Online Supplementary Material for:

Ion and Particle Size Effects on the Surface Reactivity of Anatase Nanoparticle–Aqueous Electrolyte Interfaces: Experimental, Density Functional Theory, and Surface Complexation Modeling Studies

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Table S1. Fitting parameters for the SCM for each anatase sample, in each electrolyte media. The particle size are in nm, capacitance values are in units of farad per m^2, also included are the MSC values.[1]

Particle Size	Electrolyte Media	C_1	Inner-sphere log K	Inner-sphere Complex	CD	C_2	Outer-sphere log K $\equiv TiOH^{-0.3}\cdots M^+$	Outer-sphere log K $\equiv Ti_2O^{-0.7}\cdots M^+$	Outer-sphere log K $\equiv TiOH_2^{+0.7}\cdots A^-$	Outer-sphere log K $\equiv Ti_2OH^{+0.3}\cdots A^-$	C_S	MSC
4	LiCl	0.9 ± 0.2	-0.5 ± 0.6	Bidentate, terminal	0.46 ± 0.71	3.9 ± 4.6	-2.0	-0.31 ± 0.21	-1.8	-0.4 ± 0.2	0.73	5.15
4	NaCl	0.9 ± 0.2	-1.3 ± 0.7	Bidentate, bridged	0.36 ± 0.59	3.9 ± 3.3	-2.0	-0.11 ± 0.08	-1.8	-0.2 ± 0.09	0.73	4.10
4	NaTr	0.9 ± 0.3	-1.3 ± 2.8	Bidentate, bridged	0.36 ± 1.9	3.9 ± 7.8	-2.0	-0.11 ± 0.26	-1.8	-1.3 ± 2.8	0.73	5.47
4	KCl	0.9 ± 0.4	-1.2 ± 2.1	Tetradentate	0.55 ± 2.7	3.9 ± 8.1	-2.0	-0.11 ± 0.12	-1.8	-0.5 ± 0.2	0.73	4.83
4	RbCl	0.9 ± 2.4	-2.1 ± 10	Tetradentate	0.50 ± 5.5	3.9 ± 45	-2.0	-0.11 ± 0.17	-1.8	-0.5 ± 0.2	0.73	5.37
20	LiCl	1.2 ± 0.2	-0.45 ± 0.6	Bidentate, terminal	0.46 ± 0.64	3.0 ± 1.5	-2.0	-0.31 ± 0.25	-1.8	-0.5 ± 0.3	0.86	6.17
20	NaCl	1.1 ± 0.1	-1.3 ± 0.4	Bidentate, bridged	0.36 ± 0.26	3.9 ± 1.2	-2.0	-0.11 ± 0.07	-1.8	-0.2 ± 0.1	0.86	4.89
20	NaTr	1.1 ± 0.2	-1.3 ± 2.1	Bidentate, bridged	0.36 ± 1.3	3.9 ± 4.1	-2.0	-0.11 ± 0.28	-1.8	-0.7 ± 0.9	0.86	5.65
20	KCl	1.3 ± 0.5	-1.3 ± 2.0	Tetradentate	0.55 ± 2.3	3.9 ± 4.8	-2.0	-0.11 ± 0.10	-1.8	-0.6 ± 0.2	0.97	4.81
20	RbCl	1.1 ± 3.0	-1.8 ± 7.8	Tetradentate	0.50 ± 3.3	3.9 ± 38	-2.0	-0.11 ± 0.24	-1.8	-0.5 ± 0.3	0.86	5.21
40	LiCl	1.5 ± 0.3	-0.5 ± 0.7	Bidentate, terminal	0.50 ± 0.66	3.0 ± 1.4	-2.0	-1.50 ± 1.86	-1.8	-0.2 ± 0.2	1.00	5.19
40	NaCl	1.3 ± 0.2	-1.3 ± 1.0	Bidentate, bridged	0.36 ± 0.63	3.9 ± 1.8	-2.0	-0.11 ± 0.13	-1.8	-0.2 ± 0.1	0.97	4.36
40	NaTr	1.2 ± 0.4	-1.3 ± 2.4	Bidentate, bridged	0.36 ± 1.4	3.9 ± 4.2	-2.0	-0.11 ± 0.31	-1.8	-0.5 ± 0.4	0.92	6.02
40	KCl	1.3 ± 0.3	-1.3 ± 1.6	Tetradentate	0.50 ± 1.8	3.9 ± 3.2	-2.0	-0.11 ± 0.08	-1.8	-0.3 ± 0.1	0.97	5.53
40	RbCl	1.1 ± 1.7	-1.8 ± 4.6	Tetradentate	0.50 ± 1.8	3.9 ± 21	-2.0	-0.11 ± 0.16	-1.8	-0.1 ± 0.1	0.86	5.14

[1] All log K values reflect infinite dilution. There are no error estimates for the outer-sphere log $K \equiv TiOH^{-0.3}\cdots M^+$ and log $K \equiv TiOH_2^{+0.7}\cdots A^-$ values because they were held constant for all data fitting.

Figure S1. Periodic model of anatase (101) surface with Rb^+ as a bidentate surface complex following energy minimization. The cell stoichiometry is $Ti_{48}O_{96} + 62H_2O + Rb^+ + Cl^-$, in a $15.224 \times 10.4516 \times 30.0$ Å cell. Ti atoms are in gray, O atoms red, H atoms white, Rb ion purple, and Cl ion green.
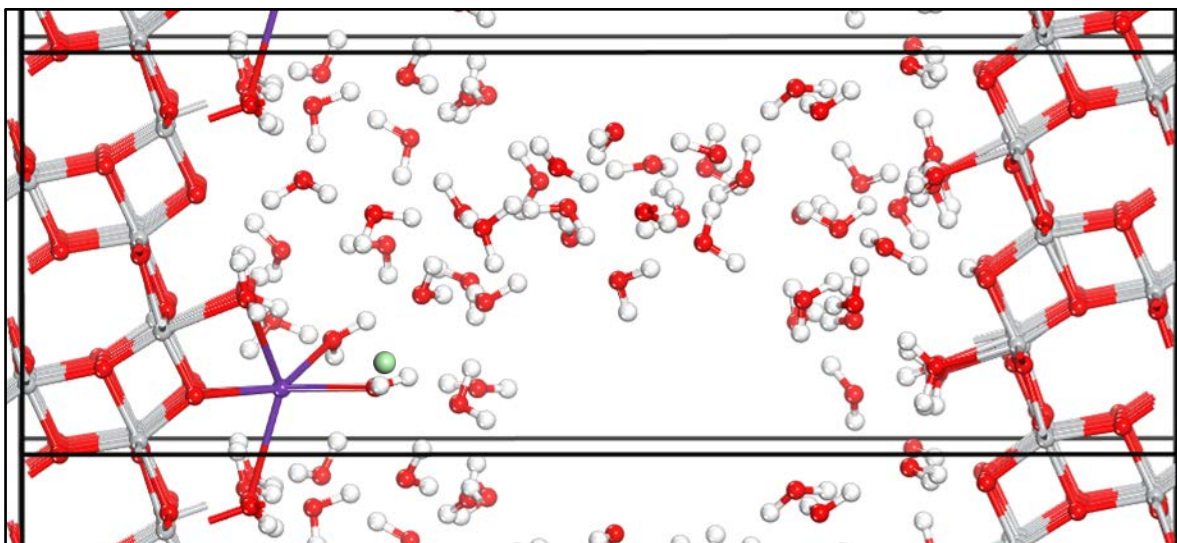
Figure S2. Effect of ionic strength on the distribution of surface species on the 4nm sized anatase sample. Data are presented for the inner-sphere (IS) and predominant outer-sphere (OS) electrolyte surface species, in NaCl media.