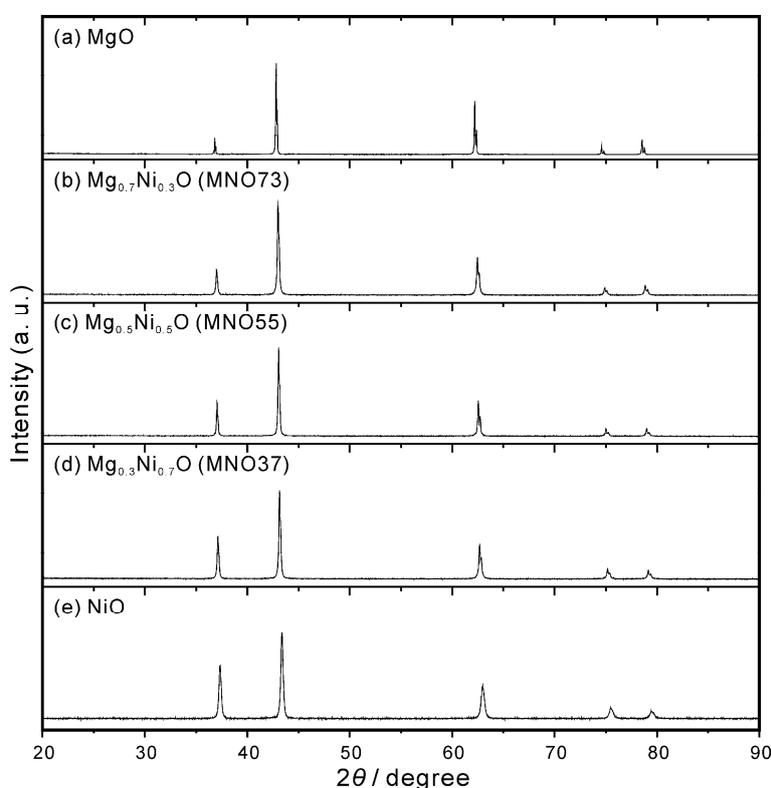


# Supplementary Materials: Correlation between Concentrations of Ni and Y in Y-doped BaZrO<sub>3</sub> Electrolyte in Co-sintered Cells: A Case of Controlled NiO Activity by Using MgO-NiO Solid Solution as Anode Substrate

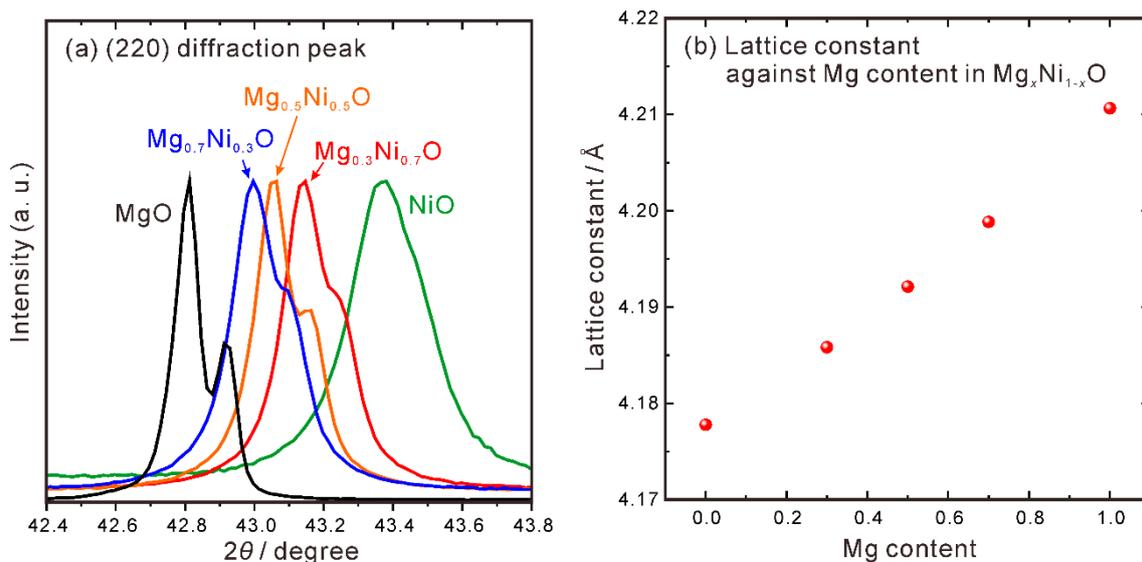
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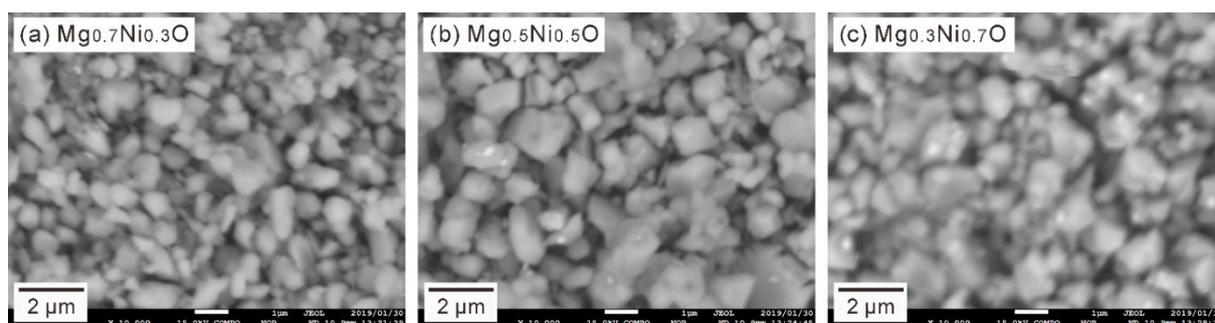
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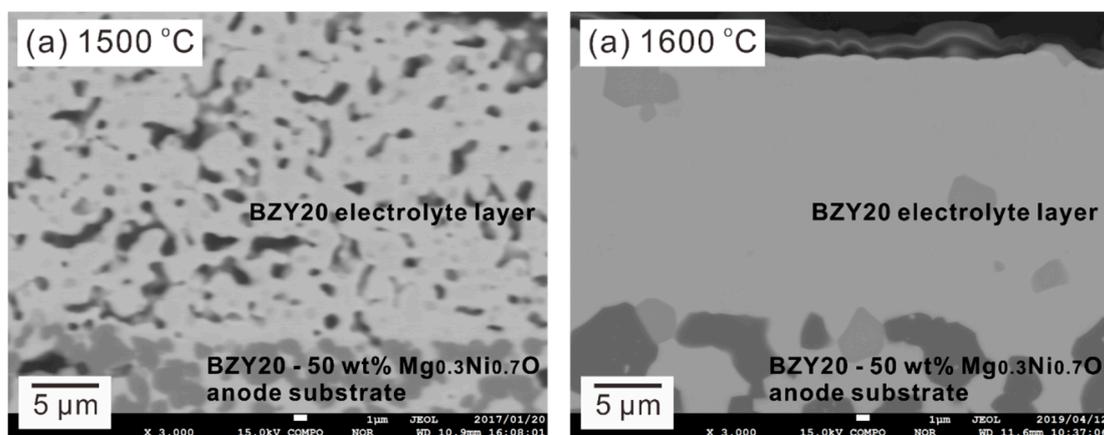
**Figure S1.** Powder XRD patterns of (a) MgO, (b) Mg<sub>0.7</sub>Ni<sub>0.3</sub>O, (c) Mg<sub>0.5</sub>Ni<sub>0.5</sub>O, (d) Mg<sub>0.3</sub>Ni<sub>0.7</sub>O, and (e) NiO. The Mg<sub>0.7</sub>Ni<sub>0.3</sub>O, Mg<sub>0.5</sub>Ni<sub>0.5</sub>O and Mg<sub>0.3</sub>Ni<sub>0.7</sub>O samples were synthesized by heating at 1300 °C for 10 h in air, and subsequently pulverized by ball-milling for 50 h.



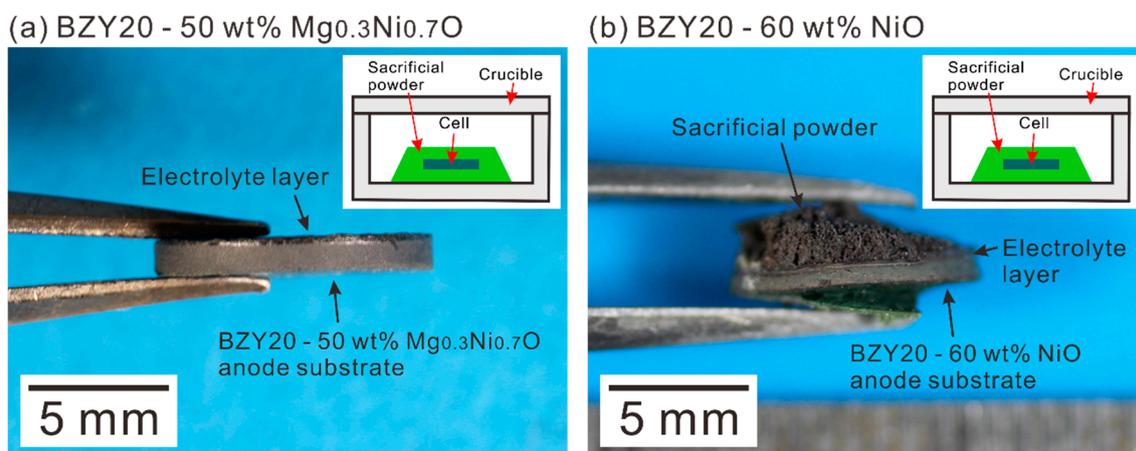
**Figure S2.** (a) Shifting of (220) diffraction peak towards low angle side, and (b) increasing lattice constant of the sample with the increasing Mg concentration, indicating that solid solution of MgO-NiO has been prepared successfully, since the six-coordinated radius of Ni(II) (0.690 Å) is smaller than Mg(II) (0.72 Å) [25].



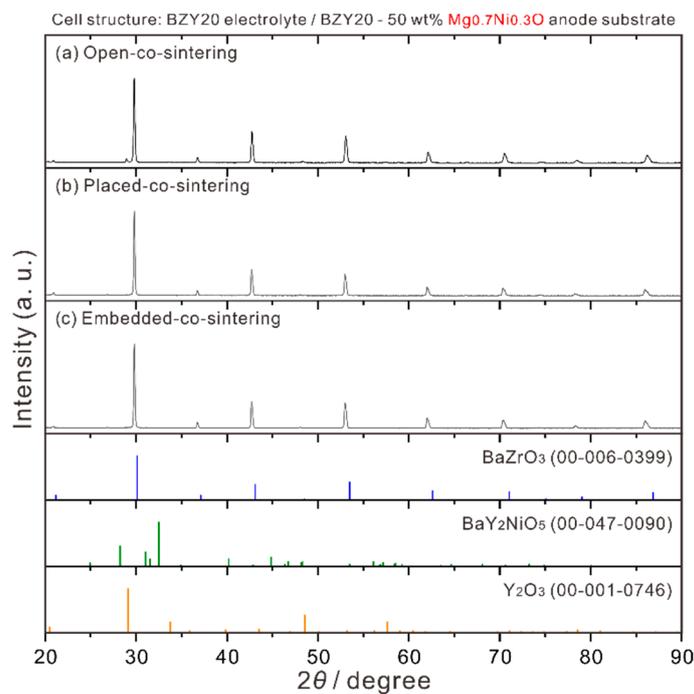
**Figure S3.** Back scattering electron images of the powders of (a) Mg<sub>0.7</sub>Ni<sub>0.3</sub>O, (b) Mg<sub>0.5</sub>Ni<sub>0.5</sub>O, and (c) Mg<sub>0.3</sub>Ni<sub>0.7</sub>O. The samples were synthesized by heating at 1300 °C for 10 h in air, and subsequently pulverized by ball-milling for 50 h.



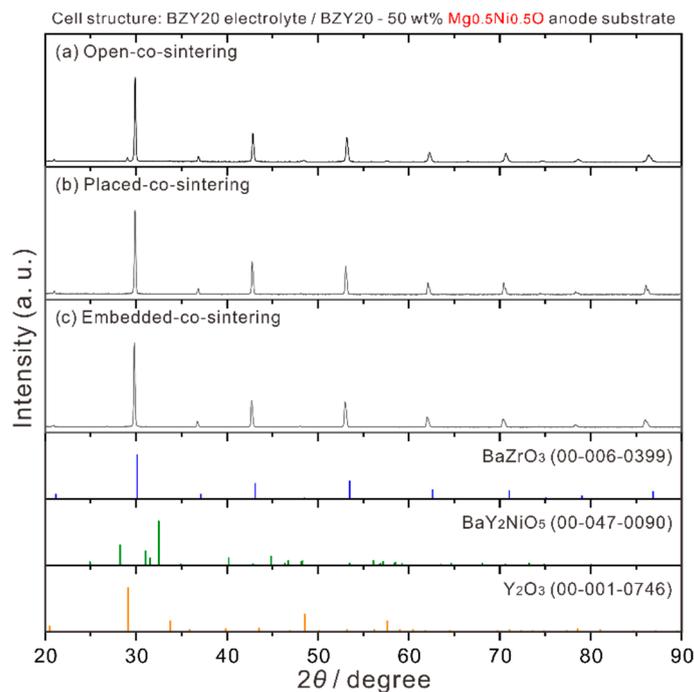
**Figure S4.** Back scattering electron images of the half cells composed of a BZY20 electrolyte layer and a BZY20-50 wt % Mg<sub>0.3</sub>Ni<sub>0.7</sub>O anode substrate, which were co-sintered at (a) 1500 °C, and (b) 1600 °C in oxygen for 10 h with the open-co-sintering method (Figure 1a).



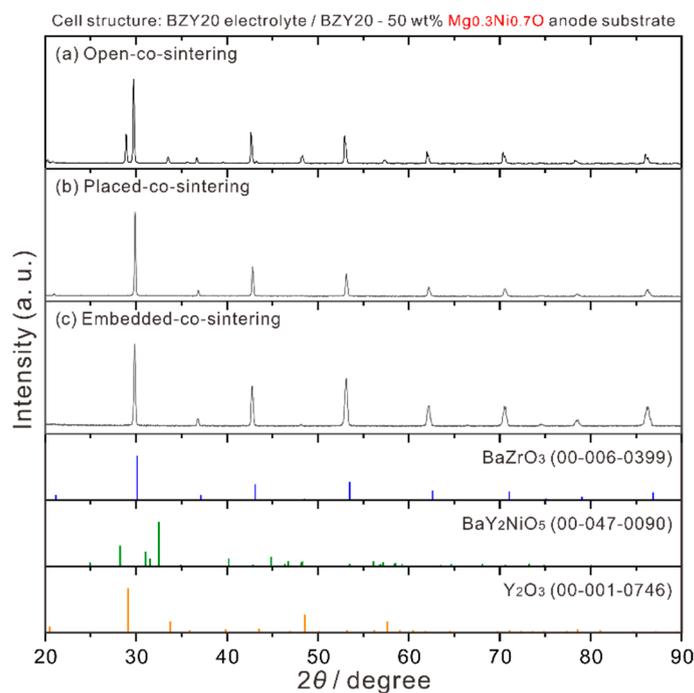
**Figure S5.** Optical images of the half cells composed of the BZY20 electrolyte layer and (a) BZY20-50 wt %  $\text{Mg}_{0.3}\text{Ni}_{0.7}\text{O}$ , and (b) BZY20-60 wt % NiO anode substrates after co-sintering at 1600 °C in oxygen for 10 h with the embedded-co-sintering (Figure 1c) method.



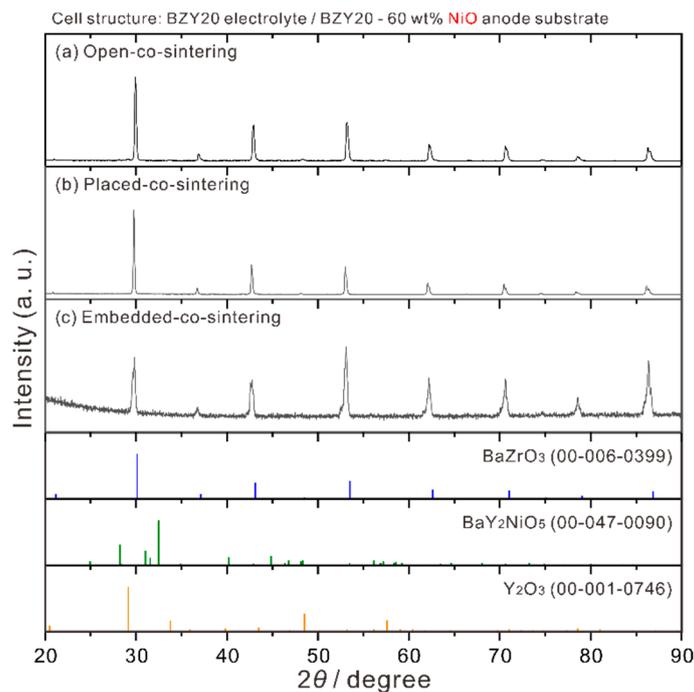
**Figure S6.** XRD patterns of the electrolyte side on the half cells composed of BZY20 electrolyte layers and BZY20-50 wt %  $\text{Mg}_{0.7}\text{Ni}_{0.3}\text{O}$  anode substrate co-sintered at 1600 °C in oxygen for 10 h using the (a) open-co-sintering, (b) placed-co-sintering, and (c) embedded-co-sintering methods.



**Figure S7.** XRD patterns of the electrolyte side on the half cells composed of BZY20 electrolyte layers and BZY20-50 wt %  $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$  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.

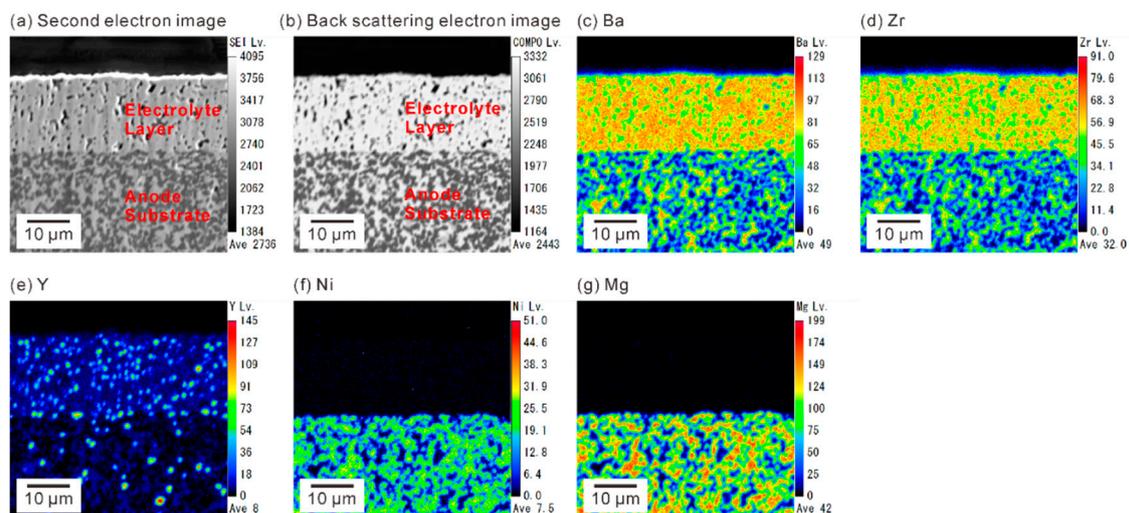


**Figure S8** XRD patterns of the electrolyte side on the half cells composed of BZY20 electrolyte layers and BZY20-50 wt %  $\text{Mg}_{0.3}\text{Ni}_{0.7}\text{O}$  anode substrate co-sintered at 1600 °C in oxygen for 10 h using the (a) open-co-sintering, (b) placed-co-sintering, and (c) embedded-co-sintering methods.



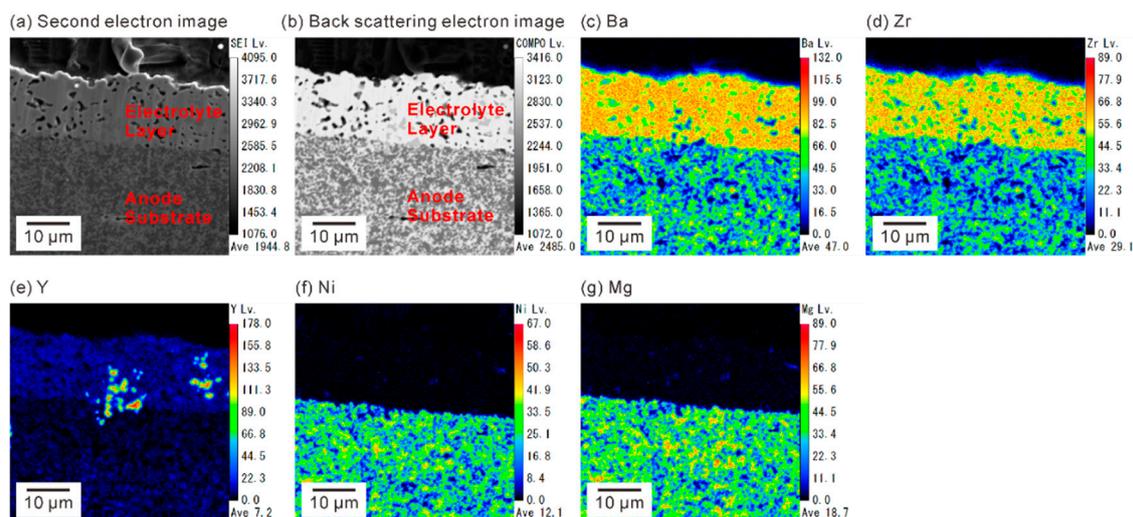
**Figure S9.** XRD patterns of the electrolyte side on the half cells composed of BZY20 electrolyte layers and BZY20-60 wt % NiO anode substrate co-sintered at 1600 °C in oxygen for 10 h using the (a) open-co-sintering, (b) placed-co-sintering, and (c) embedded-co-sintering methods.

Half cell of BZY20 electrolyte layer / BZY20 - 50 wt% Mg<sub>0.7</sub>Ni<sub>0.3</sub>O anode substrate  
Co-sintering condition: Open-co-sintering, 1600 °C, O<sub>2</sub>, 10 h



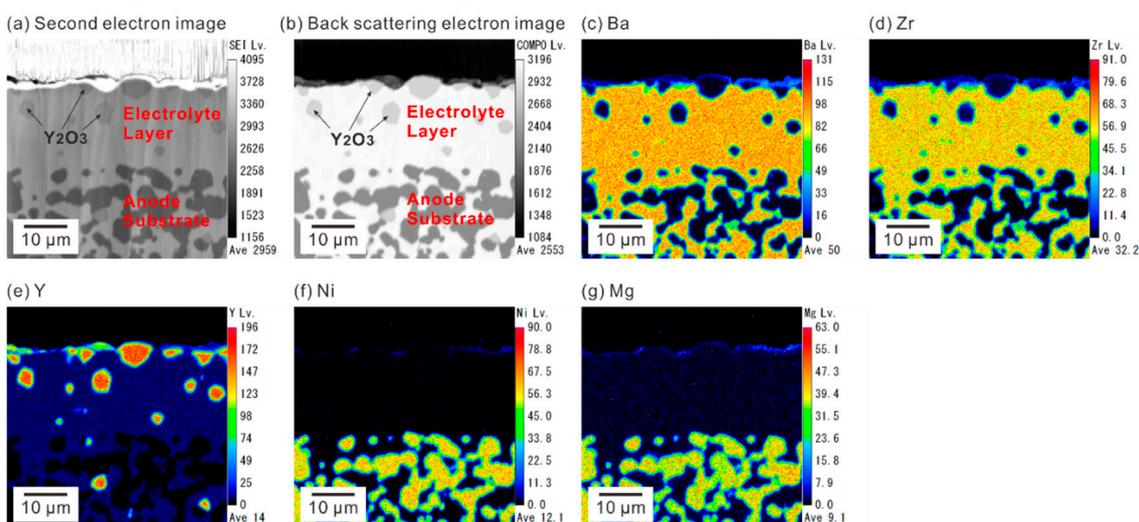
**Figure S10.** (a) The second electron image, and (b) back scattering electron image of the cross-section area of the half cell composed of a BZY20 electrolyte and a BZY20-50 wt % Mg<sub>0.7</sub>Ni<sub>0.3</sub>O anode substrate, which was co-sintered at 1600 °C in oxygen for 10 h using the open-co-sintering 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.

Half cell of BZY20 electrolyte layer / BZY20 - 50 wt%  $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$  anode substrate  
 Co-sintering condition: Open-co-sintering, 1600 °C,  $\text{O}_2$ , 10 h



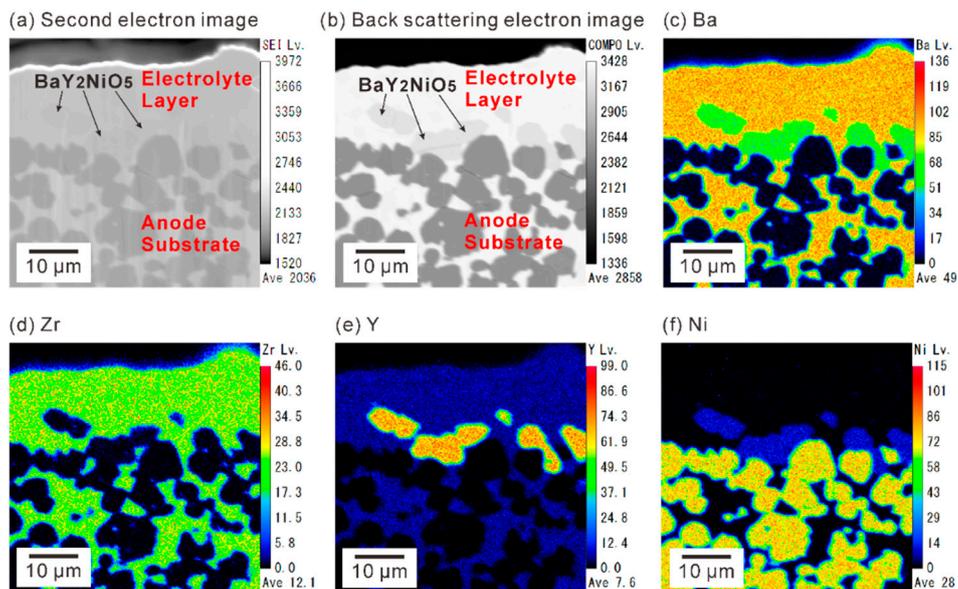
**Figure S11.** (a) The second electron image, and (b) back scattering electron image of the cross-section area of the half cell composed of a BZY20 electrolyte and a BZY20-50 wt %  $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$  anode substrate, which was co-sintered at 1600 °C in oxygen for 10 h using the 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.

Half cell of BZY20 electrolyte layer / BZY20 - 50 wt%  $\text{Mg}_{0.3}\text{Ni}_{0.7}\text{O}$  anode substrate  
 Co-sintering condition: Open-co-sintering, 1600 °C,  $\text{O}_2$ , 10 h

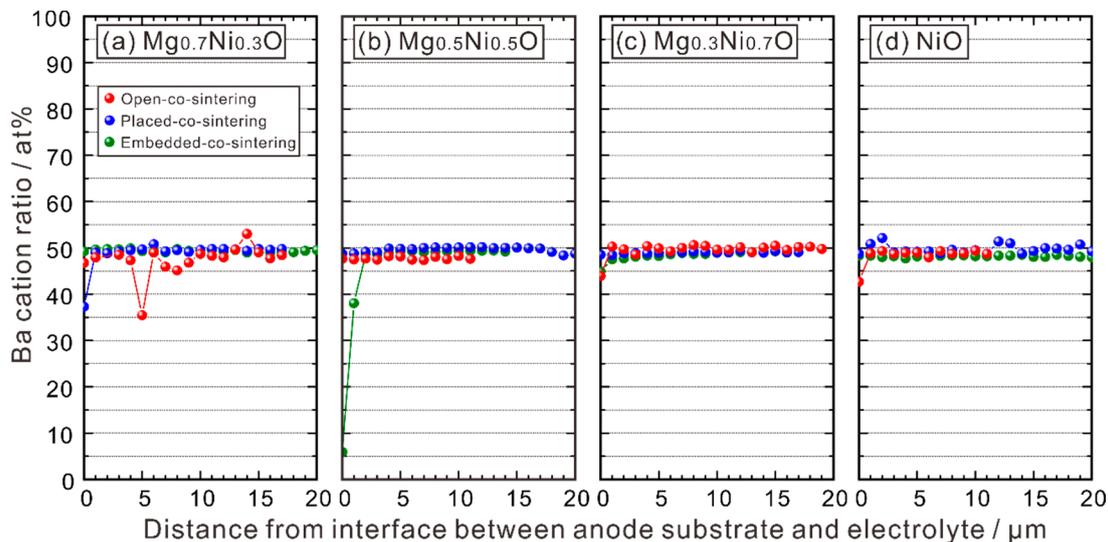


**Figure S12.** (a) The second electron image, and (b) back scattering electron image of the cross-section area of the half cell composed of a BZY20 electrolyte and a BZY20-50 wt %  $\text{Mg}_{0.3}\text{Ni}_{0.7}\text{O}$  anode substrate, which was co-sintered at 1600 °C in oxygen for 10 h using the 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.

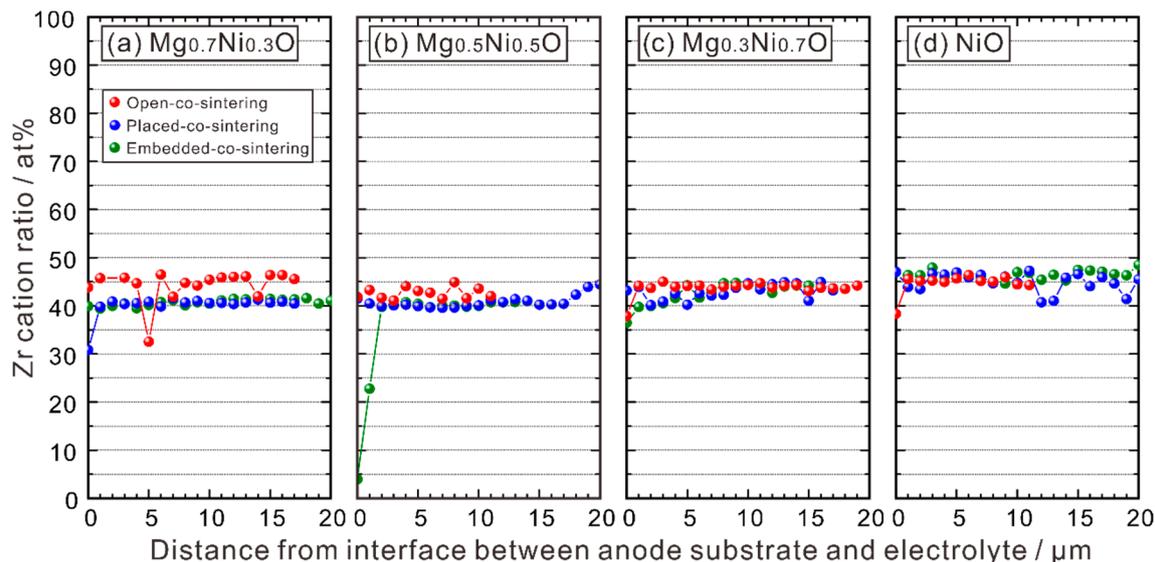
Half cell of BZY20 electrolyte layer / BZY20 - 60 wt% NiO anode substrate  
Co-sintering condition: Open-co-sintering, 1600 °C, O<sub>2</sub>, 10 h



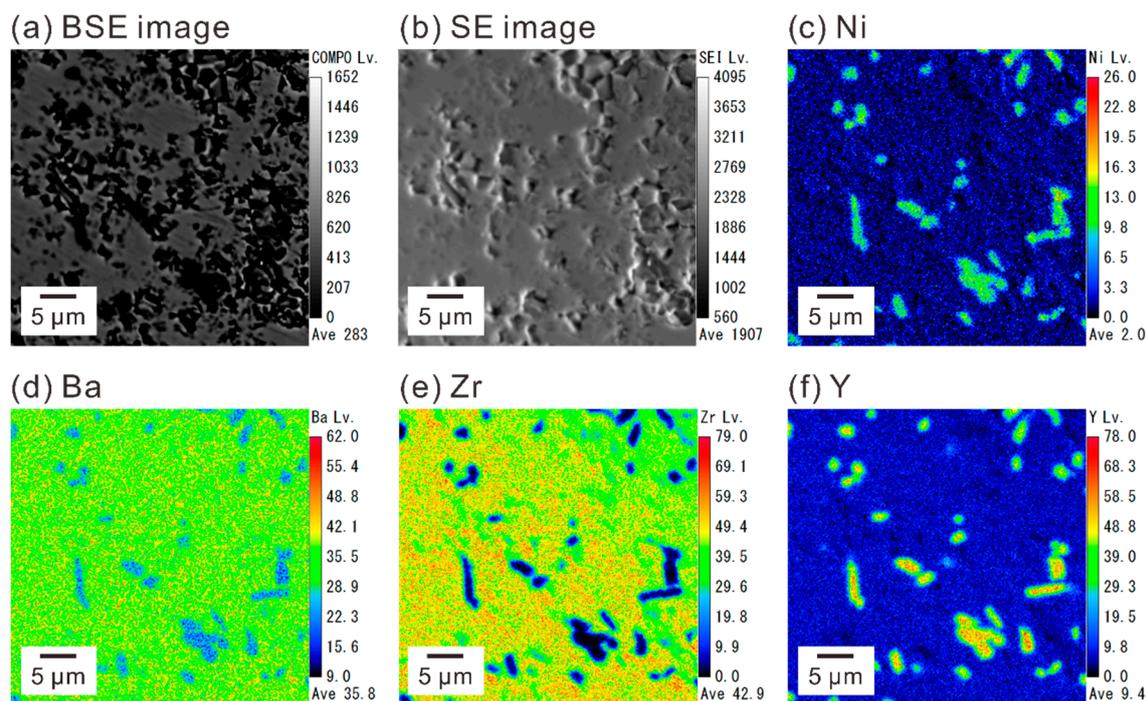
**Figure S13.** (a) The second electron image, and (b) back scattering electron image of the cross-section area of the half cell composed of a BZY20 electrolyte and a BZY20-60 wt % NiO anode substrate, which was co-sintered at 1600 °C in oxygen for 10 h using the open-co-sintering method (Figure 1a).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



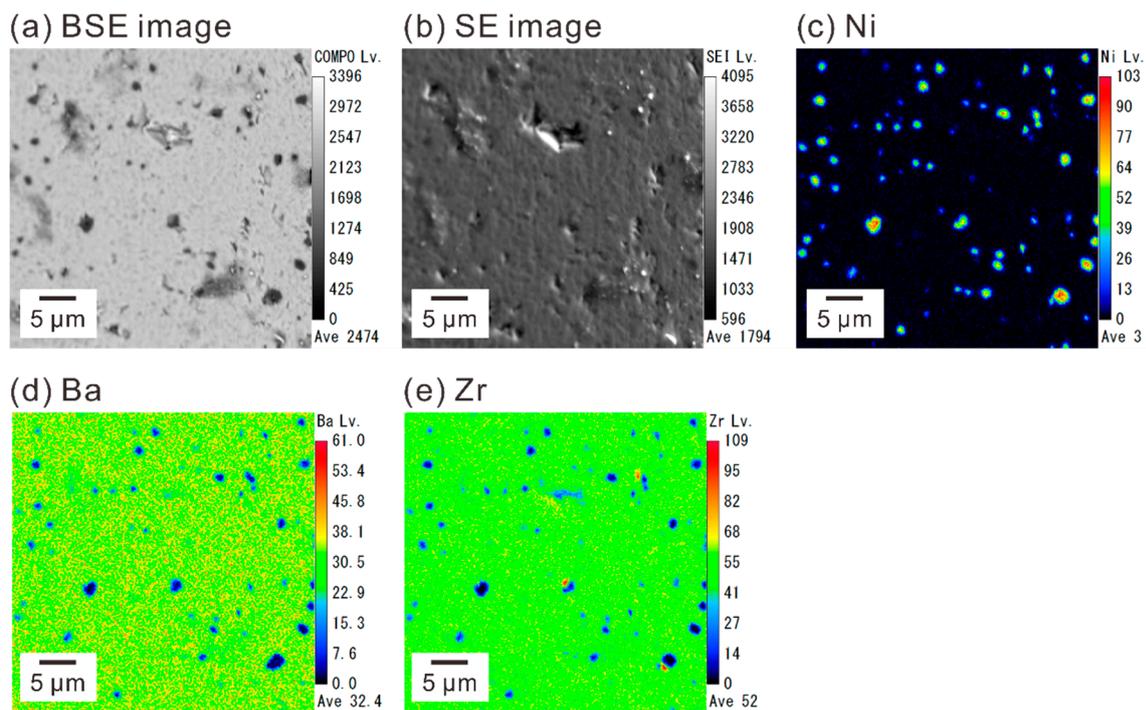
**Figure S14.** Ba cation ratio in the electrolyte layer of the half cells with the anode substrates of (a) BZY20-50 wt % Mg<sub>0.7</sub>Ni<sub>0.3</sub>O, (b) BZY20-50 wt % Mg<sub>0.5</sub>Ni<sub>0.5</sub>O, (c) BZY20-50 wt % Mg<sub>0.3</sub>Ni<sub>0.7</sub>O, and (d) BZY20-50 wt % NiO. All the half 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 %  $\text{Mg}_{0.7}\text{Ni}_{0.3}\text{O}$ , (b) BZY20-50 wt %  $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$ , (c) BZY20-50 wt %  $\text{Mg}_{0.3}\text{Ni}_{0.7}\text{O}$ , 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  $\text{BaZr}_{0.78}\text{Y}_{0.22}\text{O}_{3-\delta}$ -2 wt % NiO pellet after sintering at 1500 °C in  $\text{O}_2$  for 10 h. EPMA-WDS elemental mapping was performed to see the distribution of (c) Ni, (d) Ba, (e) Zr, and (f) Y.



**Figure S17.** (a) Back-scattering electron image and (b) second electron image of the cross-section of the BaZrO<sub>3</sub>-2 wt % NiO pellet after sintering at 1500 °C in O<sub>2</sub> 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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