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Electronic Supplementary Information

Thermally Driven In Situ Exsolution of Ni Nanoparticles from (Ni, Gd)CeO_2 for High Performance Solid Oxide Fuel Cells

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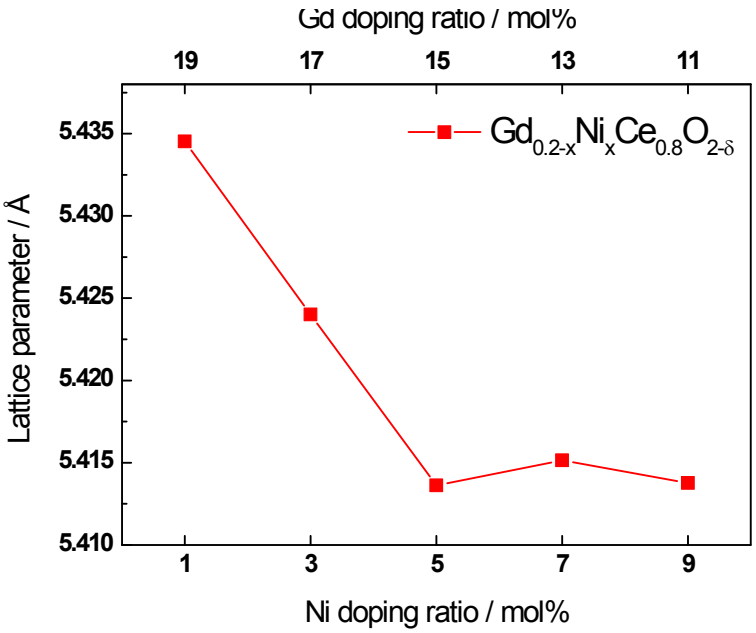

Fig. S1 Calculated lattice parameter of GNDC*x* as a function of Ni doping ratio (*x* mol%).

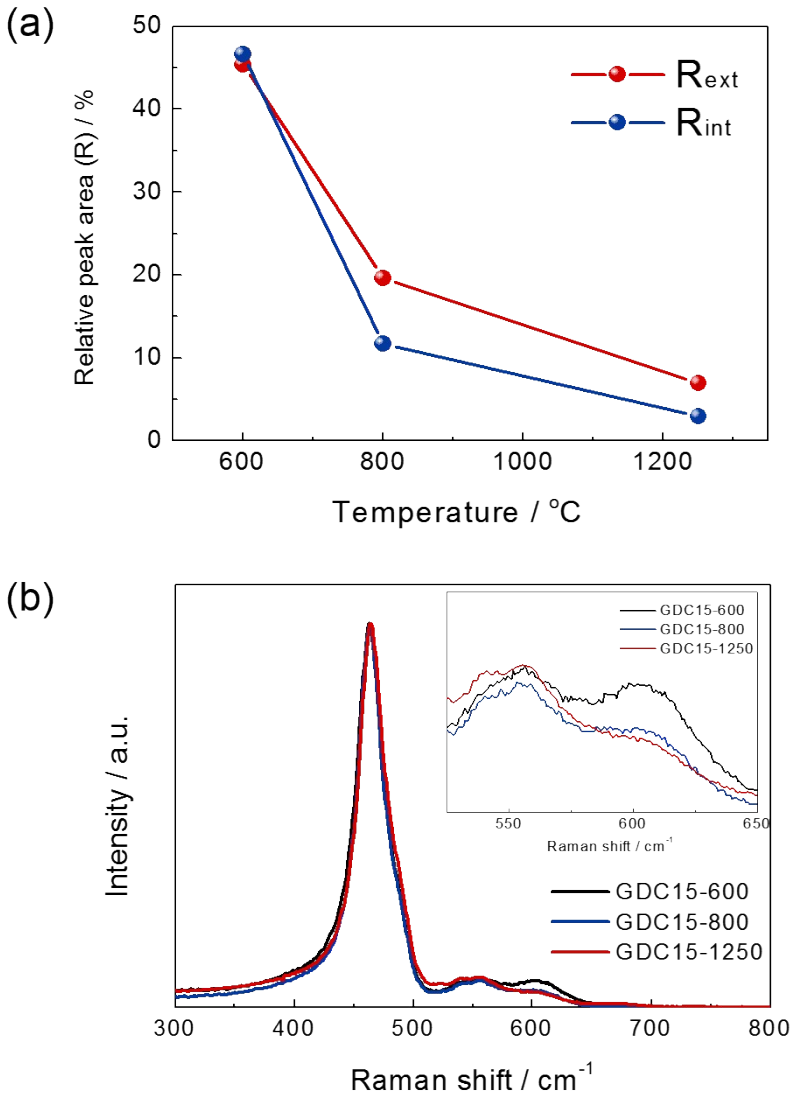

Fig. S2 (a) Relative peak area of the deconvoluted non-degenerate mode with respect to F_{2g} peak area obtained from GNDC5 as a function of annealing temperature. R_{ext} (= A_{ext}/A_{F2g}) and R_{int} (= A_{int}/A_{F2g}) correspond to the relative amount of extrinsic and intrinsic oxygen vacancies, respectively. (b) Raman spectra of GDC15 powder calcinated at 600 °C and annealed at 800 °C and 1250 °C. Only the intrinsic vacancy peak attenuated after annealing while the extrinsic vacancy peak remains almost unchanged (inset).

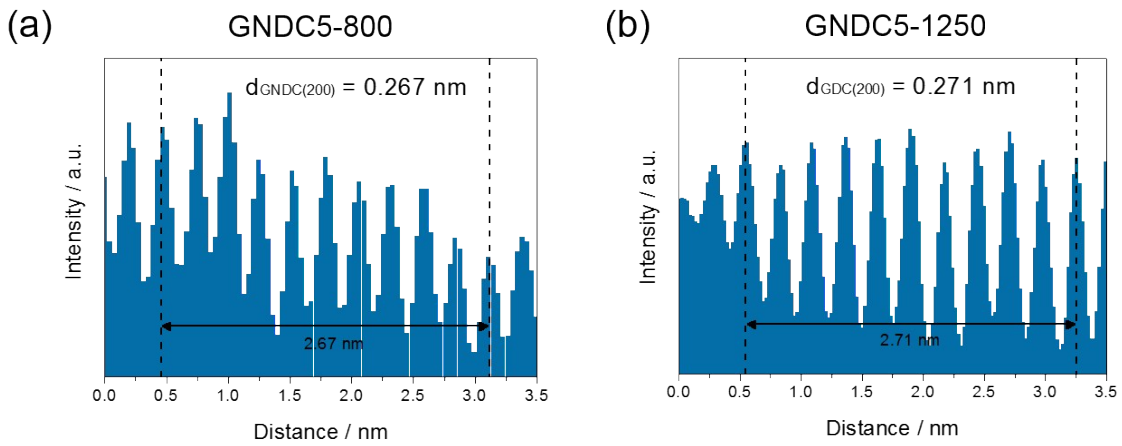

Fig. S3 Scattering intensities of lattice fringe obtained from HR-TEM images (Figure 3). Lattice spacing of (a) GNDC (200) planes from GNDC5-800 and (b) GDC (200) planes from GNDC5-1250. All lattice spacings are obtained by averaging ten intervals of the intensity peaks.

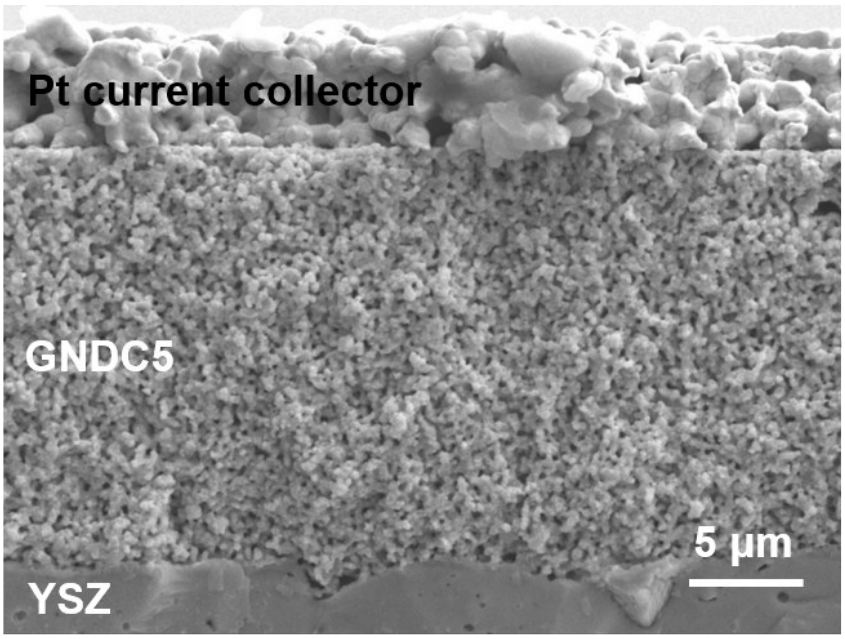

Fig. S4 Cross-sectional SEM image of GNDC5 symmetrical cell after EIS measurement confirming the electrode thickness (~20 µm).

Table S1. Comparison of R_p of different powder-processed Ni-ceria electrodes.

#	Electrode	Fabrication process	R_p @ temperature	Cell type	Electrode thickness
This study	GNDC	GNDC powder screen printing	1.04 Ω cm^2 @ 650 ^{o}C	symmetric	~20 µm
This study	Ni-GDC	NiO-GDC powder screen printing	1.38 Ω cm^2 @ 650 ^{o}C	symmetric	~20 µm
[S1]	Ni-GDC	GDC powder spray coating / Ni impregnation	1.13 Ω cm^2 @ 850 ^{o}C	symmetric	10-20 µm
[S2]	Ni/Ag-GDC	GDC powder screen printing / Ag electroless deposition / Ni electrodeposition	1.59 Ω cm^2 @ 650 ^{o}C	symmetric	~8 µm
[S3]	Ni-GDC	NiO powder slurry painting / Gd, Ce impregnation	1.5 Ω cm^2 @ 700 ^{o}C	3-electrode	20-38 µm
[S4]	Ni-GDC	NiO-GDC powder screen printing	1.22 Ω cm^2 @ 650 ^{o}C	3-electrode	20-40 µm
[S5]*	Ni-SDC	NiO-GDC powder spin coating	~1 Ω cm^2 @ 650 ^{o}C	3-electrode	~10 µm
[S6]	Pd/Ni-GDC	NiO-GDC powder slurry painting / Pd impregnation	1.66 Ω cm^2 @ 650 ^{o}C	3-electrode	~30 µm

* R_p at 650 ^{o}C was estimated from the given Arrhenius plot

[1] *Journal of The Electrochemical Society*, **2002**, *149*, A1466-A1472

[2] *International Journal of Hydrogen Energy*, **2016**, *41*, 9627-9637

[3] *Electrochemical and Solid-State Letters*, **2004**, *7*, A282-A285

[4] *Ceramics International*, **2014**, *40*, 13105–13113

[5] *Journal of Membrane Science*, **2009**, *334*, 138–147

[6] *Journal of The Electrochemical Society*, **2009**, *156*, B1022-B1029

Table S2. Resistance and constant phase element (CPE) values obtained from deconvolution of EIS data.

	R_s (Ω cm^2)	R_{HF} (Ω cm^2)	CPE_{HF} (F cm^{-2})	R_{LF} (Ω cm^2)	CPE_{LF} (F cm^{-2})
GNDC5	4.97	0.6475*	0.3721	1.46*	0.4979
Ni-GDC composite	4.69	0.9014*	0.1996	1.79*	0.0424

* It should be noted that one half of fitted value corresponds to polarization of one electrode.

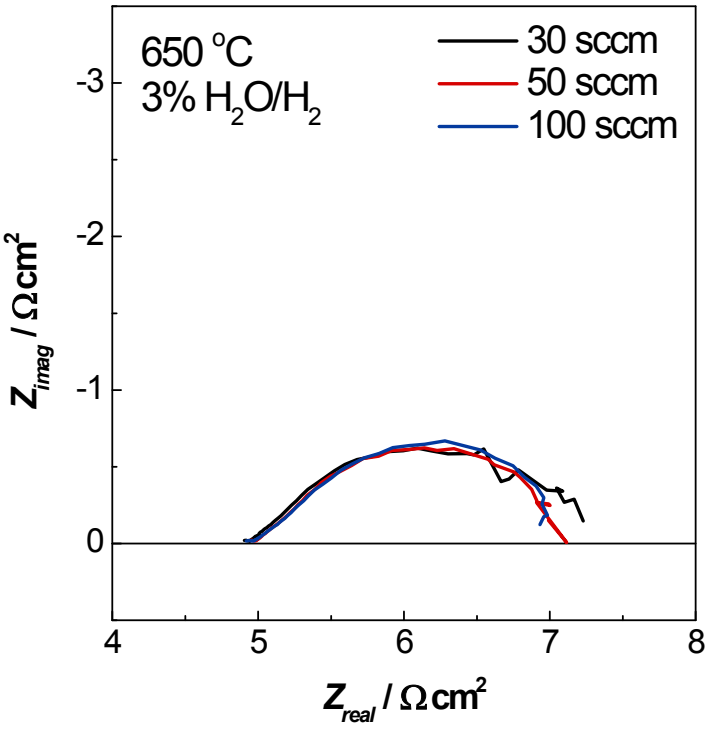

Fig. S5 Nyquist plot of GNDC5 electrode as a function of gas flow rate. Both R_s and R_p are almost identical regardless of gas flow rate, indicating that gas diffusion limit is negligible.

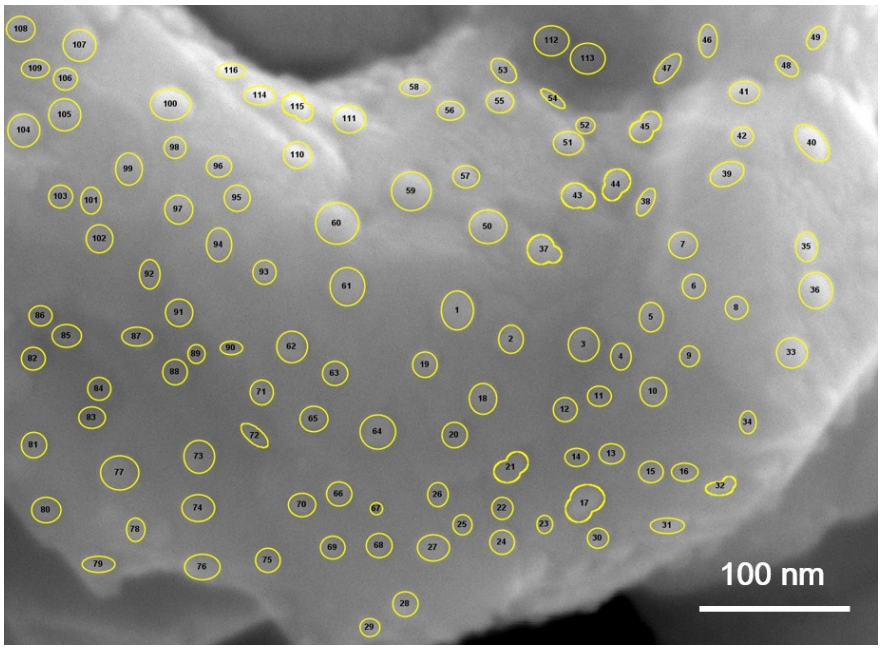

Fig. S6 SEM image analysis of GNDC5 electrode (Figure 5c) to estimate TPB density induced by Ni nanocatalyst. Total perimeter of Ni nanocatalyst (yellow circles) measured using ImageJ software was 6.683 µm. The calculated TPB density was ~ 2448 m/cm^2 or ~ 2.4 x 10^7 m/cm^3 assuming an electrode depth of 1 µm.

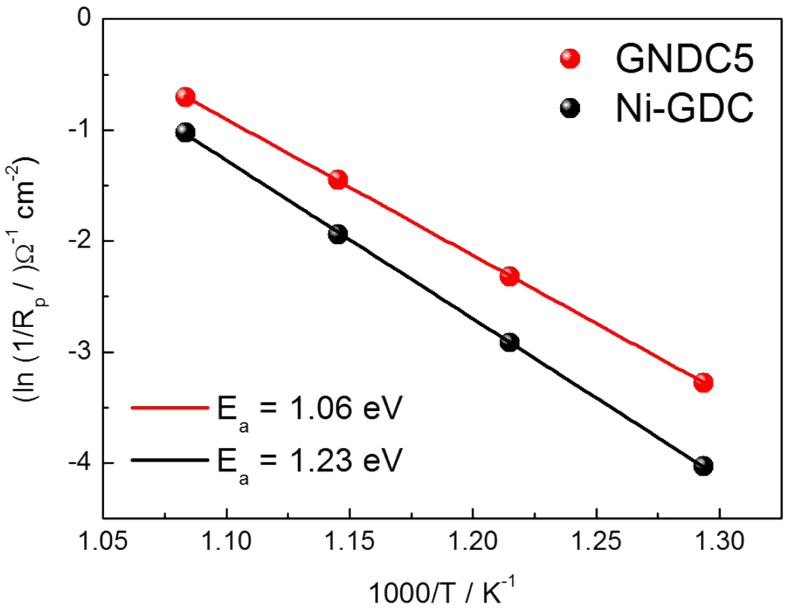

Fig. S7 Arrhenius plot for GNDC5 and mechanically mixed Ni-GDC composite electrode showing the E_a of 1.06 ± 0.001 eV and 1.23 ± 0.001 eV, respectively.

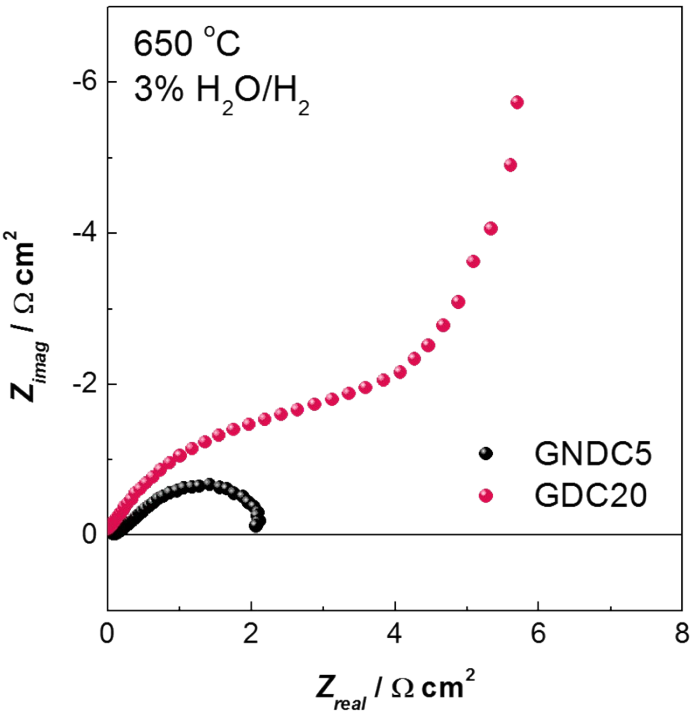

Fig. S8 Nyquist plot showing R_p for GDC20 (*i.e.*, without Ni doping)-based symmetrical cells sintered at 1250 °C and reduced at 650 °C. R_p becomes significantly large without Ni nanocatalyst.

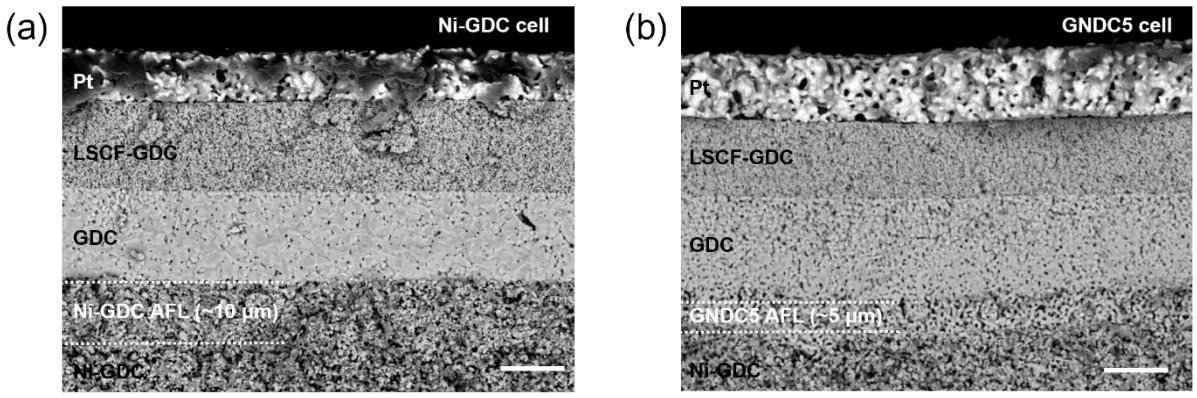

Fig. S9 Cross-sectional SEM images obtained by backscattering electron mode to confirm the AFL thickness of (a) Ni-GDC cell and (b) GNDC5 cell (scale bar = 10 μm).

Table S3. The R_s and R_p of two full cells measured at 650, 600, and 550 °C.

	650 °C		600 °C		550 °C	
	R_s (Ω cm^2)	R_p (Ω cm^2)	R_s (Ω cm^2)	R_p (Ω cm^2)	R_s (Ω cm^2)	R_p (Ω cm^2)
GNDC5 cell	0.096	0.103	0.223	0.281	0.659	0.924
Ni-GDC cell	0.087	0.122	0.199	0.398	0.564	1.492

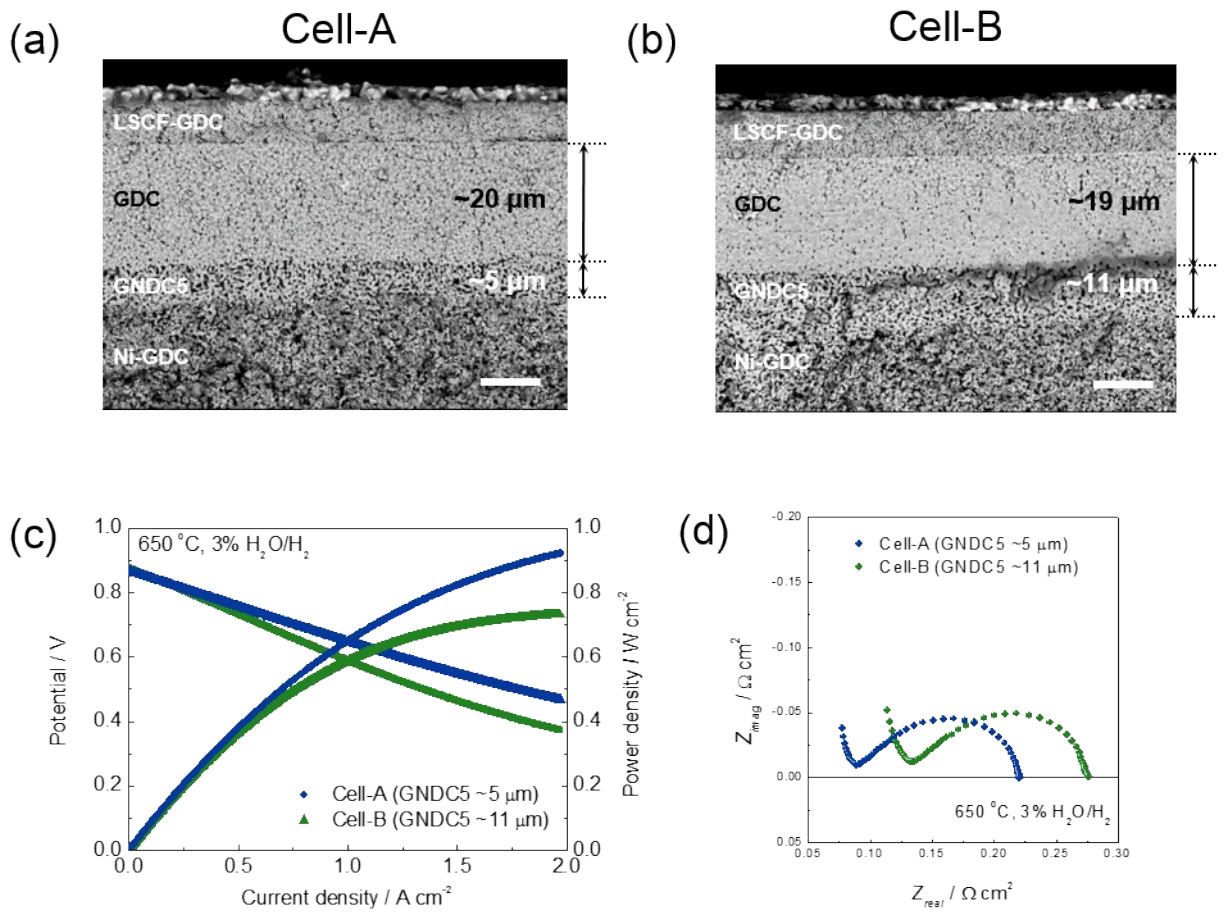

Fig. S10 Cross-sectional SEM image obtained by backscattering electron mode to confirm the thicknesses of GNDC5 AFL and GDC electrolyte in (a) cell-A and (b) cell-B (scale bar = 10 μm). Solid loadings of 2.2 vol% and 2.5 vol% for GNDC5 AFL dip-coating slurry were used for fabricating cell-A and cell-B, respectively. (c) I-V characteristics and (d) EIS data are shown for comparison.