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

Supporting Information

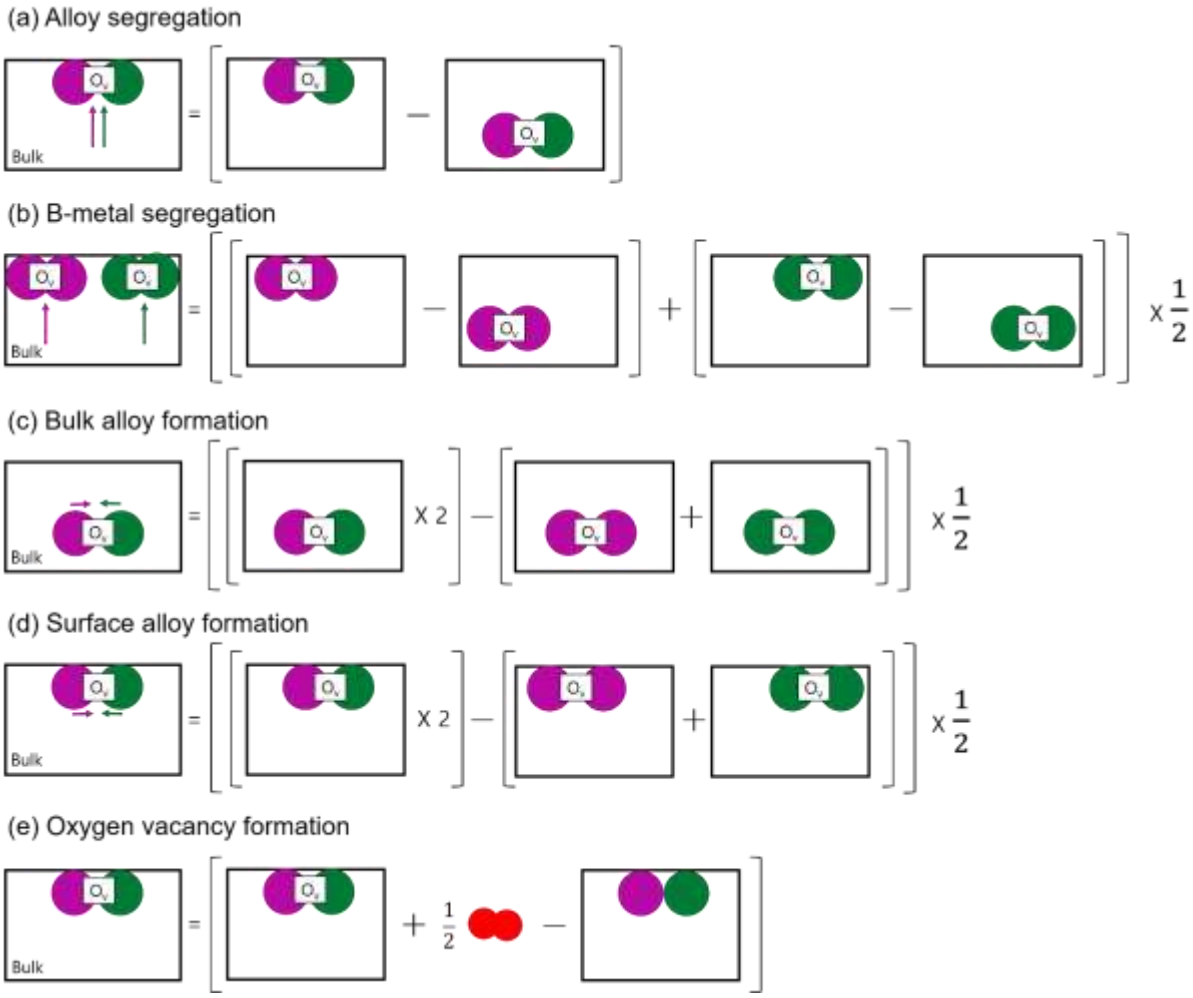

Fig. S1 Schematic illustration for DFT-calculated energetics at each elementary step. (a) The alloy segregation energy was defined by the total energy difference between the systems with Co-O_v-Ni alloy located at surface and in bulk. (b) To compare the segregation energy of Co-O_v-Ni alloy with the separate segregation of Co-O_v-Co and Ni-O_v-Ni, we used the normalized segregation energies of Co-O_v-Co and Ni-O_v-Ni. The alloy formation energies (c) in the bulk and (d) at the surface were defined by the total energy difference between the systems where two different B-site metals are separated and aggregated. (e) The oxygen vacancy formation energy was defined by total energy difference of the supercells with and without an oxygen vacancy.

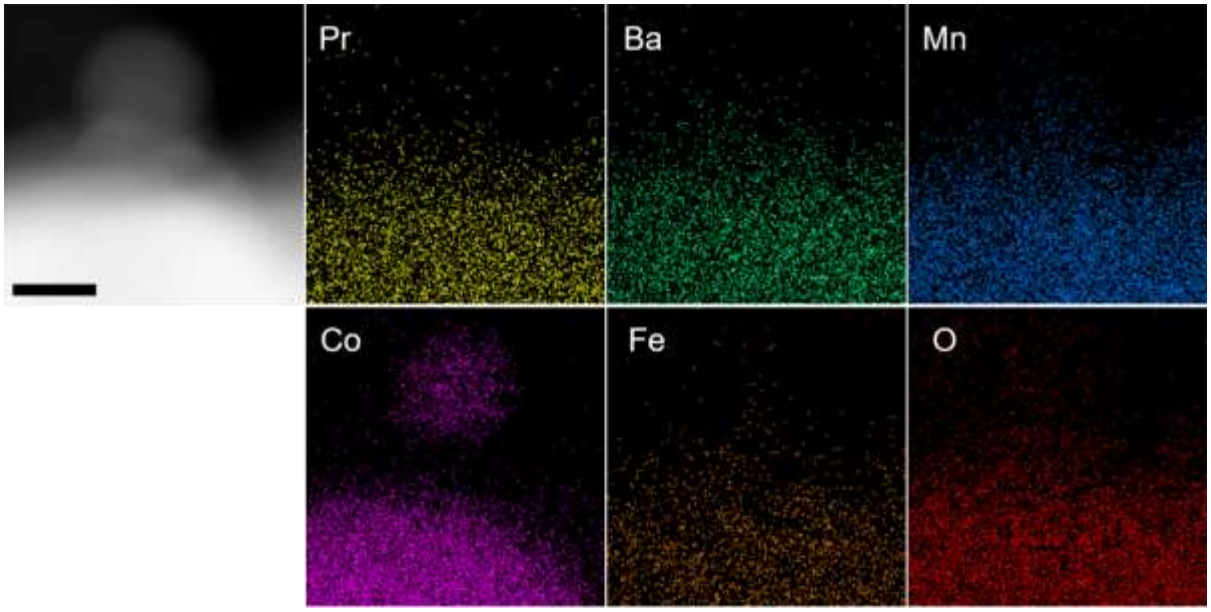

Fig. S2 High-angle annular dark-field (HADDF) image of the $PrBaMn_{1.7}Co_{0.1}Fe_{0.2}O_{5+\delta}$ with the EDS elemental map of Pr, Ba, Mn, Co, Fe, and O; scale bar 25 nm.

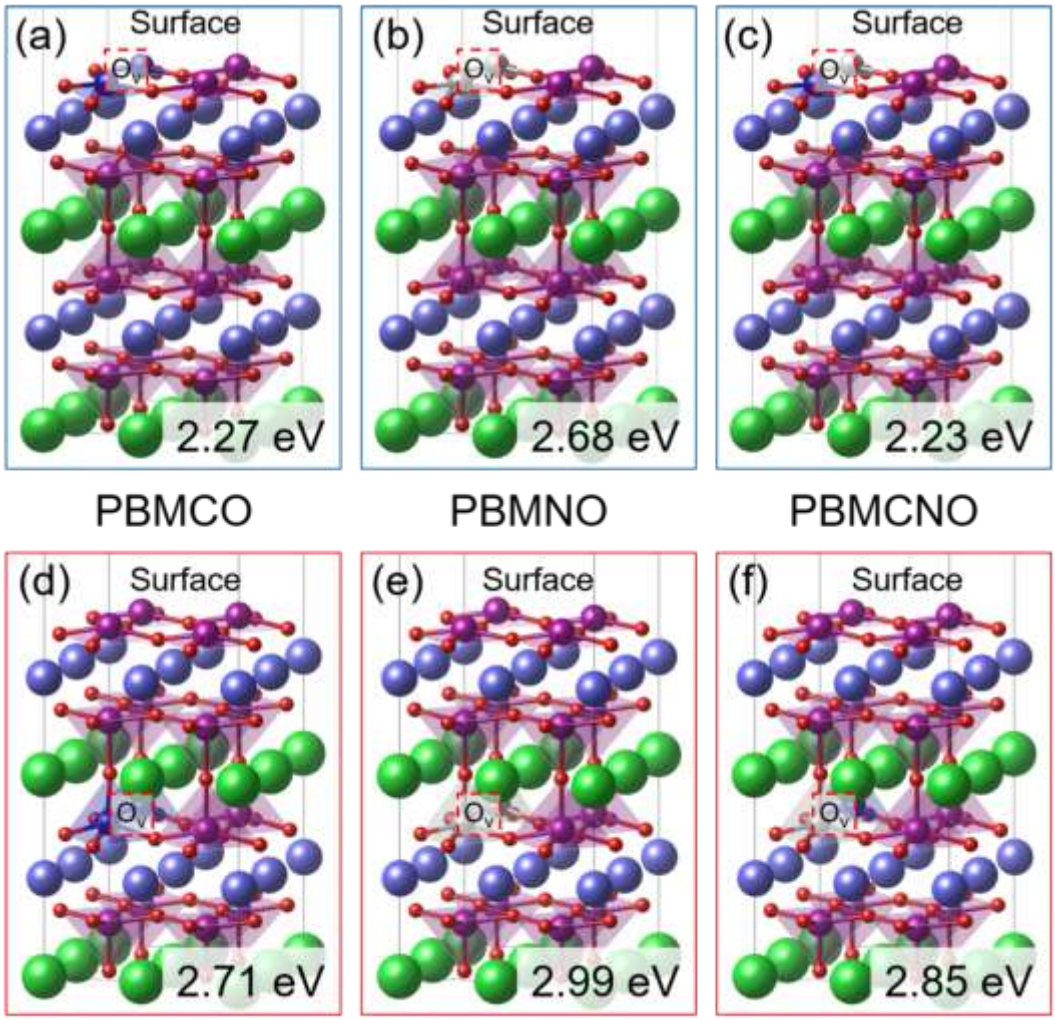

Fig. S3 Oxygen vacancy formation energies (a)-(c) at the surface or (d)-(f) in the bulk of Co, Ni, and Co-Ni doped PBMO, respectively. Pr, Ba, Mn, Co, Ni, and O atoms are shown as dark blue, green, purple, blue, grey, and red, respectively. The O_v in red rectangular indicates an oxygen vacancy.

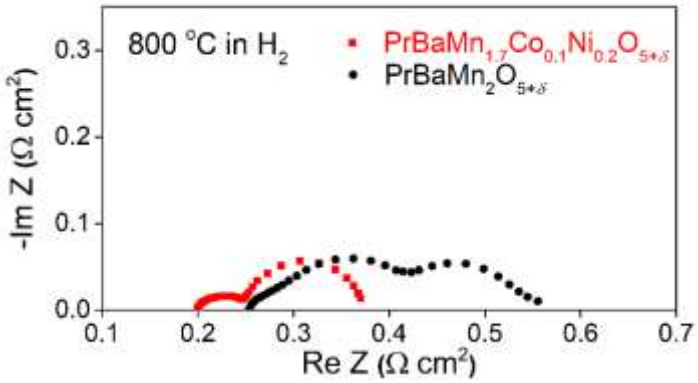

Fig. S4 Impedance spectra of fuel cells with the $PrBaMn_2O_{5+\delta}$ and $PrBaMn_{1.7}Co_{0.1}Ni_{0.2}O_{5+\delta}$ anodes using humidified (3% H_2O) H_2 and ambient air as the oxidant at 800 °C.

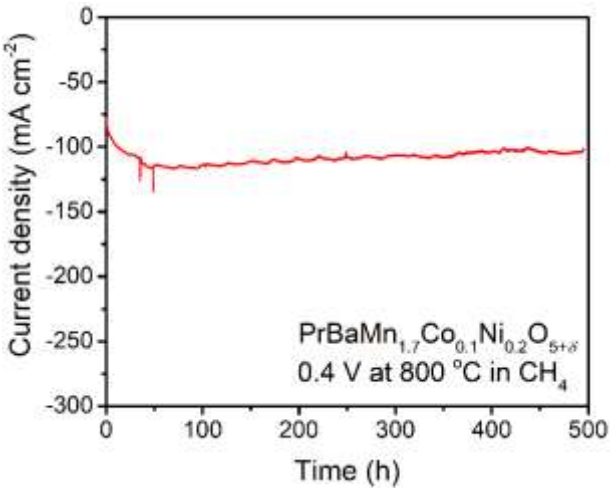

Fig. S5 Electrochemical performance of fuel cell with $PrBaMn_{1.7}Co_{0.1}Ni_{0.2}O_{5+\delta}$ anode in CH_4 at 800 °C under a constant voltage of 0.4 V.

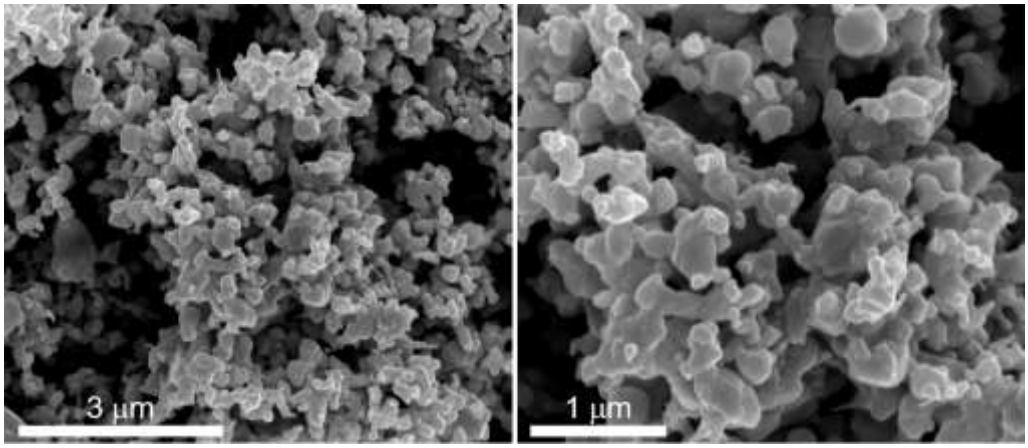

Fig. S6 Scanning electron microscope images of $PrBaMn_{1.7}Co_{0.1}Ni_{0.2}O_{5+\delta}$ anode after stability test in CH_4 at 800 ^oC under a constant voltage of 0.4 V.