Supporting Information

Structural Engineering of The Barrier Oxide Layer of Nanoporous Anodic Alumina for Iontronic Sensing

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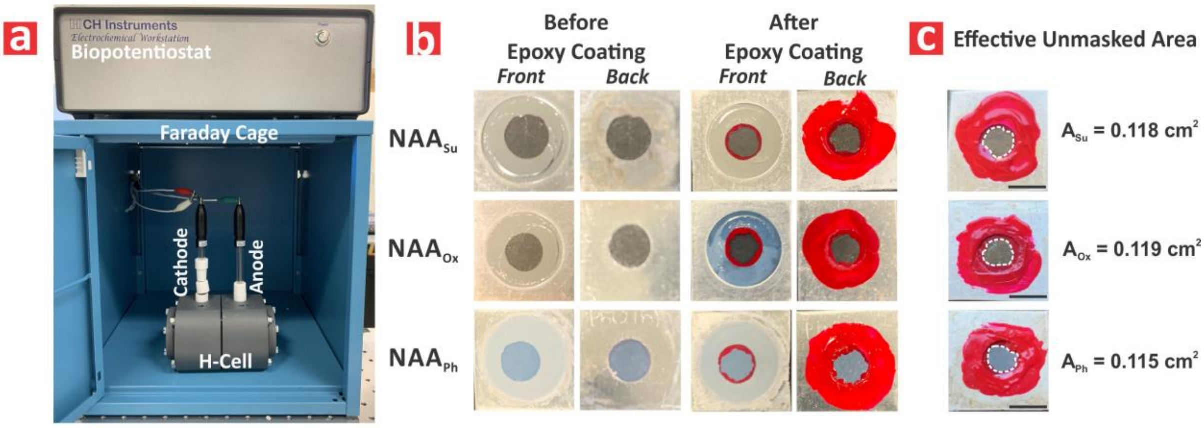

Figure S1. Iontronic characterization of NAA membranes. (a) Iontronic setup showing details of the H-cell comprising two half H cells between which NAA membranes were sandwiched, and electrodes immersed in KCl in each half H cell. (b) Digital pictures of NAA membranes (front and back) before and after coating. (c) Measurement of effective unmask area outlined by white dotted lines of three representative NAA membranes (scale bars: 0.5 cm; image analysis was performed using ImageJ).

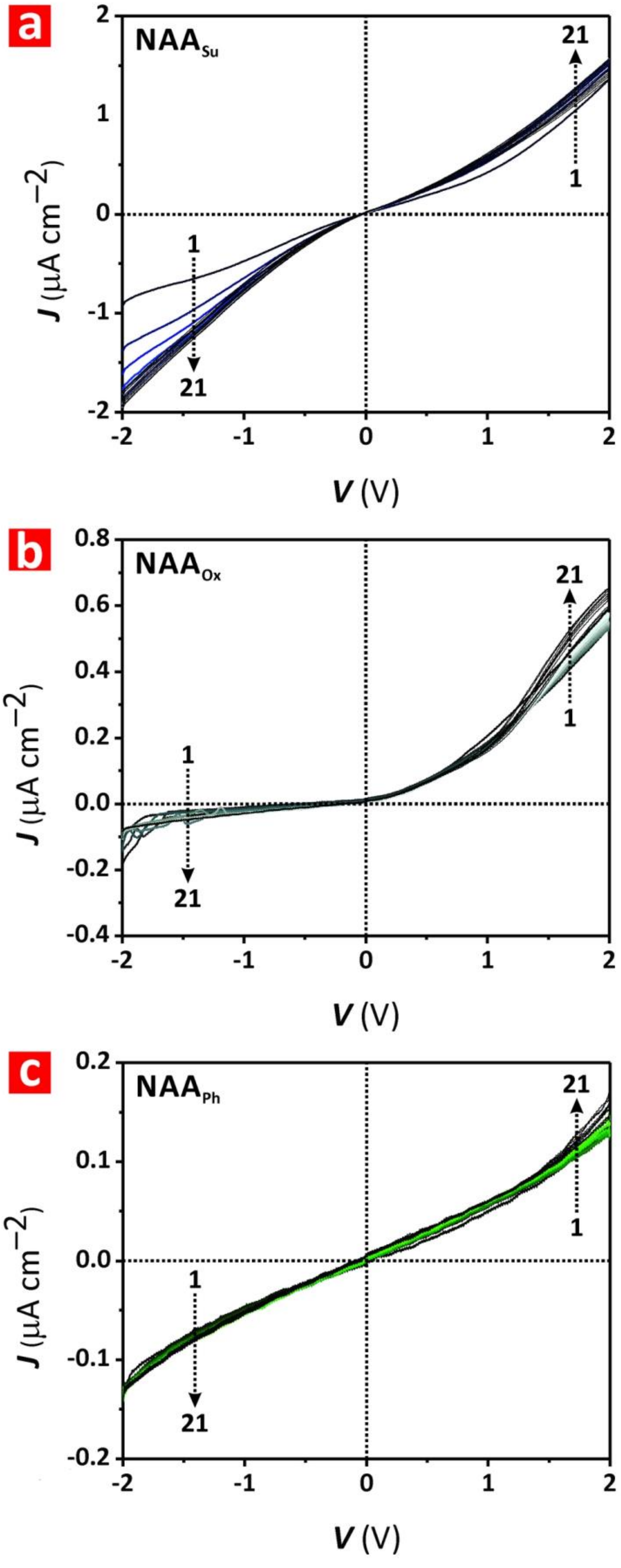

Figure S2. Dynamic change in ionic *J*–*V* characteristic in Milli–Q water during 21 cycles of the reset process for NAA membranes produced by the two-step anodization process in (a) sulfuric, (b) oxalic, and (c) phosphoric acid electrolytes.

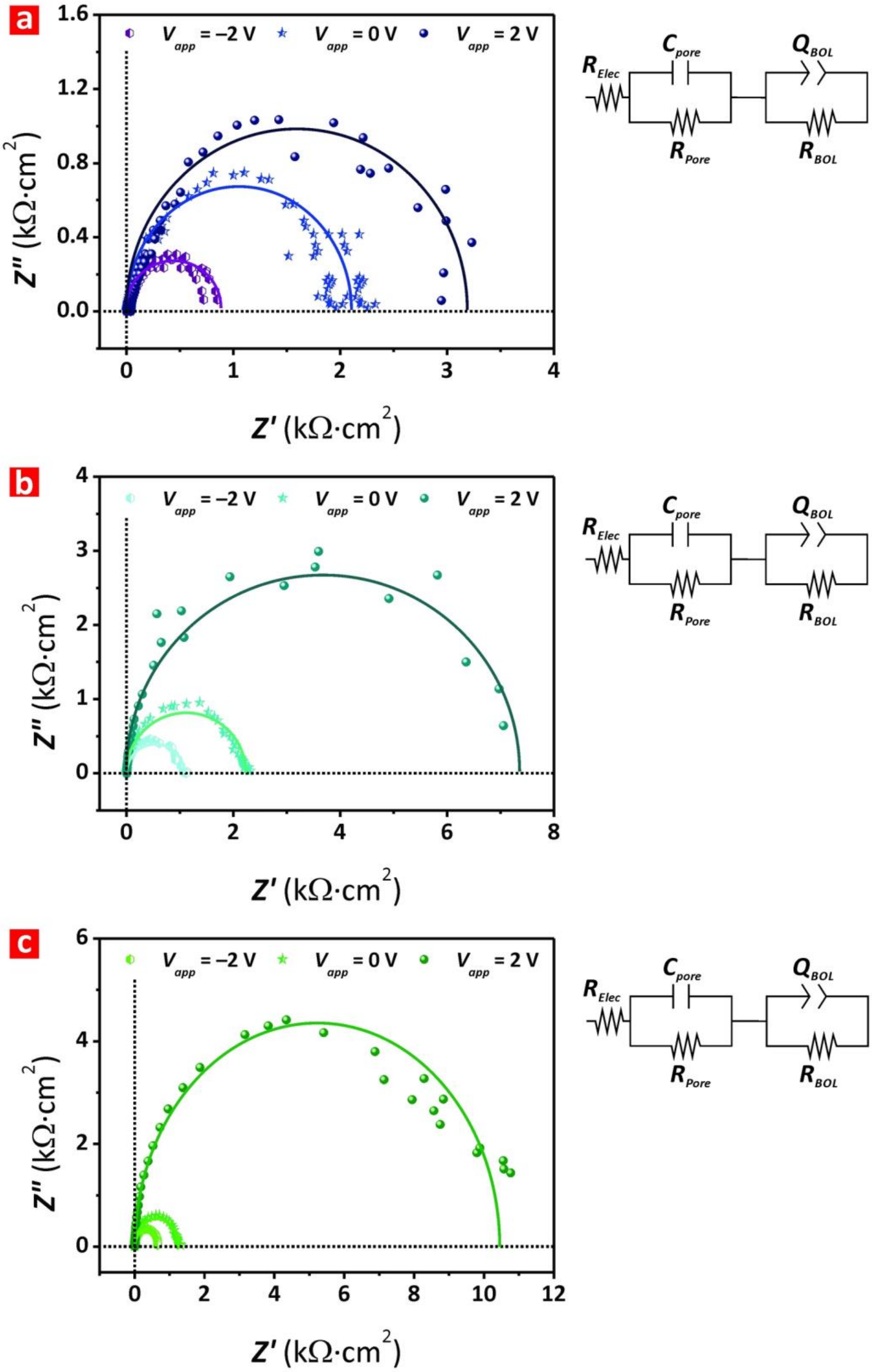

Figure S3. Nyquist impedance spectra and fitting lines of as-produced blind-hole NAA membranes in 0.1 M KCl electrolyte along with the equivalent circuit used to estimate key electronic parameters (NB: R_{Elec} = electrolyte resistance, R_{Pore} = nanopore resistance, R_{BOL} = barrier oxide layer resistance, Q_{Pore} = nanopore capacitance, and Q_{BOL} = barrier oxide layer capacitance). (a) NAA_{Su} membranes at V_{app} = –2 V, 0 V, and 2 V. (b) $NAA0_{Ox}$ membranes at V_{app} = –2 V, 0 V, and 2 V. (c) NAA_{Ph} membranes at V_{app} = –2 V, 0 V, and 2 V.

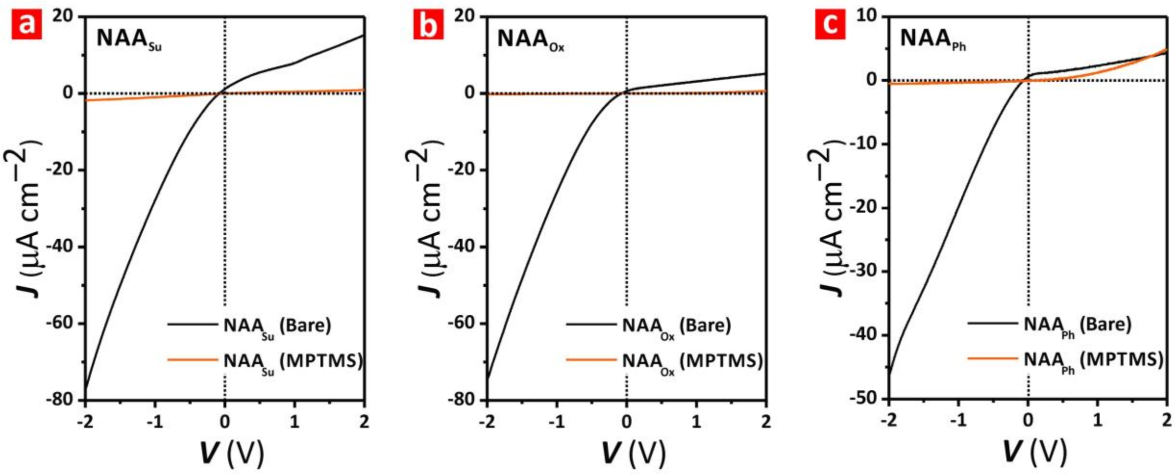

Figure S4. Ionic *J*–*V* characteristic of blind-hole NAA membranes before in 0.1 M KCl at pH = 6 before and after MPTMS functionalization. (a) NAA_{Su} membranes. (b) $NAA0_{Ox}$ membranes. (c) NAA_{Ph} membranes.

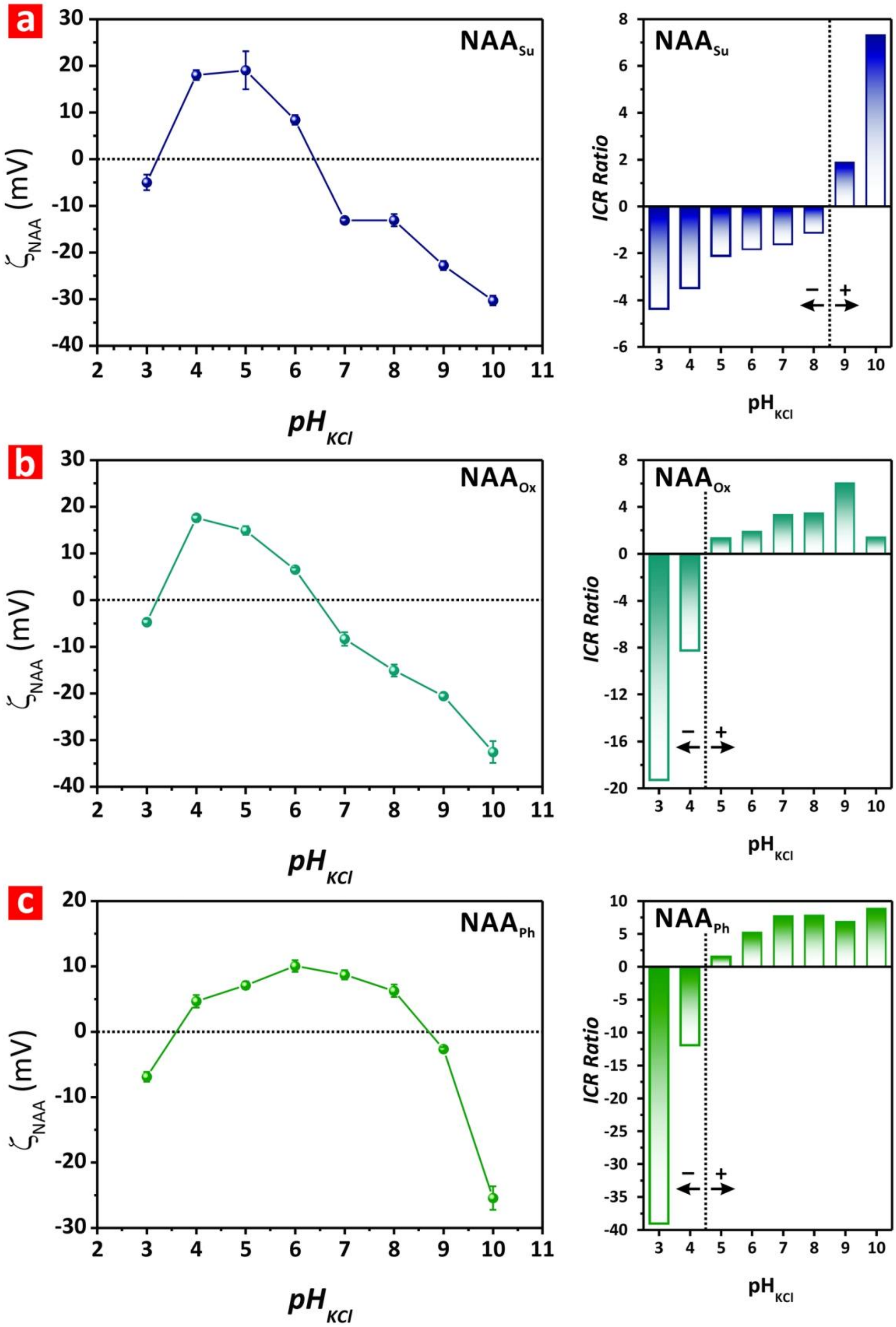

Figure S5. Dependence of zeta potential (ζ_{NAA}) and ionic current rectification (ICR) ratio in engineered MPTMS-functionalized NAA membranes with pH, from 3 to 10, in 0.1 M KCl (NB: all blind-hole NAA membranes were subjected to the reset process prior to J–V characterization). (a) ζ_{NAA} (left) and ICR ratio (right) for NAA$_{Su}$ membranes. (b) ζ_{NAA} (left) and ICR ratio (right) for NAA$_{Ox}$ membranes. (c) ζ_{NAA} (left) and ICR ratio (right) for NAA$_{Ph}$ membranes.

Table S1. Estimated values of key electronic parameters characterizing the impedance spectroscopy analysis shown in **Figure S1** (NB: R_{Elec} = electrolyte resistance, R_{Pore} = nanopore resistance, R_{BOL} = barrier oxide layer resistance, C_{Pore} = nanopore capacitance, C_{Pore} = barrier oxide layer capacitance, Q_{BOL} = barrier oxide layer pseudocapacitance, ε_0 = vacuum permittivity, ε_r = relative permittivity of anodic aluminum oxide, σ_{BOL} = barrier oxide layer conductivity, and n = constant phase element component of the barrier oxide)†.

NAA	V_{app} (V)	R_{Elec} (kΩ·cm²)	R_{Pore} (kΩ·cm²)	R_{BOL} (kΩ·cm²)	C_{Pore} (μF·cm⁻²)	Q_{BOL} (sⁿΩ⁻¹·cm⁻²)	***n***	C_{BOL} (μF·cm⁻²)	σ_{BOL} (nS·cm⁻¹)
NAA_{Su}	–2	0.0048	0.071	0.6	85.1	0.00006	0.919	30.1	0.041
	0	0.0042	0.135	1.8	77.4	0.00008	0.892	30.5	0.015
	2	0.0042	0.126	2.8	79.4	0.00008	0.884	29.9	0.001
NAA_{Ox}	–2	0.0027	0.002	1.0	0.06	0.00001	0.987	9.4	0.085
	0	0.0047	0.418	1.8	37.9	0.00003	0.616	0.1	4.060
	2	0.0049	3.124	4.5	16.9	0.00006	0.890	22.6	0.008
NAA_{Ph}	–2	0.0041	0.252	0.5	7.6	0.000005	0.992	4.3	0.434
	0	0.0041	0.092	1.2	1847.5	0.000003	0.988	2.7	0.240
	2	0.0041	1.124	8.3	94.5	0.00004	0.914	16.0	0.006

†Values estimated from **Equations S1 and S2**

$$C_{BOL} = Q_{BOL}^{1/n} \cdot \left(\frac{1}{R_{Elec}} + \frac{1}{R_{BOL}}\right)^{n-1/n} \tag{S1}$$

$$\sigma_{BOL} = \frac{\varepsilon_r \cdot \varepsilon_0}{R_{BOL} \cdot C_{BOL}} \tag{S2}$$