

Supplementary Information

# The Origin of the Non-Constancy of the Bulk Resistance of Ion-Selective Electrode Membranes within the Nernstian Response Range

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## SUMMARY

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Number of Figures: 3

Number of Tables: 3

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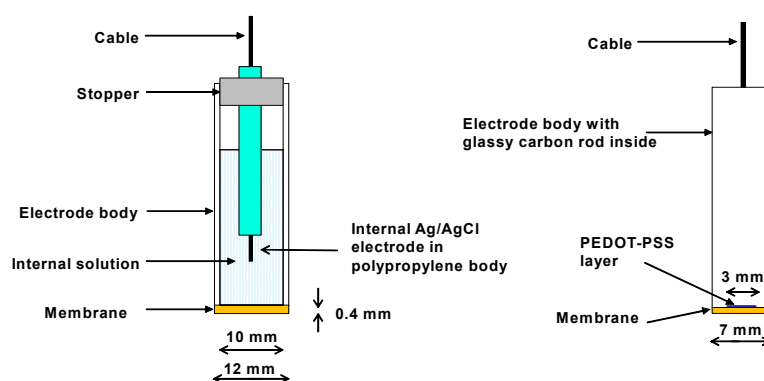
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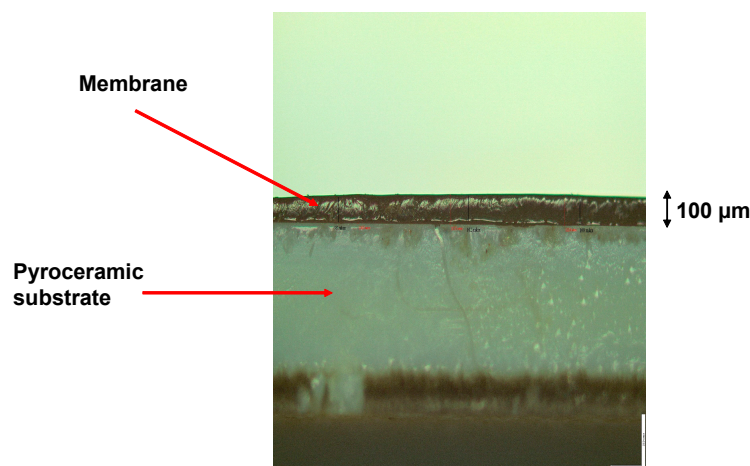
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**Figure S1.** Electrode constructs. Left: classical Ion-Selective Electrode (ISE) with internal reference solution and internal reference electrode. Right: solid-contact electrode.



**Figure S2.** Cross-section of the membrane with thickness of 100  $\mu\text{m}$  on a pyroceramic substrate.

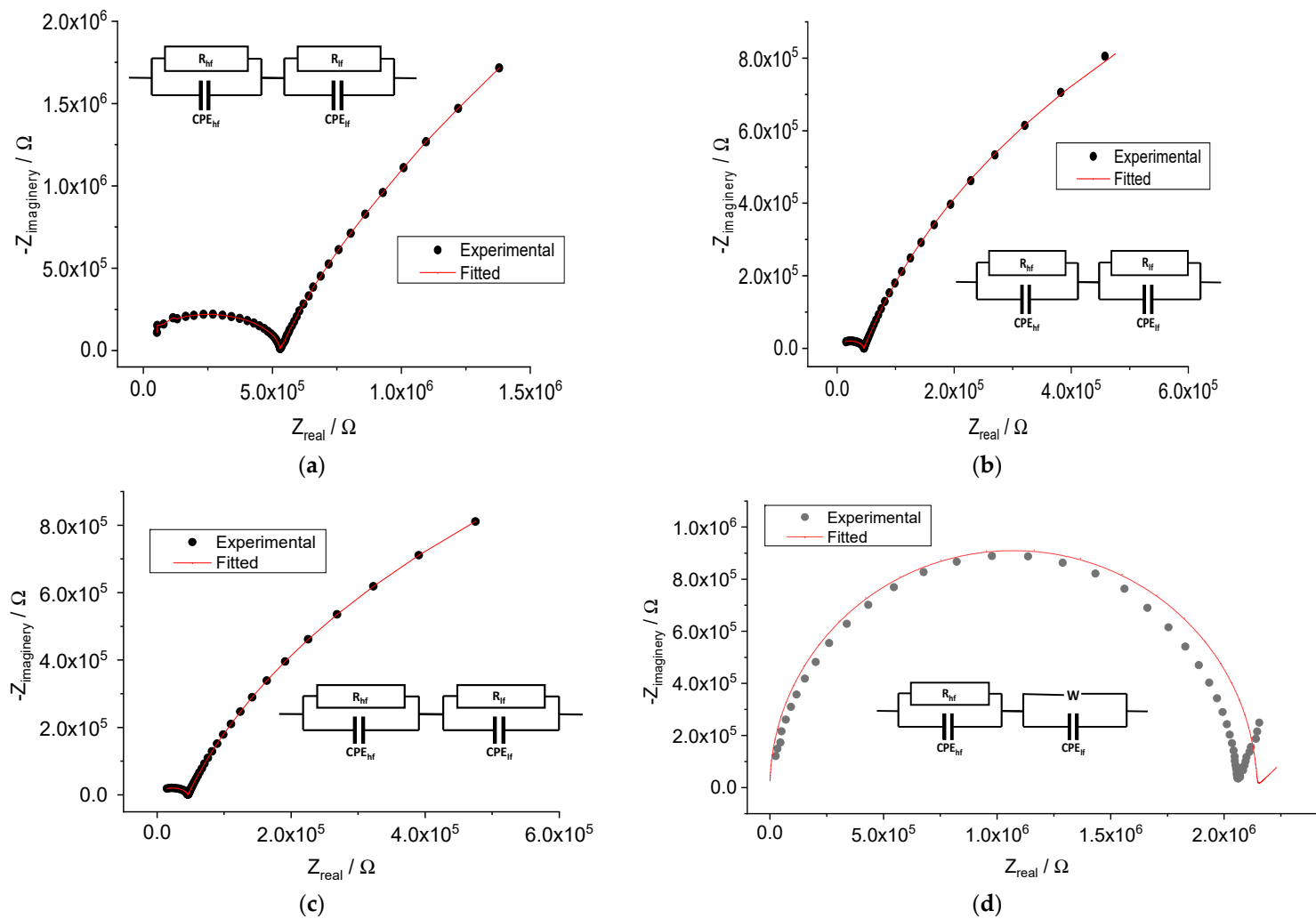
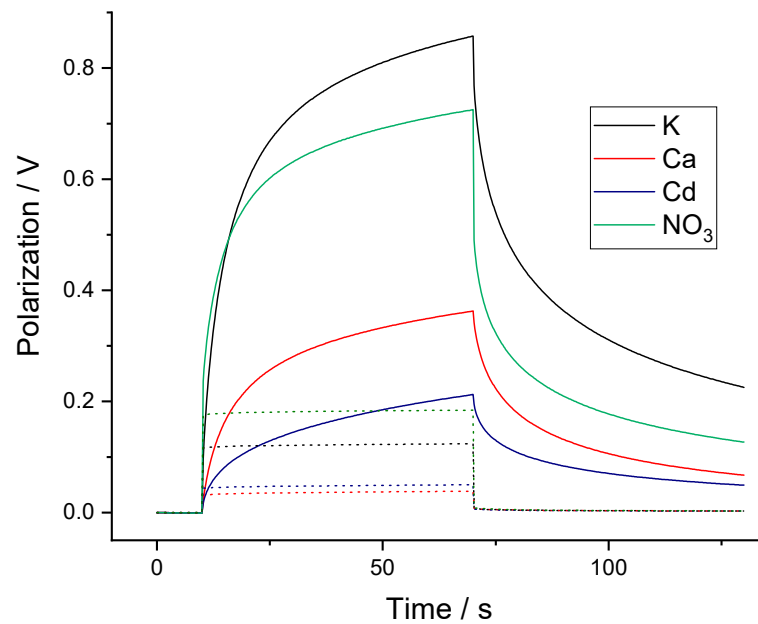


Figure S3. Nyquist plots of the impedance spectra of dry membranes. (a) K<sup>-</sup>; (b) Ca; (c) Cd; (d) NO<sub>3</sub>.



**Figure S4.** Chronopotentiometric curves (“slow” protocol) obtained by passing current with density of  $1.27 \cdot 10^{-7}$  A/cm<sup>2</sup> across dry membranes (solid lines) and membranes equilibrated with Solution #10 (dotted lines).

**Table S1.** Ohmic drops (V) registered in “fast” and “slow” chronopotentiometric measurements, and S/F: the ratio of the value obtained in “slow” protocol over that obtained in “fast” protocol.

logTCI	logIS	K-ISE			Ca-ISE			Cd-ISE			NO <sub>3</sub> -ISE		
		Fast	Slow	S/F	Fast	Slow	S/F	Fast	Slow	S/F	Fast	Slow	S/F
-1.02	-1.28	0.107	0.109	1.02	0.019	0.019	1.02	0.025	0.026	1.02	0.180	0.180	1.01
-1.28	-1.46	0.134	0.138	1.03	0.029	0.030	1.03	0.028	0.028	1.03	0.173	0.177	1.03
-1.46	-1.47	0.108	0.110	1.02	0.020	0.020	1.00	0.025	0.026	1.03	0.175	0.177	1.02
-1.78	-1.88	0.107	0.109	1.02	0.019	0.019	1.02	0.026	0.026	1.02	0.180	0.185	1.03
-1.79	-1.79	0.115	0.117	1.02	0.025	0.025	1.01	0.025	0.026	1.03	0.155	0.159	1.02
-2.27	-2.37	0.098	0.101	1.03	0.017	0.018	1.03	0.024	0.025	1.02	0.156	0.160	1.03
-2.65	-2.94	0.109	0.111	1.02	0.020	0.020	1.03	0.028	0.029	1.02	0.152	0.156	1.02
-2.75	-2.86	0.113	0.113	1.01	0.021	0.022	1.02	0.028	0.029	1.02	0.155	0.157	1.01
-2.82	-3.03	0.117	0.120	1.02	0.021	0.022	1.02	0.031	0.031	1.01	0.163	0.164	1.00
-3.57	-3.82	0.113	0.116	1.03	0.030	0.031	1.03	0.043	0.044	1.02	0.170	0.176	1.03
-4.15	-4.30	0.168	0.172	1.02	0.067	0.069	1.02	0.083	0.086	1.03	0.255	0.259	1.01
Dry membranes		0.047	0.058	0.059	1.03	0.053	0.054	1.03	0.006	0.006	1.03	0.125	1.02

**Table S2.** Resistivity of the ISE membranes (MΩ·m) obtained by chronopotentiometric (fast protocol) and impedance measurements.

log(TCI)	log(IS)	K-ISE		Ca-ISE		Cd-ISE		NO <sub>3</sub> -ISE	
		Chrono-potentiometry	Impedance	Chrono-potentiometry	Impedance	Chrono-potentiometry	Impedance	Chrono-potentiometry	Impedance
-1.02	-1.28	0.171	0.166	0.025	0.025	0.055	0.054	0.395	0.391
-1.28	-1.46	0.214	0.213	0.038	0.037	0.060	0.059	0.380	0.377
-1.46	-1.47	0.172	0.169	0.026	0.024	0.055	0.053	0.384	0.380
-1.78	-1.88	0.171	0.171	0.025	0.024	0.056	0.055	0.396	0.388
-1.79	-1.79	0.184	0.180	0.033	0.032	0.054	0.053	0.341	0.336
-2.27	-2.37	0.157	0.150	0.023	0.022	0.052	0.050	0.343	0.331
-2.65	-2.94	0.174	0.169	0.026	0.025	0.061	0.060	0.335	0.329
-2.75	-2.86	0.180	0.178	0.028	0.027	0.061	0.060	0.341	0.335
-2.82	-3.03	0.187	0.183	0.028	0.027	0.067	0.065	0.359	0.349
-3.57	-3.82	0.181	0.178	0.040	0.039	0.093	0.092	0.375	0.372
-4.15	-4.30	0.268	0.266	0.089	0.083	0.180	0.169	0.562	0.536
Dry membrane		0.092	0.090	0.070	0.069	0.012	0.012	0.274	0.273

**Table S3.** Water uptake (weight %) by the membranes equilibrated with mixed solutions.

log(TCI)	K-membrane		Ca-membrane		Cd-membrane		NO <sub>3</sub> -membrane	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
-1.02	0.32	0.30	2.59	0.36	4.05	0.24	0.40	0.27
-1.28	0.33	0.26	2.55	0.25	4.18	0.35	0.36	0.19
-1.46	0.34	0.17	2.58	0.36	4.07	0.34	0.40	0.20
-1.78	0.34	0.17	2.60	0.26	4.05	0.37	0.48	0.22
-1.79	0.34	0.27	2.67	0.27	4.26	0.35	0.57	0.28
-2.27	0.37	0.19	2.51	0.27	4.39	0.36	0.33	0.31
-2.65	0.40	0.30	2.81	0.24	4.36	0.33	0.36	0.39
-2.75	0.40	0.20	2.81	0.28	4.37	0.36	0.41	0.32
-2.82	0.42	0.21	2.80	0.29	4.47	0.37	0.59	0.17
-3.57	0.50	0.36	3.04	0.31	4.80	0.37	1.00	0.24
-4.15	0.59	0.29	3.42	0.24	5.35	0.44	1.71	0.42