Supporting Information

Adventitious Water Sorption in a Hydrophilic and a Hydrophobic Ionic Liquid: Analysis and Implications

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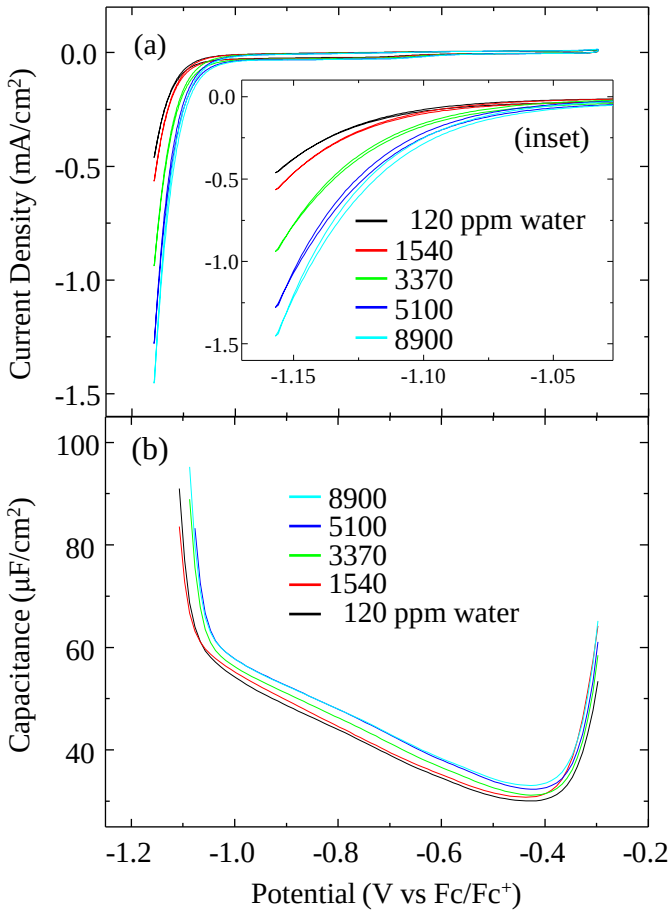

Figure S1. Cyclic voltammograms (a) and capacitance curves (b) from an Ag electrode in EAN solutions of varying water contents as noted. Inset in (a) shows cathodic limit to illustrates lower HER overpotentials at higher water concentrations. CV sweep rate is 50 mV/s. Capacitance frequency and amplitude are 10 Hz and 5 mV, respectively.

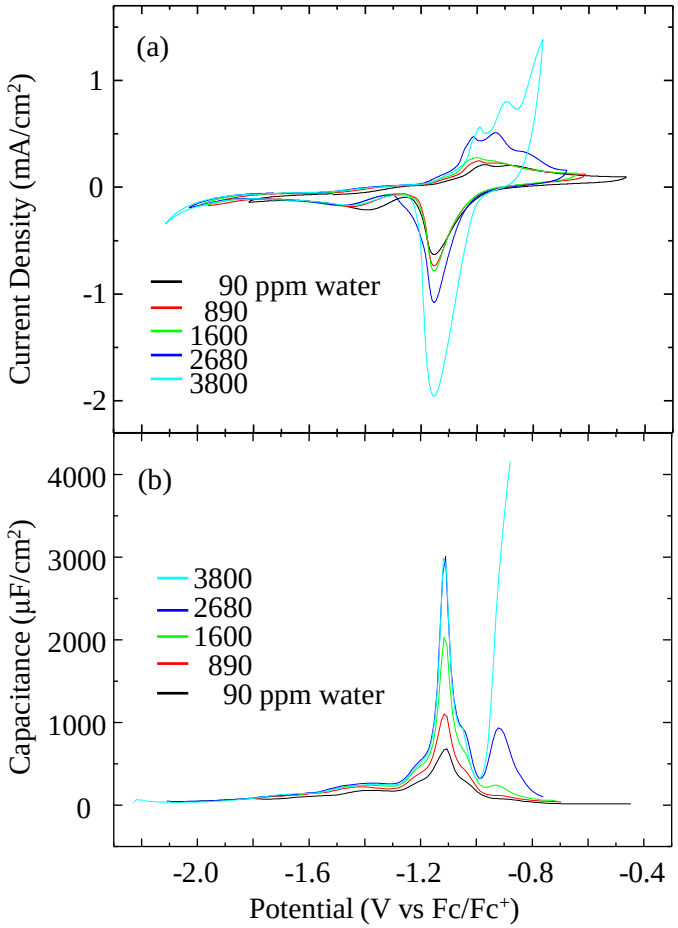

Figure S2. Cyclic voltammograms (a) and capacitance curves (b) for an Ag electrode in N1114 TFSI solutions with varying water concentration as noted. CV sweep rate is 50 mV/s. Capacitance frequency and amplitude are 10 Hz and 5 mV, respectively.

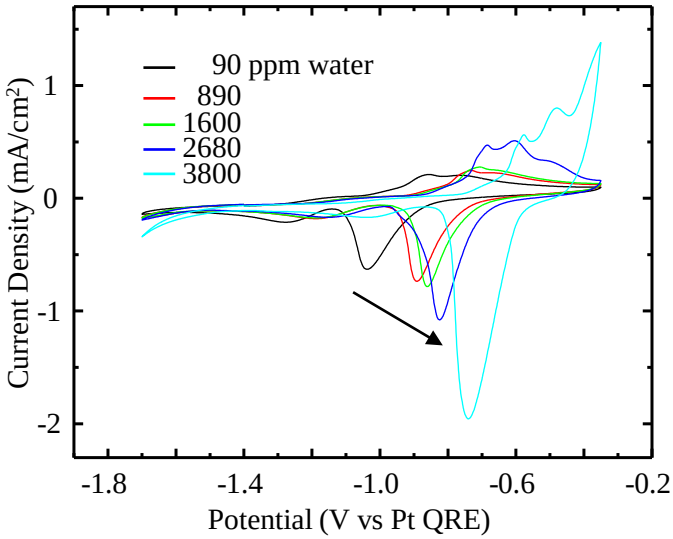

Figure S3. Cyclic voltammograms at 50 mV/s demonstrating the shift in the cathodic peak feature as a function of water uptake in N1114 TFSI. This drift was corrected for by normalizing cathodic peaks to that of the driest sample (< 100 ppm water), located at -1.1 V vs Pt QRE. Ag cathode used.

Electrochemical data N1114 TFSI show a drift in the potential axis ascribed to significant oxidation of the Pt quasi-reference electrode used here. This is evidenced by the cathodic feature at ca. -1 V vs Pt QRE, corresponding to reduction of Ag-oxide from the working electrode, clearly shifting to more positive potentials as the concentration of water is increased. It is generally understood that Pt quasi-reference electrode potentials are established through formation of oxides on the Pt metal surface. However, the exact chemistry is likely to vary depending on the system being studied as the electrode interacts with components in the surrounding solution.[31] To allow useful evaluation of the data, the location of the Ag-oxide reduction is normalized to that of the driest IL sample (90 ppm H_2O) at ca. -1 V vs Pt QRE. This is reasonable as the formal reduction potential for the Ag/Ag_2O redox couple should not change appreciably.

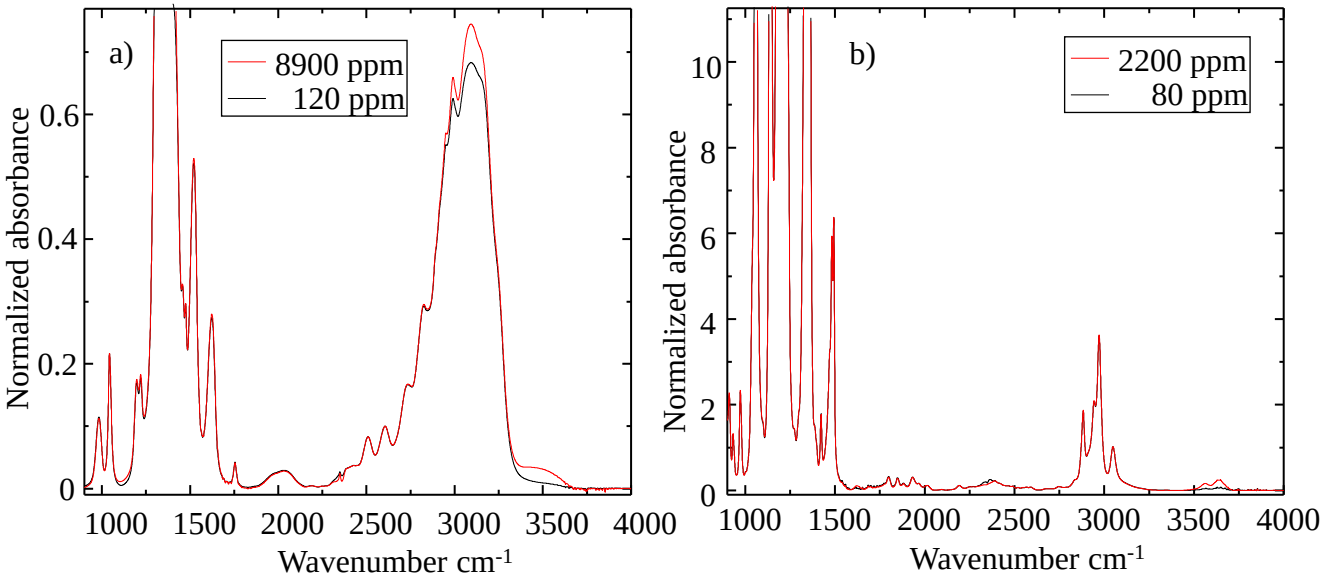

Figure S4. FTIR spectra of EAN (a) and N1114 TFSI (b) with varying concentration of water.

Table S1. Water content measurements in EAN using Karl Fisher titration.

Time	Water content (ppm)			Mean	Std dev	Total mean	Pooled std dev
0 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	133	104	126	121	15	117	12
Trial 2	158	142		150	11		
Trial 3	78	84		81	4		
5 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	1525	1552		1539	19	1139	51
Trial 2	808	930	933	890	71		
Trial 3	988	988		988	0.4		
10 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	3326	3405		3365	56	2486	53
Trial 2	2633	2678		2655	31		
Trial 3	1369	1474	1471	1438	60		
15 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	4962	5256		5109	208	3615	120
Trial 2	3421	3579		3500	111		
Trial 3	2213	2225	2272	2237	31		
20 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	8775	8995		8885	155	5999	167
Trial 2	5523	5707	5387	5539	160		
Trial 3	3369	3606	3743	3573	189		

Table S2. Water content measurements in N1114 TFSI using Karl Fisher titration.

Time	Water content (ppm)			Mean	Std dev	Total mean	Pooled std dev
0 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	56	55		56	0.7	78	12
Trial 2	86	88	105	93	10		
Trial 3	71	97		84	19		
20 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	432	443	450	442	9	579	20
Trial 2	874	913		894	27		
Trial 3	382	420		401	27		
40 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	815	824		819	7	1061	22
Trial 2	1594	1602	1620	1605	13		
Trial 3	785	730		758	39		
60 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	1097	1083	1116	1099	17	1704	20
Trial 2	2704	2659		2682	31		
Trial 3	1327	1333		1330	4		
80 mins	Aliquot 1	Aliquot 2	Aliquot 3				
Trial 1	1637	1634		1636	3	2548	70
Trial 2	3904	3708		3806	138		
Trial 3	2190	2209	2211	2204	12		