Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Non-ohmic conduction in sodium bismuth titanate: the influence of oxide-ion conduction

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X-ray diffraction and SEM

An XRD pattern (Figure S1) of an $NB_{0.51}T$ pellet shows it to be phase-pure. The crystal structure was refined on a rhombohedral cell (Space group *R3c*) with lattice parameters a = 5.4927 and c = 13.4904 Å. An SEM image (Figure S2) of a thermally-etched surface of an $NB_{0.51}T$ ceramic revealed an average grain size of ~ 1-2 µm.

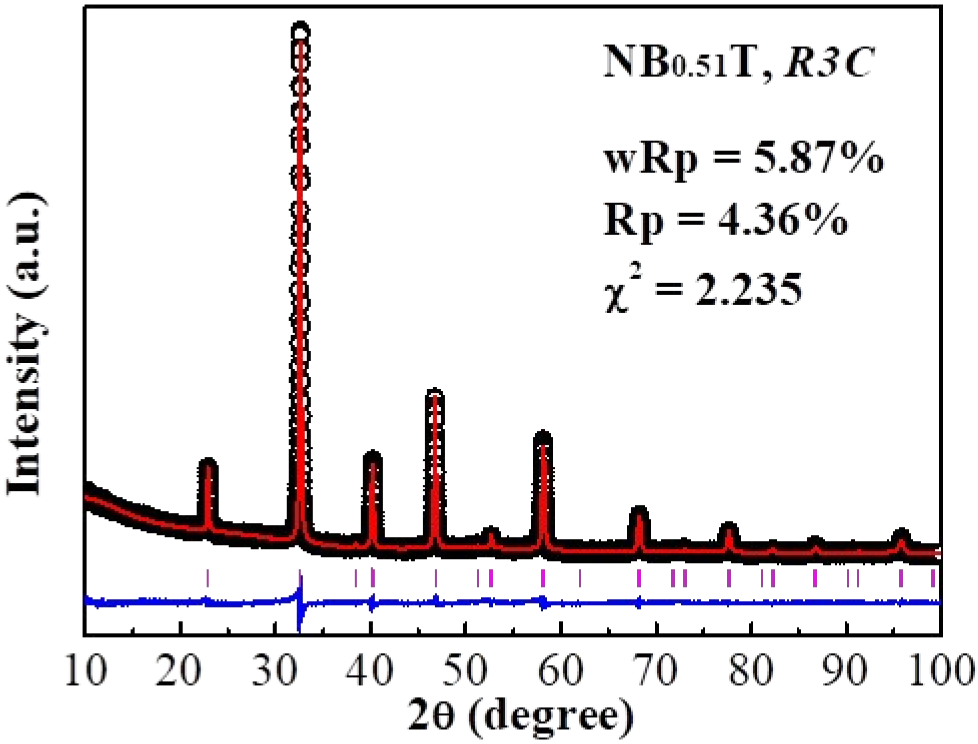

Figure S1. Rietveld refinement of the room temperature XRD pattern of $NB_{0.51}T$ ceramic. The hollow circles represent the observed pattern and the solid line shows the calculated fit. The reflection markers for the *R3c* structure are shown as vertical lines with the difference pattern below the diffraction pattern.

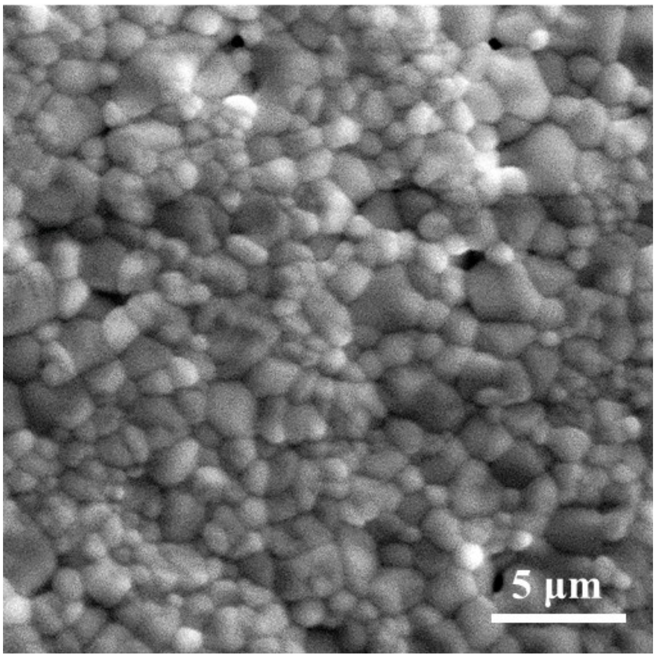

Figure S2. An SEM image of a thermally-etched surface of an $NB_{0.51}T$ ceramic.

Permittivity-T and M'' spectroscopic plot of $NB_{0.51}T$

According to the Joule heating model, at 600 ºC, the temperature rise caused by the heat generated by the 10 V *dc* bias in 30 minutes is estimated to be ~ 30 ºC. Based on the temperature dependence of permittivity of $NB_{0.51}T$ (Figure S3), a temperature rise from 600 to 630 ^{o}C will lead to a permittivity drop from 850 to 760, as indicated by the arrow in the figure. However this is contrary to experimental observation where permittivity increases (*M*''-log*f* peak height decreases) under the dc bias (Figure S3b). This gives evidence that Joule heating is not the origin of the enhanced σ of $NB_{0.51}T$ under *dc* bias. Further evidence from equivalent circuit fittings also support the conclusion that Joule heating is not the reason behind the enhanced σ of $NB_{0.51}T$.

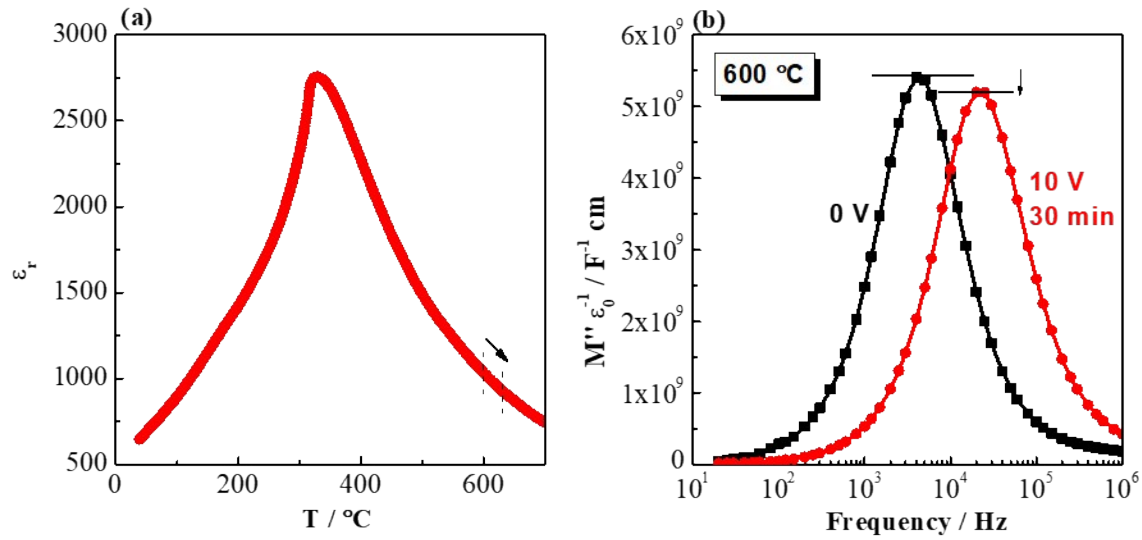

Figure S3. (a) Temperature dependence of permittivity of $NB_{0.51}T$ at 1 MHz. The arrow in the figure indicates a decrease of permittivity with a temperature rise from 600 to 630 °C. (b) Comparison of the M'' peak height before and after applying a 10 V dc bias for 30 min.

Equivalent circuit fitting of EIS data

*Z** plots of $NB_{0.51}T$ ceramics without a dc bias in the frequency range ~ 20 Hz to 2 MHz show a single arc. An equivalent circuit of R-CPE-C (Figure S4a) was used to fit the data. The fitting results are presented in different formats (Figure S4b-4e). The impedance residuals, defined as $Z_{residual} = (Z_{measured} - Z_{fitted})/|Z_{measured}|$, are used to present the difference between the measured and fitted data. The impedance residuals are less than 2% within the frequency range, indicating the validity of the selected equivalent circuit.

Under a 10 V dc bias, *Z** plots still show a single arc; however, additional plateaus appear on Y'-log*f* and C'-log*f* spectroscopic plots. Another R-C element was added in series with the R-CPE-C element to fit the impedance data (Figure S5a). This R-C element is attributed to the oxygen vacancy-rich and/or the depletion layers near the cathode and anode regions, respectively. The fitting results presented in different formats are shown in Figure S5b-5e. The impedance residuals are less than 1% within the frequency range, indicating the validity of the selected equivalent circuit.

The above equivalent circuit fitting parameters are listed in Table S1.

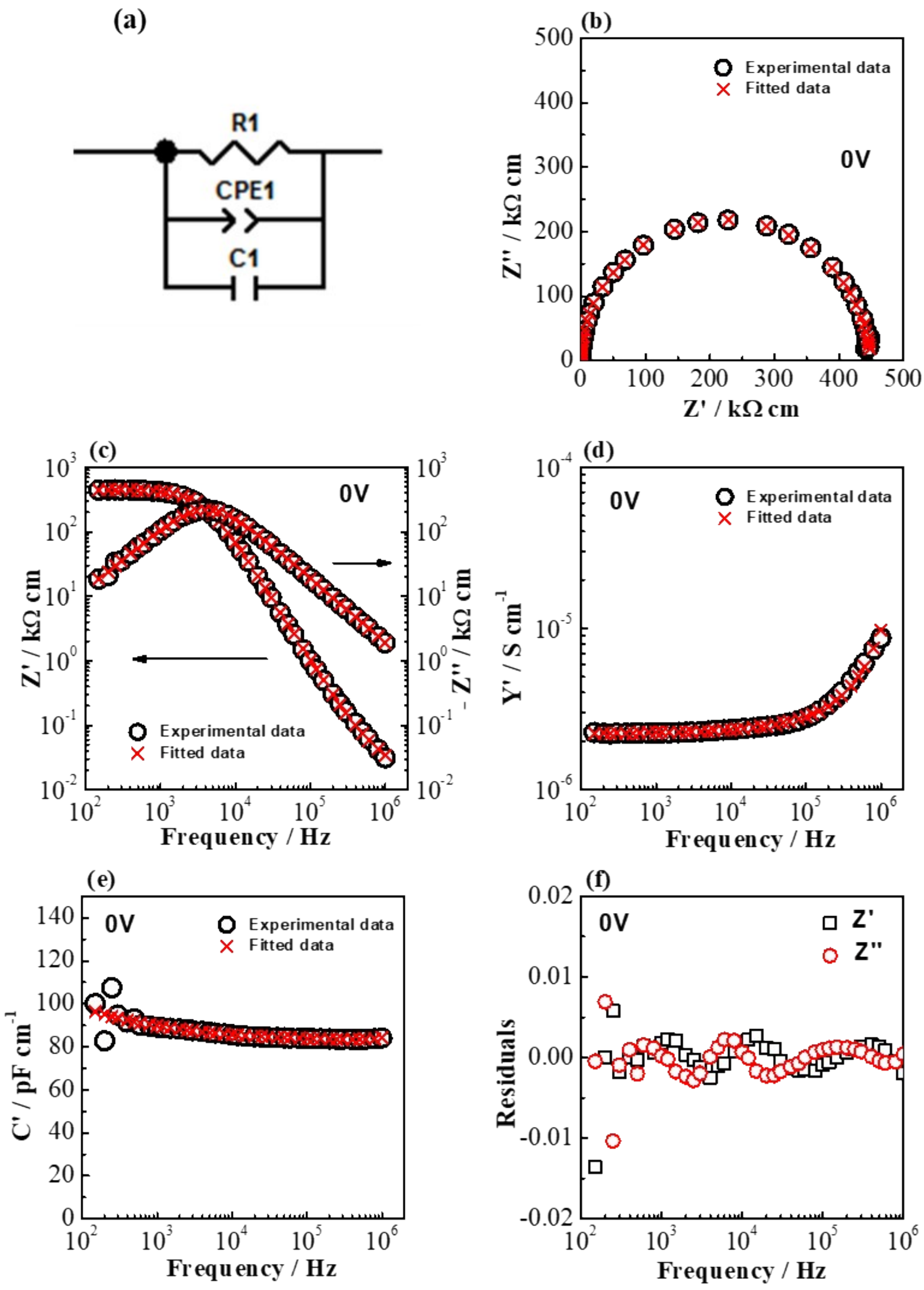

Figure S4. (a) Equivalent circuit used to fit impedance spectra of $NB_{0.51}T$ without dc bias; (b)-(e) impedance and fitting results presented in different formats: (b) Z*, (c) Z'-log*f* and Z''-log*f*, (d) Y'-log*f* and (e) C'-log*f*; (f) impedance residuals showing the quality of fit. Measurement was carried out at 600 °C in air.

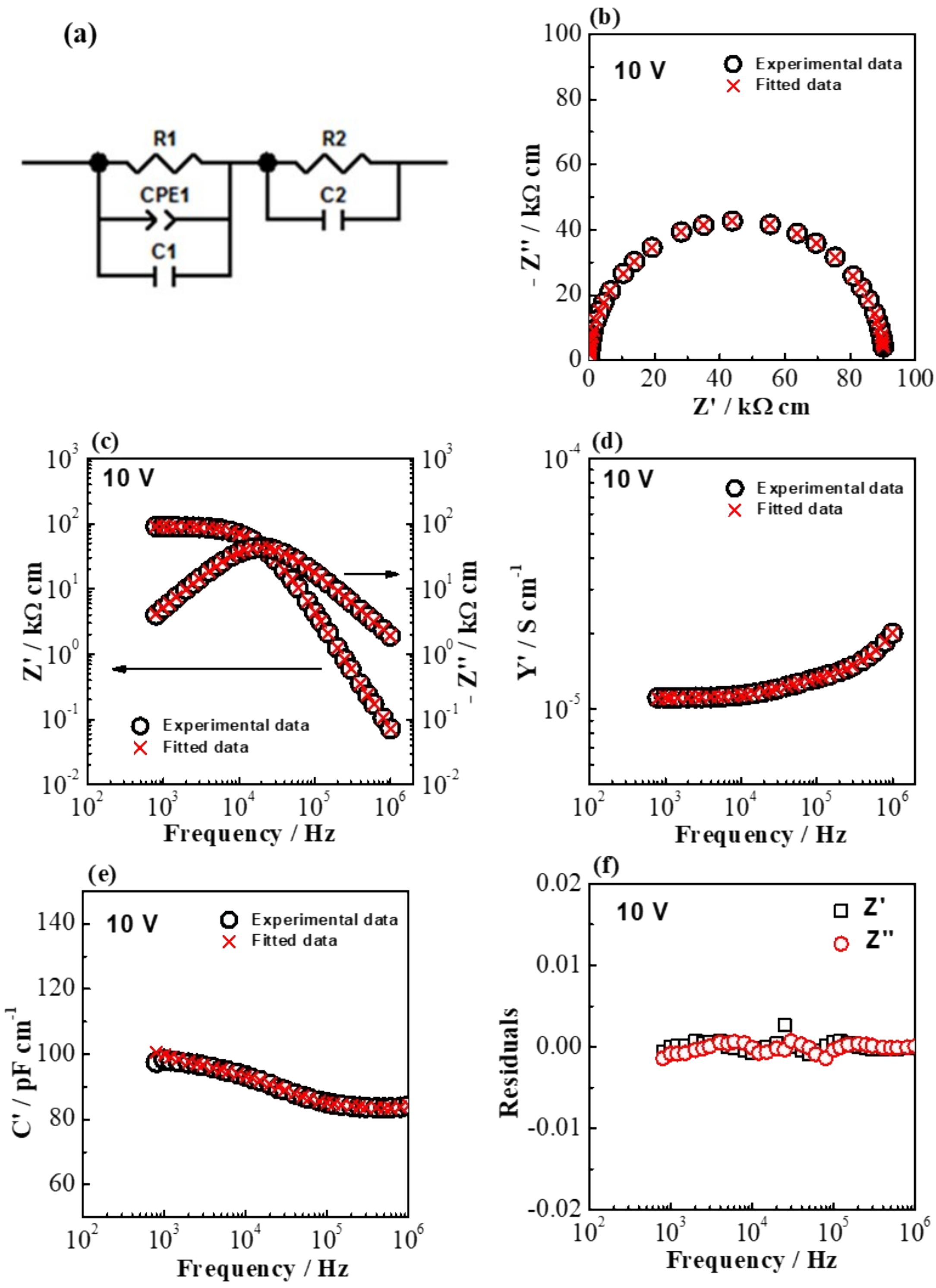

Figure S5. (a) Equivalent circuit used to fit impedance spectra of $NB_{0.51}T$ under dc bias for 30 minutes; (b)- (e) impedance and fitting results presented in different formats: (b) Z*, (c) Z'-log*f* and Z''-log*f*, (d) Y'-log*f* and (e) C'-log*f*; (f) impedance residuals showing the quality of fit. Measurement was carried out at 600 °C in air.

Table S1. Equivalent circuit fitting parameters for $NB_{0.51}T$ without dc bias and under 10 V dc bias for 30 minutes.

	R_1 (kΩ cm)	Q_1 (pS cm^{-1} Hz^{-n})	n_1	C_1 (pF cm^{-1})	R_2 (kΩ cm)	C_2 (pF cm^{-1})
0 V	450.45 ± 0.43	213.80 ± 35.49	0.63 ± 0.02	82.47 ± 0.12	NA	NA
10 V 30 min	80.43 ± 0.50	114.30 ± 9.92	0.82 ± 0.01	98.45 ± 0.61	10.20 ± 0.48	391.05 ± 3.28