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

Supplementary Information

Oxygen vacancy redistribution and ferroelectric polarization relaxation on epitaxial perovskite film during the electrocatalytic process

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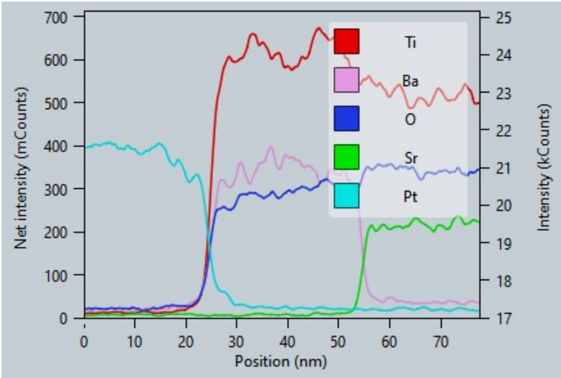

Figure S1. The EDS line scan of STO/BTO/Pt film.

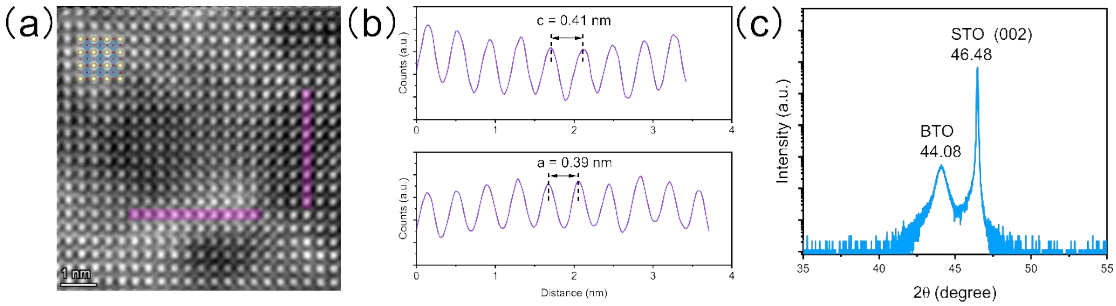

Figure S2. Lattice parameters of epitaxial BTO film. (a) Gaussian filter-corrected HAADF-STEM image. (b) The corresponding intensity profiles in the vertical and horizontal directions in (a). (c) The 2θ-ω XRD scan.

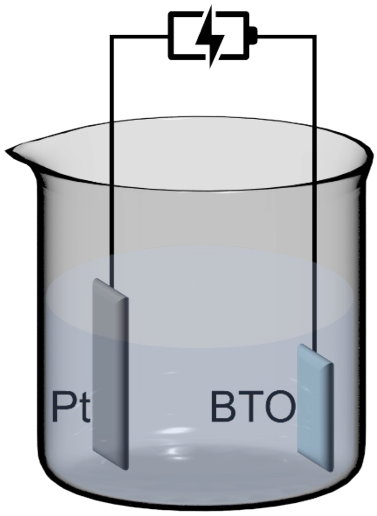

Figure S3. Illustration of ferroelectric polarization with an electrochemical method. When the positive bias is applied to BTO, the ferroelectric polarization of BTO is positive, otherwise, negative.

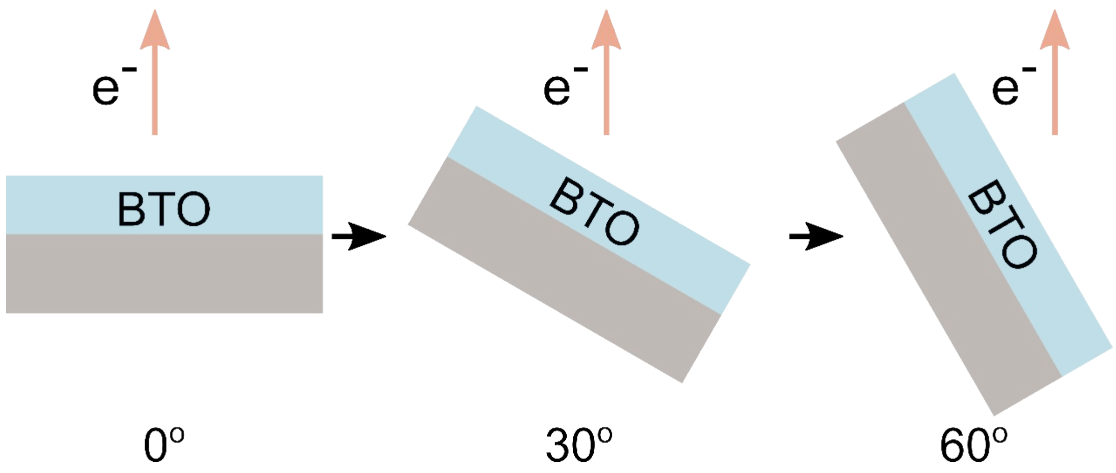

Figure S4. Illustration of AR-XPS with a tilt angle from 0° to 60°.

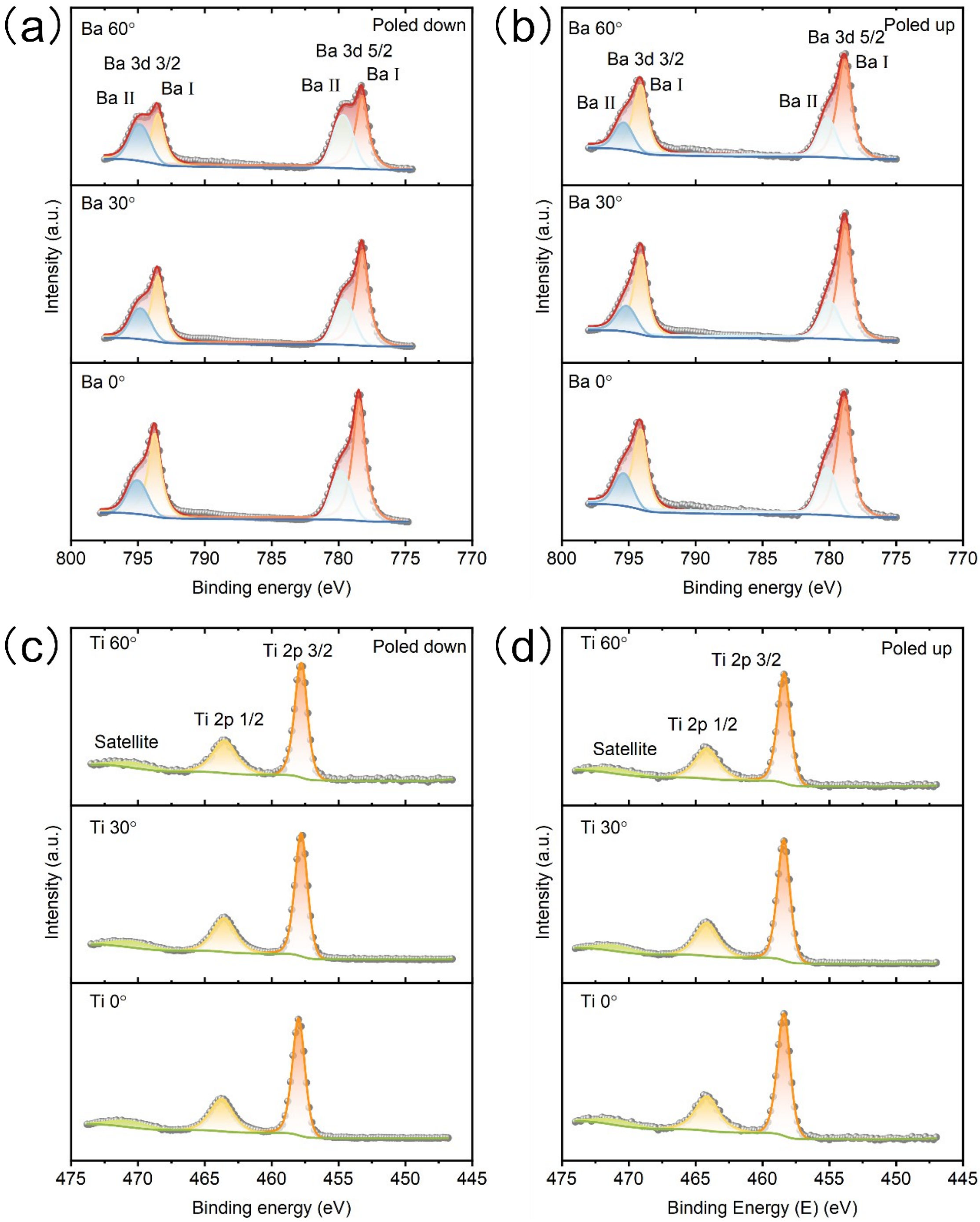

Figure S5. AR-XPS measurements of BTO film. Ba 3d high-resolution XPS spectra after poled down (a) and poled up (b). Ti 2p high-resolution XPS spectra after poled down (c) and poled up (d).

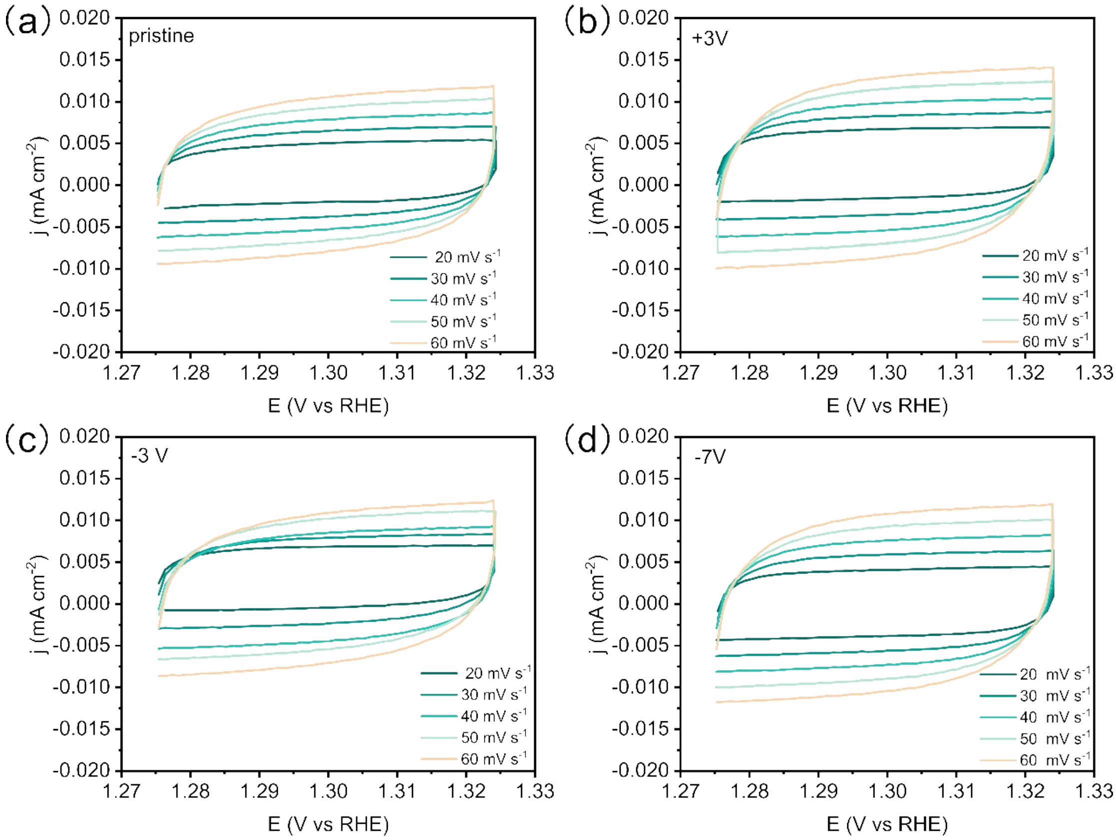

Figure S6. CV tests under different scan rates: (a) pristine BTO film, (b) + 3V poled-up BTO film, (c) -3V, and (d) -7V poled-down BTO film.

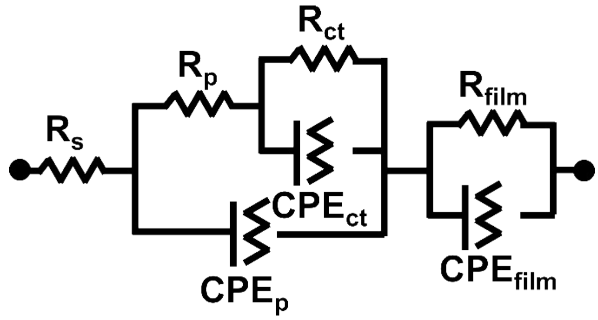

Figure S7. Equivalent circuit for modeling the measured EIS. This mode considers the dielectric property more suitable for the ferroelectric film system[1,2]. R_s is the solution resistance. R_p and R_{ct} refer to the resistance of adsorption and the interfacial charge transfer. CPE_{ct} and CPE_p represent the relaxation of the charge associated with the adsorbed intermediate and the double-layer capacitance, respectively. R_{film} and CPE_{film} model the resistance and dielectric properties of BTO film, respectively.

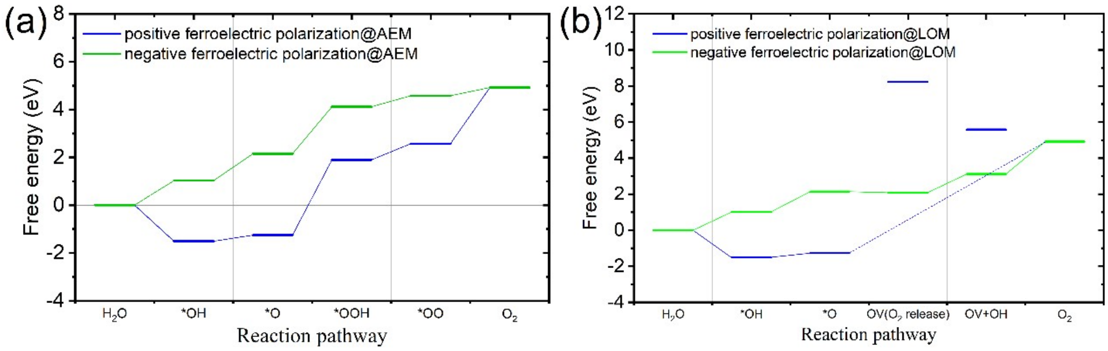

Figure S8. Free energy profile of OER over positive and negative ferroelectric polarization with adsorbate evolution mechanism (AEM) (a) and lattice oxygen mechanism (LOM) (b).

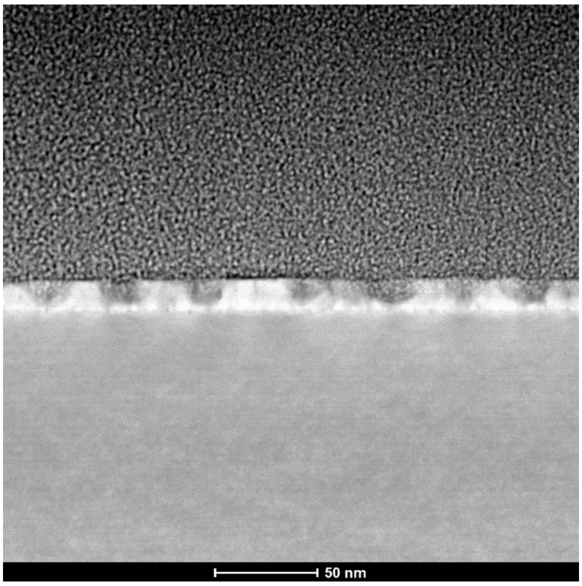

Figure S9. TEM image of BTO film after long time OER performance.

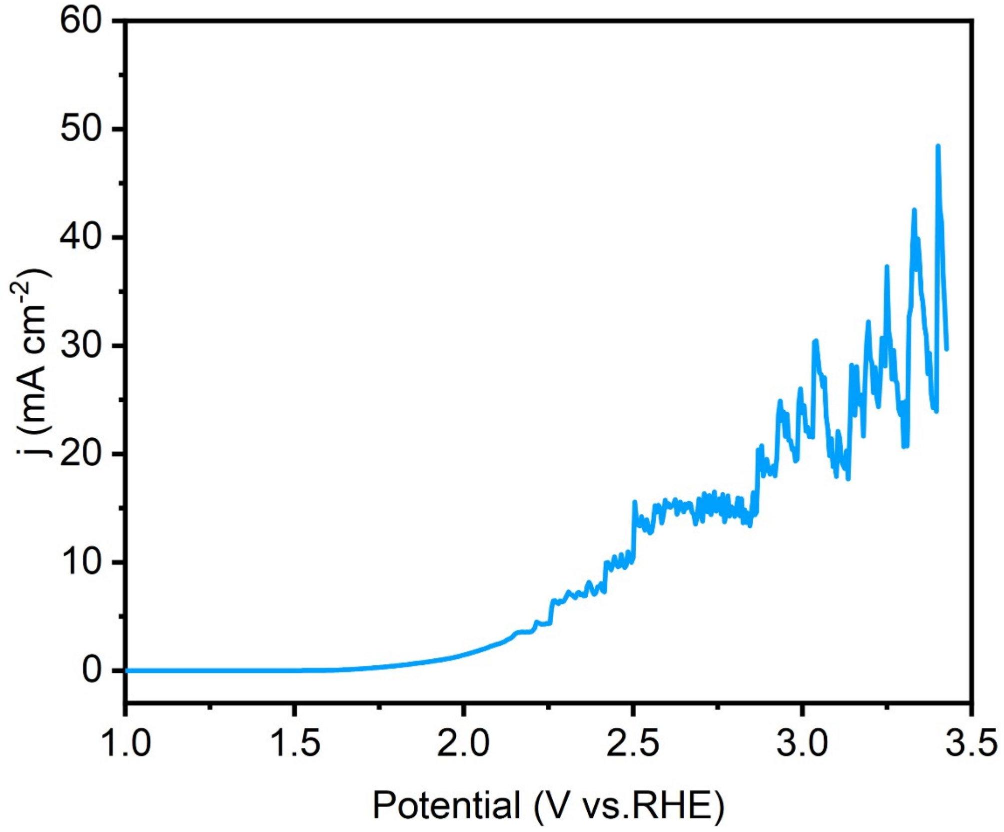

Figure S10. LSV of BTO film within a large range of potential.

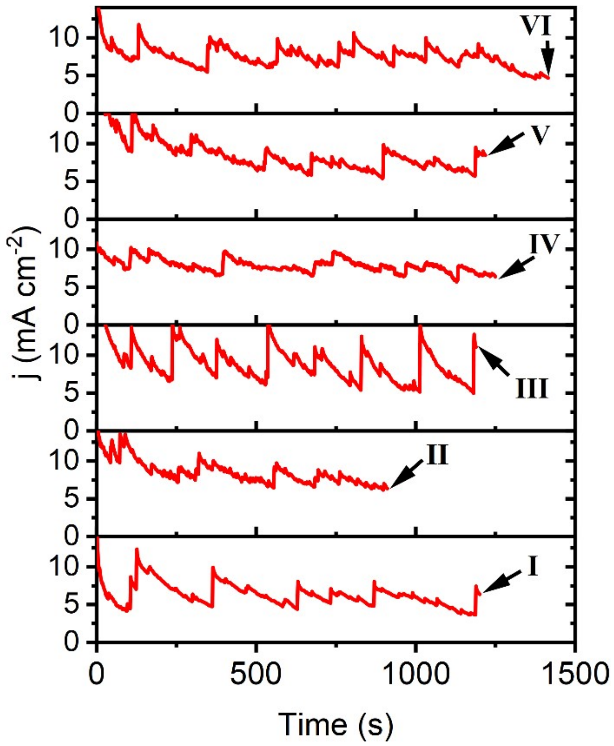

Figure S11. CA response of BTO film stopped at different times under 2.262 V (vs. RHE). I, III, and V for the highest current density, while II, IV, and VI for lowest current density.

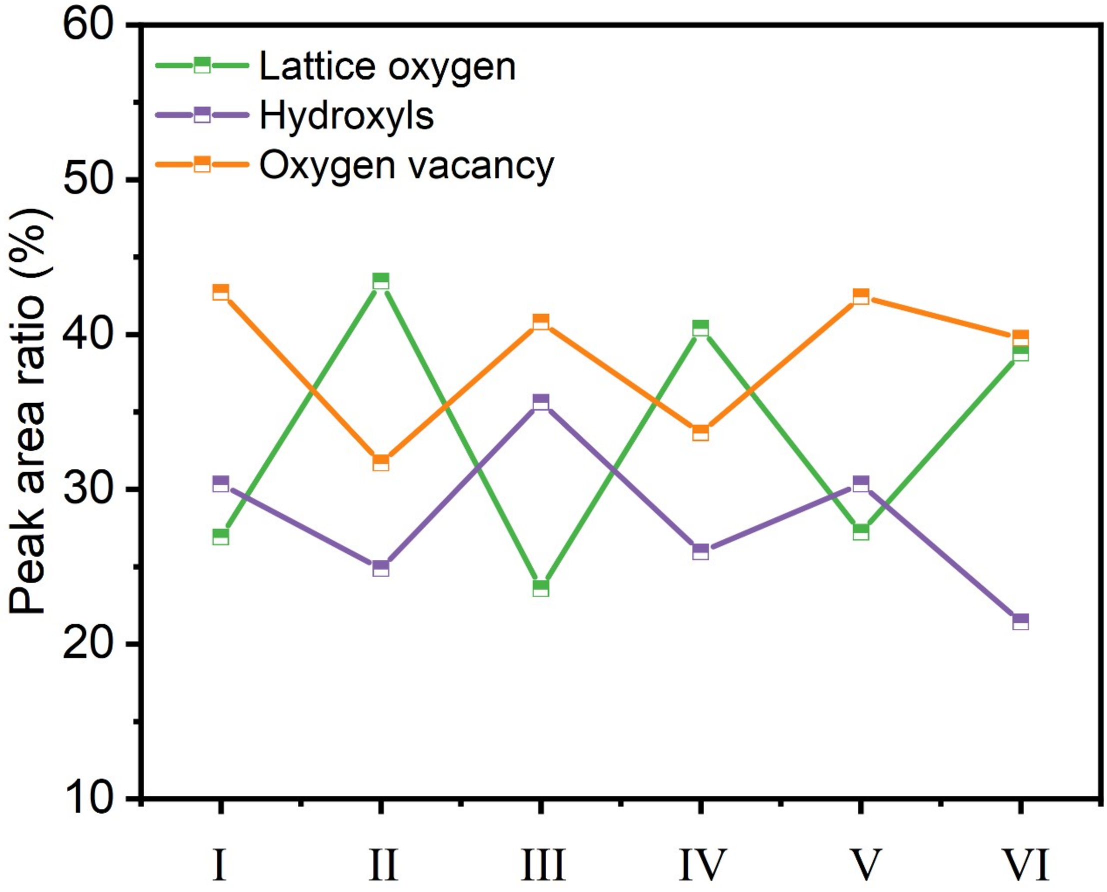

Figure S12. Evolution of lattice oxygen, hydroxyls, and oxygen vacancy of BTO film at different points on the CA curve.

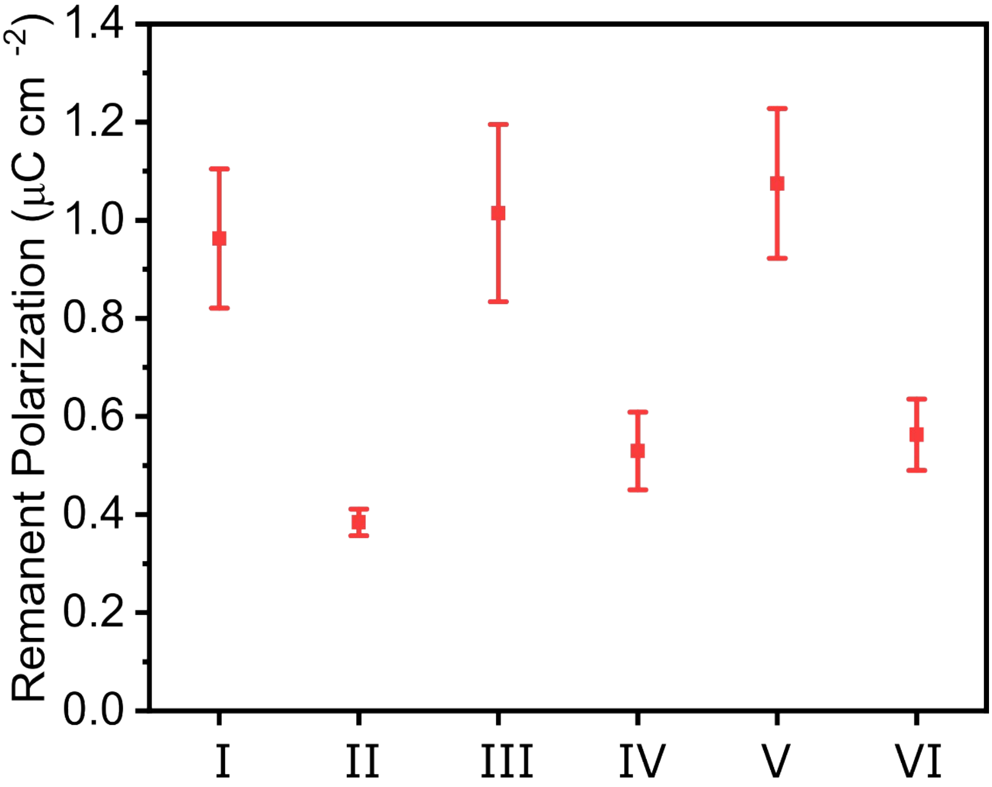

Figure S13. Remanent polarization extracted from P-E loops.

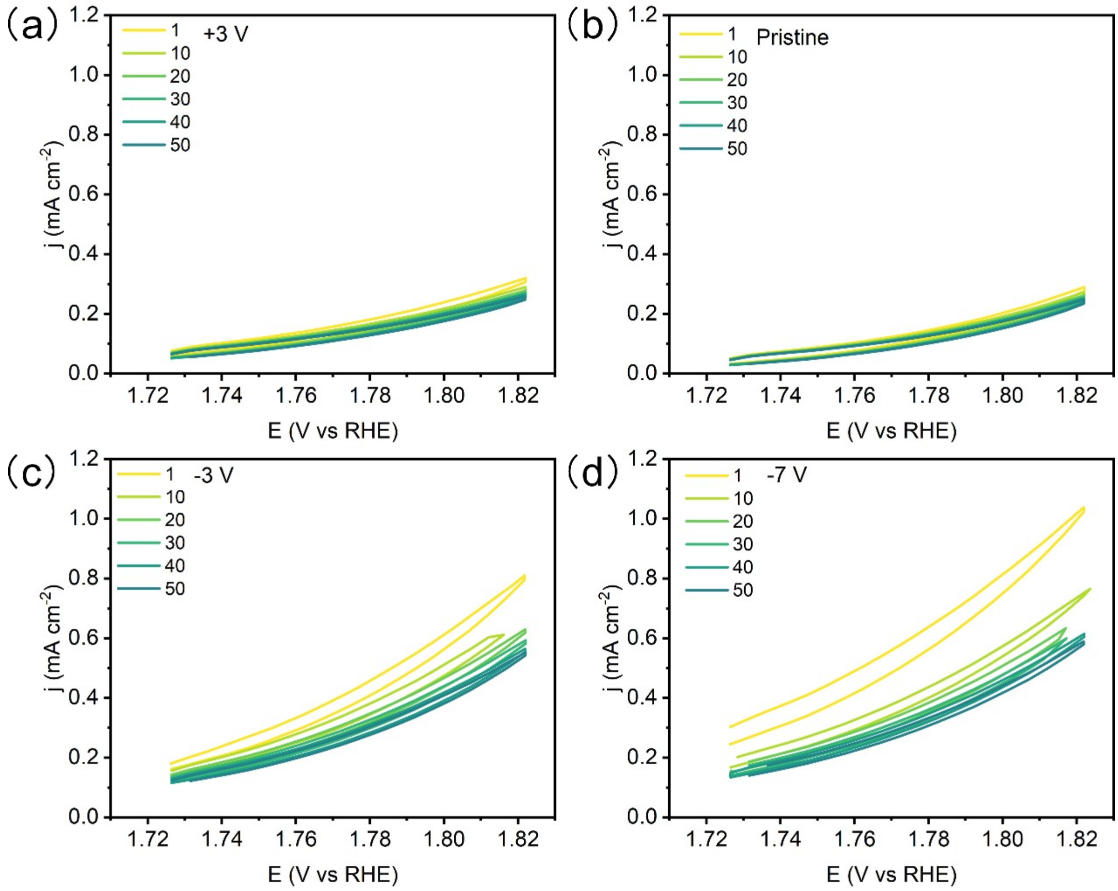

Figure S14. Time dependent CV test of BTO film with different ferroelectric polarization. The number is the circle of CV tests.

Table S1. Parameters of EIS fitting data for BTO film with different ferroelectric polarizations.

	R_p (Ω)	R_{ct} (Ω)	CPE_{ct} (mF)	CPE_p (mF)	R_{film} (Ω)	CPE_{film} (mF)
+3V	12	2156	0.06	0.0055	221	0.14
pristine	13	1195	0.08	0.01	512	0.16
-3V	4	984	0.11	0.0002	226	0.12
-7V	22	32	0.12	0.0029	366	0.12

Table S2. Comparison of OER performance of BTO film with other ferroelectric film catalysts.

Electrocatalysts	Tafel ($mv\ dec^{-1}$)	Overpotential ($10\ mA\ cm^{-2}$)	Reference
$BaTiO_3$	90		This work
$K_{0.4}Sr_{0.4}Ba_{0.4}Nb_{1.7}Co_{0.3}O_{6-\delta}$		40	Advanced Functional Materials, 2023, 33(6): 2210194.
$Bi_5CoTi_3O_{15}$ with in-situ $BiCoO_3$	320	34	Nature communications, 2019, 10(1): 1409.
$SrIrO_3/Pb(Mg_{1/3}Nb_{2/3})_{0.7}Ti_{0.3}O_3$	83.5	316	Physical Chemistry Chemical Physics, 2023, 25(36): 24976-24984.

Supplementary References

1 Z. Xiao, Y. C. Huang, C. L. Dong, C. Xie, Z. Liu, S. Du, W. Chen, D. Yan, L. Tao, Z. Shu, G. Zhang, H. Duan, Y. Wang, Y. Zou, R. Chen, S. Wang, J Am Chem Soc 2020, 142, 12087.

2 M. E. G. Lyons, M. P. Brandon, Journal of Electroanalytical Chemistry 2009, 631, 62.