Supplementary Materials: Correlation between Concentrations of Ni and Y in Y-doped BaZrO$_3$ Electrolyte in Co-sintered Cells: A Case of Controlled NiO Activity by Using MgO-NiO Solid Solution as Anode Substrate

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Figure S1. Powder XRD patterns of (a) MgO, (b) Mg$_{0.7}$Ni$_{0.3}$O, (c) Mg$_{0.5}$Ni$_{0.5}$O, (d) Mg$_{0.3}$Ni$_{0.7}$O, and (e) NiO. The Mg$_{0.7}$Ni$_{0.3}$O, Mg$_{0.5}$Ni$_{0.5}$O and Mg$_{0.3}$Ni$_{0.7}$O samples were synthesized by heating at 1300 °C for 10 h in air, and subsequently pulverized by ball-milling for 50 h.
Figure S2. (a) Shifting of (220) diffraction peak towards low angle side, and (b) increasing lattice constant of the sample with the increasing Mg concentration, indicating that solid solution of MgO-NiO has been prepared successfully, since the six-coordinated radius of Ni(II) (0.690 Å) is smaller than Mg(II) (0.72 Å) [25].

Figure S3. Back scattering electron images of the powders of (a) Mg_{0.7}Ni_{0.3}O, (b) Mg_{0.5}Ni_{0.5}O, and (c) Mg_{0.3}Ni_{0.7}O. The samples were synthesized by heating at 1300 °C for 10 h in air, and subsequently pulverized by ball-milling for 50 h.

Figure S4. Back scattering electron images of the half cells composed of a BZY20 electrolyte layer and a BZY20-50 wt % Mg_{0.3}Ni_{0.7}O anode substrate, which were co-sintered at (a) 1500 °C, and (b) 1600 °C in oxygen for 10 h with the open-co-sintering method (Figure 1a).
Figure S5. Optical images of the half cells composed of the BZY20 electrolyte layer and (a) BZY20-50 wt % Mg0.3Ni0.7O, and (b) BZY20-60 wt % NiO anode substrates after co-sintering at 1600 °C in oxygen for 10 h with the embedded-co-sintering (Figure 1c) method.

Figure S6. XRD patterns of the electrolyte side on the half cells composed of BZY20 electrolyte layers and BZY20-50 wt % Mg0.3Ni0.7O anode substrate co-sintered at 1600 °C in oxygen for 10 h using the (a) open-co-sintering, (b) placed-co-sintering, and (c) embedded-co-sintering methods.
Figure S7. XRD patterns of the electrolyte side on the half cells composed of BZY20 electrolyte layers and BZY20-50 wt % Mg0.5Ni0.5O anode substrate co-sintered at 1600 °C in oxygen for 10 h using the (a) open-co-sintering, (b) placed-co-sintering, and (c) embedded-co-sintering methods.

Figure S8. XRD patterns of the electrolyte side on the half cells composed of BZY20 electrolyte layers and BZY20-50 wt % Mg0.3Ni0.7O anode substrate co-sintered at 1600 °C in oxygen for 10 h using the (a) open-co-sintering, (b) placed-co-sintering, and (c) embedded-co-sintering methods.
Figure S9. XRD patterns of the electrolyte side on the half cells composed of BZY20 electrolyte layers and BZY20-60 wt % NiO anode substrate co-sintered at 1600 °C in oxygen for 10 h using the (a) open-co-sintering, (b) placed-co-sintering, and (c) embedded-co-sintering methods.

Figure S10. (a) The second electron image, and (b) back scattering electron image of the cross-section area of the half cell composed of a BZY20 electrolyte and a BZY20-50 wt % Mg0.7Ni0.3O anode substrate, which was co-sintered at 1600 °C in oxygen for 10 h using the open-co-sintering method (Figure 1a). EPMA-WDS elemental mapping analysis was performed to evaluate the distribution of (c) Ba, (d) Zr, (e) Y, (f) Ni and (g) Mg.
Figure S11. (a) The second electron image, and (b) back scattering electron image of the cross-section area of the half cell composed of a BZY20 electrolyte and a BZY20-50 wt % Mg0.5Ni0.5O anode substrate, which was co-sintered at 1600 °C in oxygen for 10 h using the open-co-sintering method (Figure 1a). EPMA-WDS elemental mapping analysis was performed to evaluate the distribution of (c) Ba, (d) Zr, (e) Y, (f) Ni and (g) Mg.

Figure S12. (a) The second electron image, and (b) back scattering electron image of the cross-section area of the half cell composed of a BZY20 electrolyte and a BZY20-50 wt % Mg0.3Ni0.7O anode substrate, which was co-sintered at 1600 °C in oxygen for 10 h using the open-co-sintering method (Figure 1a). EPMA-WDS elemental mapping analysis was performed to evaluate the distribution of (c) Ba, (d) Zr, (e) Y, (f) Ni and (g) Mg.
Figure S13. (a) The second electron image, and (b) back scattering electron image of the cross-section area of the half cell composed of a BZY20 electrolyte and a BZY20-60 wt % NiO anode substrate, which was co-sintered at 1600 °C in oxygen for 10 h using the open-co-sintering method (Figure 1a). EPMA-WDS elemental mapping analysis was performed to evaluate the distribution of (c) Ba, (d) Zr, (e) Y and (f) Ni.

Figure S14. Ba cation ratio in the electrolyte layer of the half cells with the anode substrates of (a) BZY20-50 wt % Mg0.7Ni0.3O, (b) BZY20-50 wt % Mg0.5Ni0.5O, (c) BZY20-50 wt % Mg0.3Ni0.7O, and (d) BZY20-50 wt % NiO. All the half cells were co-sintered at 1600 °C in oxygen for 10 h with the method shown in Figure 1. The Ba cation ratio was measured with EPMA-WDS line analysis following the position shown in Figure 2 (red line) from the interface between the anode substrate and the electrolyte.
Figure S15. Zr cation ratio in the electrolyte layer of the half cells with the anode substrates of (a) BZY20-50 wt % Mg0.7Ni0.3O, (b) BZY20-50 wt % Mg0.5Ni0.5O, (c) BZY20-50 wt % Mg0.3Ni0.7O, and (d) BZY20-50 wt % NiO. All the half cells were co-sintered at 1600 °C in oxygen for 10 h with the method shown in Figure 1. The Zr cation ratio was measured with EPMA-WDS line analysis following the position shown in Figure 2 (red line) from the interface between the anode substrate and the electrolyte.

Figure S16. (a) Back-scattering electron image and (b) second electron image of the cross-section of the BaZr0.78Y0.22O3-δ-2 wt % NiO pellet after sintering at 1500 °C in O2 for 10 h. EPMA-WDS elemental mapping was performed to see the distribution of (c) Ni, (d) Ba, (e) Zr, and (f) Y.
Figure S17. (a) Back-scattering electron image and (b) second electron image of the cross-section of the BaZrO$_3$-2 wt % NiO pellet after sintering at 1500 °C in O$_2$ for 10 h. EPMA-WDS elemental mapping was performed to see the distribution of (c) Ni, (d) Ba, (e) Zr, and (f) Y.

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