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

Determination of Fe oxidation states in the B-site ordered perovskite-type $Ba_2Ca_{0.67}Fe_{0.33}NbO_{6-\delta}$ at surface (nano-scale) and bulk using variable temperature XPS and TGA and its impact on electrochemical catalysis

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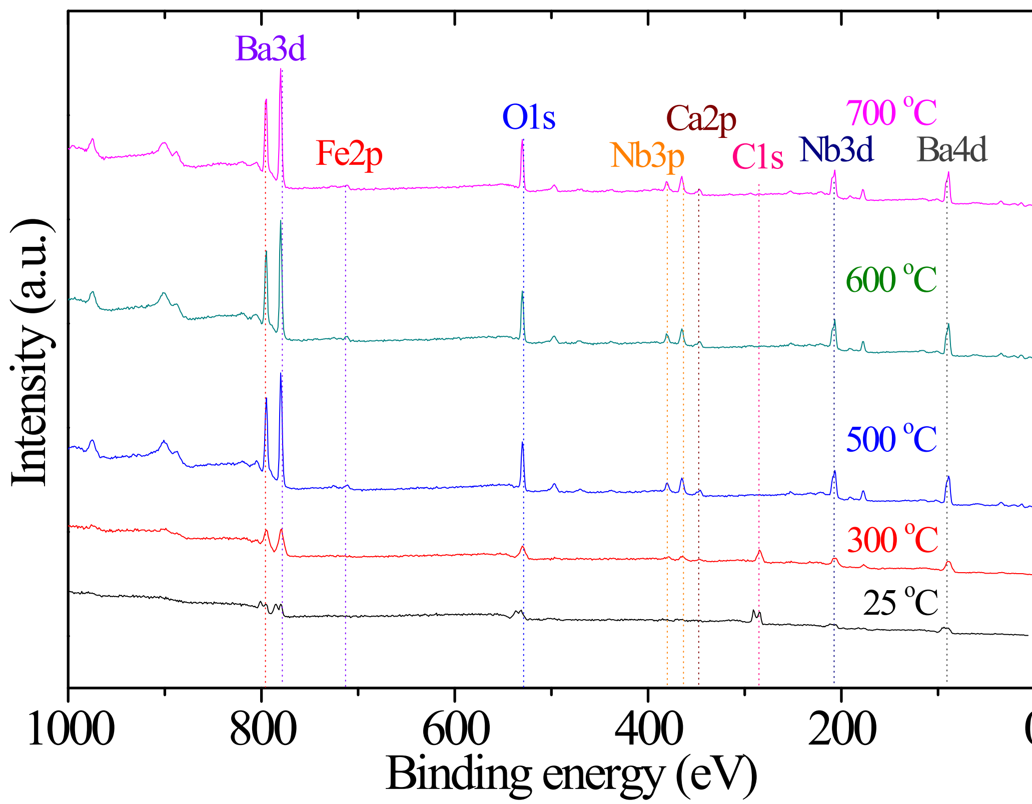
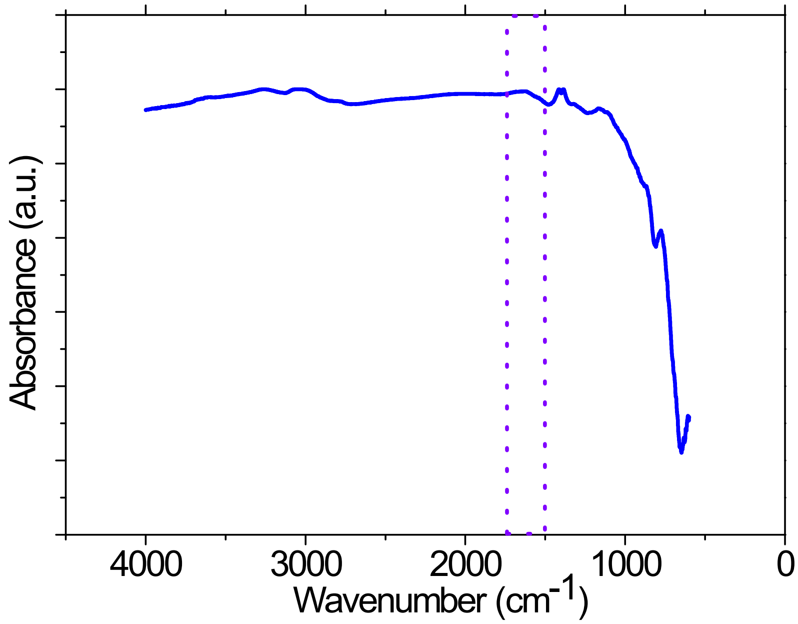
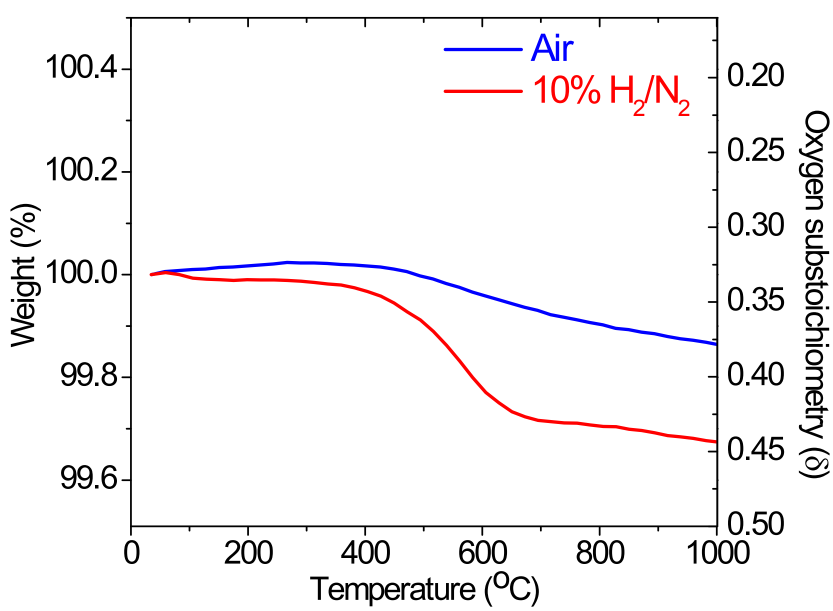
Supporting information



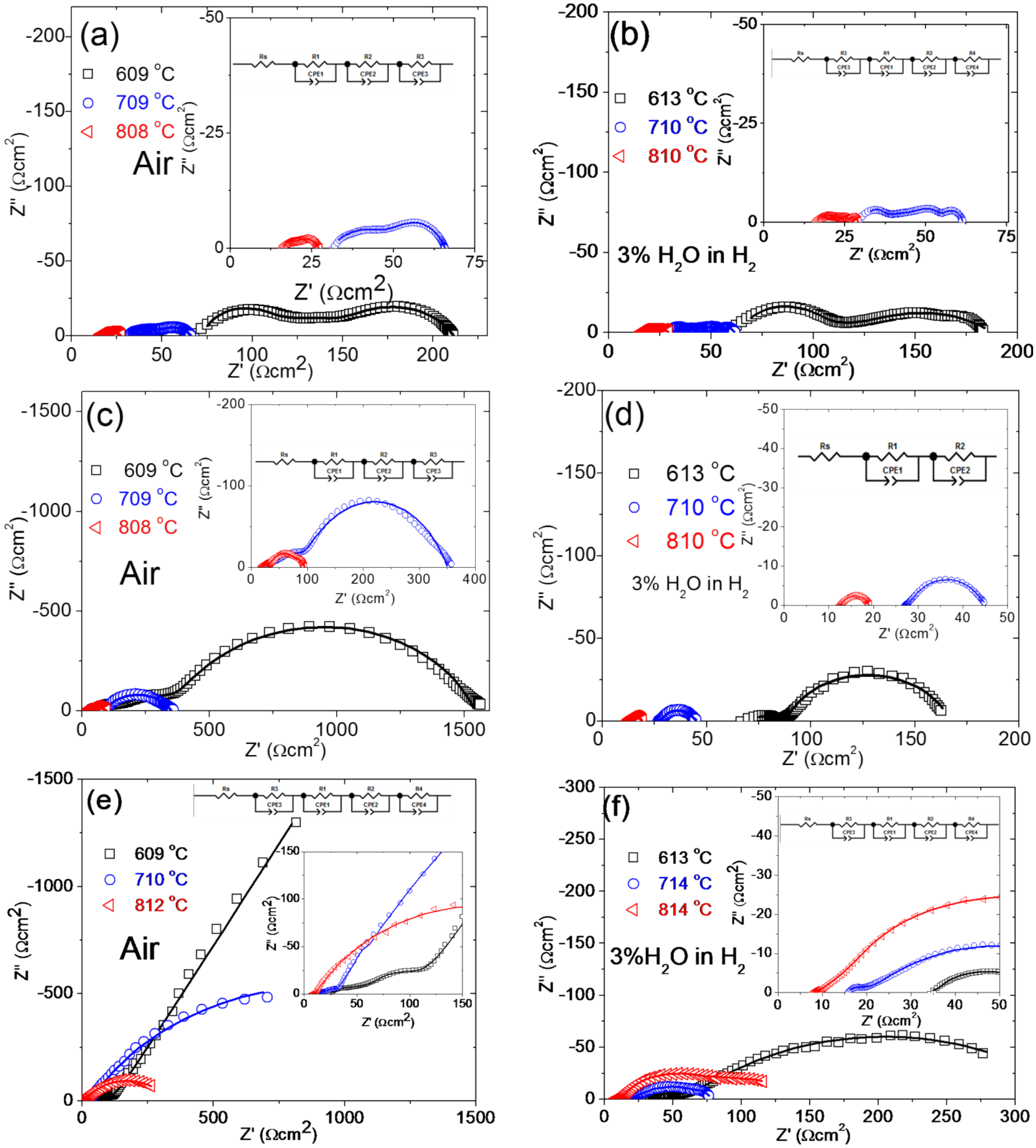
S. Figure 1. Variable temperature XPS elemental analysis on the near surface of $Ba_2Ca_{0.67}Fe_{0.33}NbO_{6-\delta}$ as a function of temperature.



S. Figure 2. FTIR spectrum of the as-prepared $Ba_2Ca_{0.67}Fe_{0.33}NbO_{6-\delta}$. The characteristic peak at ca. 1500-1700 cm^{-1} (purple dotted box) was not observed for carbonate species.



S. Figure 3. Thermogravimetric analysis of the as-prepared $Ba_2Ca_{0.67}Fe_{0.33}NbO_{6-\delta}$ in air and 10% H_2/N_2.



S. Figure 4. Electrochemical impedance spectra of two-electrode half-cell of $Ba_2Ca_{0.67}M_{0.33}NbO_{6-\delta}$ (M = Mn in (a), Fe in (b), and Co in (c)) as a function of temperature. The solid line passing through data points represents the best-fit line.

Table S1. Variable temperature XPS elemental analysis on the near surface of $Ba_2Ca_{0.67}Fe_{0.33}NbO_{6-\delta}$.

Temperature (^oC)	Ba3d	Ca2p	Nb3p	Fe2p	O1s		Fe^{2+}: Fe^{3+}
700	5.42	1.76	2.70	1.00	18.71		10.7:89.3
600	5.50	1.93	2.80	1.00	19.35		9.1:90.9
500	5.75	2.01	3.40	1.00	20.09		8.5:91.5
300	6.16	2.04	3.07	1.00	29.65		
25	6.53	2.17	3.10	1.00	74.87		
Theoretical	6	2	3	1	17.2		