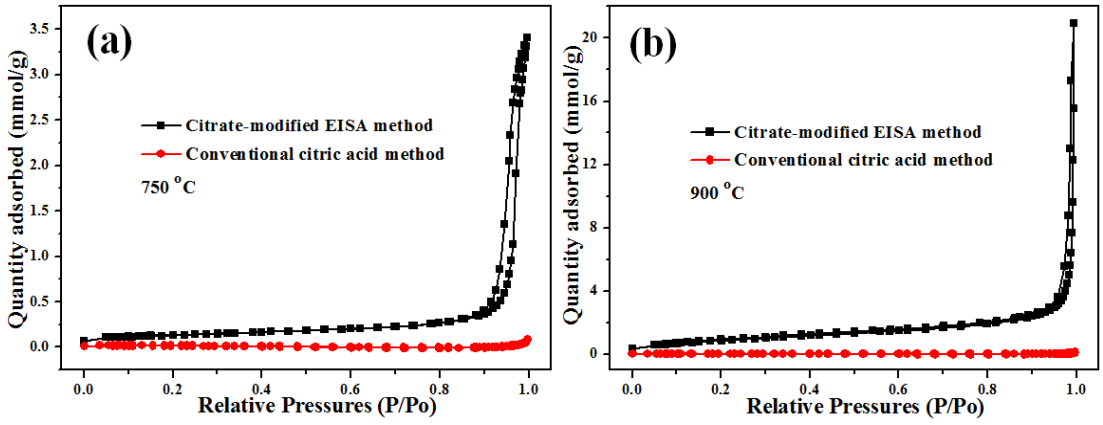

Figure S9. N_2 adsorption/desorption curves of $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$ after calcination at different temperatures for 2 h: (a) 750 °C, (b) 900 °C. The BET surface areas for $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$ using conventional citric acid method after calcination at 750 and 900 °C for 2 h are 0.72 and 0.25 m^2/g, respectively. The pore volumes for $La_{1.7}Ca_{0.3}Ni_{0.75}Cu_{0.25}O_{4-\delta}$ using conventional citric acid method after calcination at 750 and 900 °C for 2 h are both about 0.002 cm^3/g.