Potential dependent capacitance of [EMIM][TFSI], [N_{1114}][TFSI] and [PYR_{13}][TFSI] ionic liquids

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Electronic Supporting Information

Mean Field Theory Fit: The fits were performed in Origin 2017. α, γ^+, γ^-, and C_D were the fit parameters. The Levenberg Marquardt iteration method was used for a maximum of 500 iterations or a reduced chi square value of 10^{-15}.

Description of notation: The notation for **Figures S.1-6** follow this trend: Potentials closest to PZC are indicated by open squares followed by open circles, open triangles, and most positive/negative potential given by the black open diamond. Within the shape scheme the color scheme (from closest to PZC to furthest) is black, red, blue, magenta, purple, burgundy. The potentials are all given explicitly in **Figures S.2, S.4** and **S.6** for [EMIM][TFSI],[PYR_{13}][TFSI], and [N_{1114}][TFSI] respectively, and the symbol notation is consistent allowing for direct identification of the potentials in the other graphs.

Table S.1. Anodic and cathodic limits of the dried ionic liquids vs. Fc|Fc^+ measured at a cutoff current of 0.23 mA/cm^2, the respective electrochemical windows (EW), and the EWs reported in the literature. The water content of the 'dry' ILs are given in Table 1 of the manuscript.

Ionic Liquid	Anodic Limit	Cathodic Limit	Measured EW	Reported EW
[EMIM][TFSI]	1.54	-2.76	4.3	4.3 [1]
[PYR_{13}][TFSI]	2.40	-2.70	5.1	5.3 [2]
[N_{1114}][TFSI]	2.46	-3.24	5.7	5 [3]

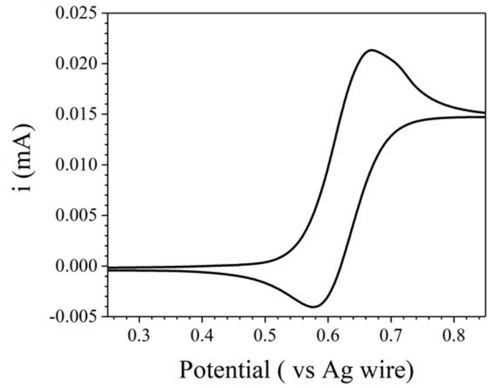

Figure S.1: Cyclic voltammetry of 2 mM Fc in acetonitrile containing 0.1 M TEAP. Used for the determination of the electrochemically active surface area of the glassy carbon working electrode

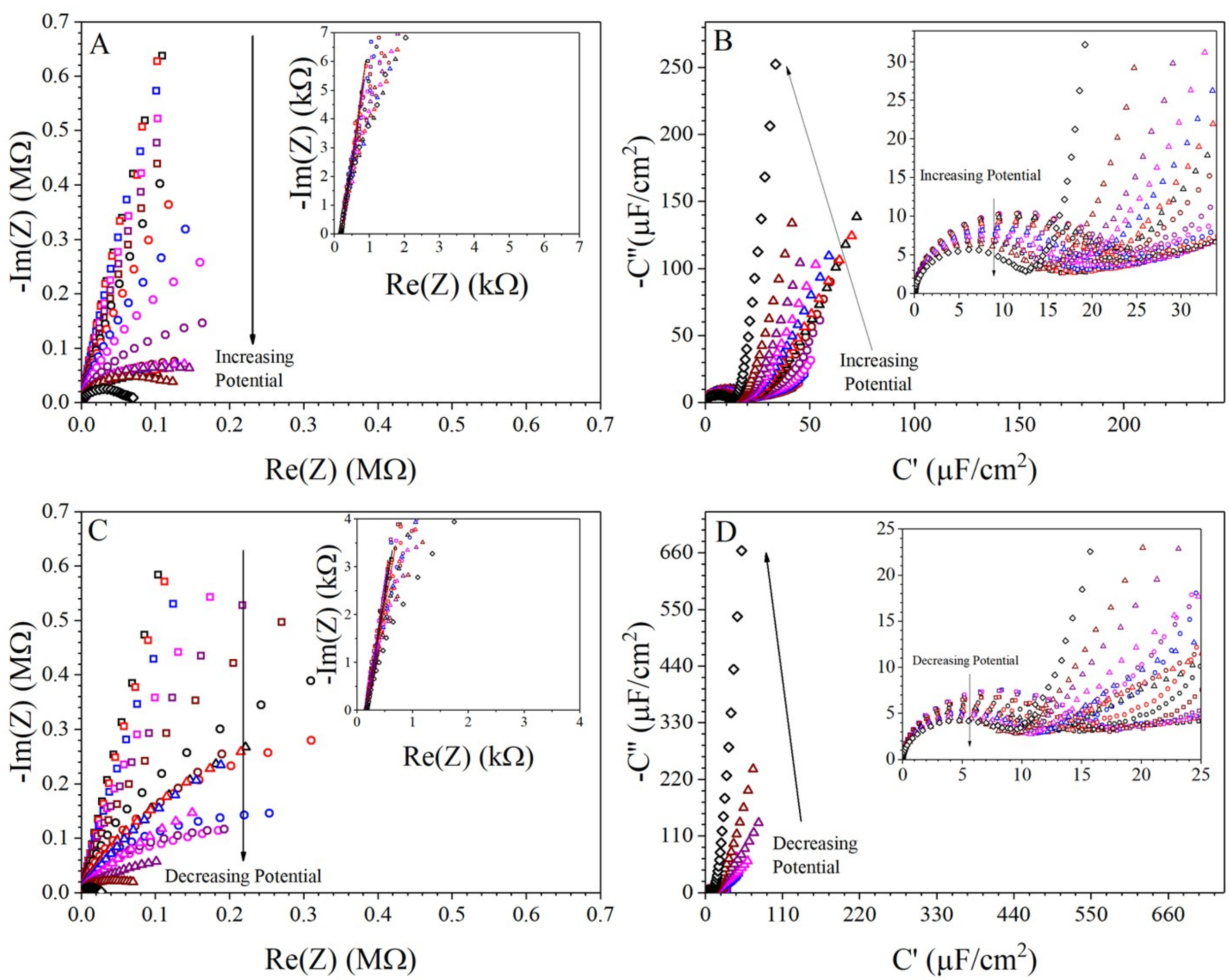

Figure S.2 Complex impedance (A and C) and complex capacitance (B and D) representations for [EMIM][TFSI] over the positive (A and B) and negative (C and D) potentials. Inset shows the equivalent circuit fits.

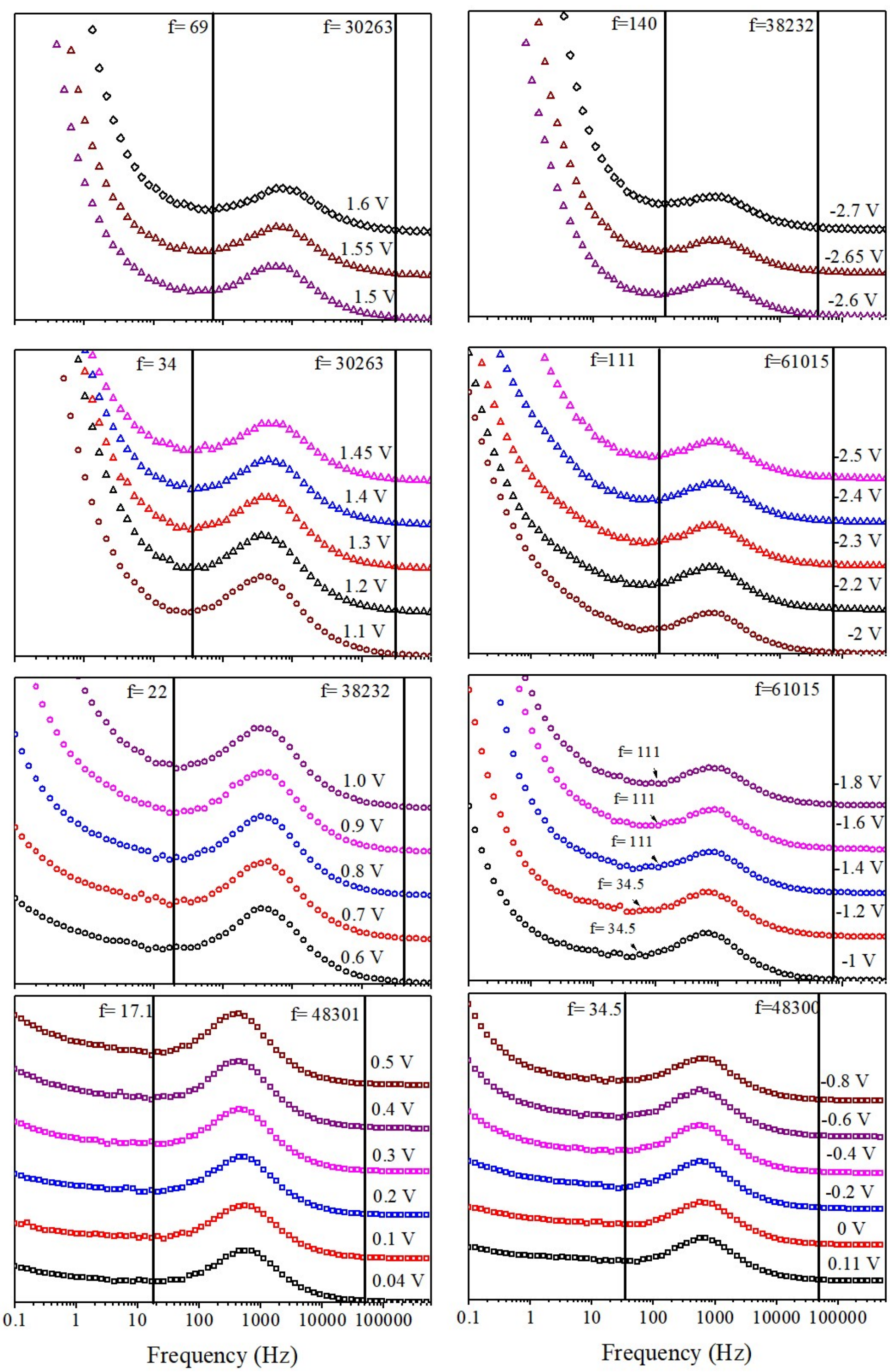

Figure S.3 Complex capacitance with respect to frequency for [EMIM][TFSI] at all potentials. The vertical lines indicate the frequency range used for the equivalent circuit fit. Y axis is Complex capacitance, but all values have been offset to show trends in the curvature. Reported potentials are with respect to the Ag quasi reference. Fc|Fc$^+$ redox peak occurred at 0.065 V vs Ag wire in [EMIM][TFSI].

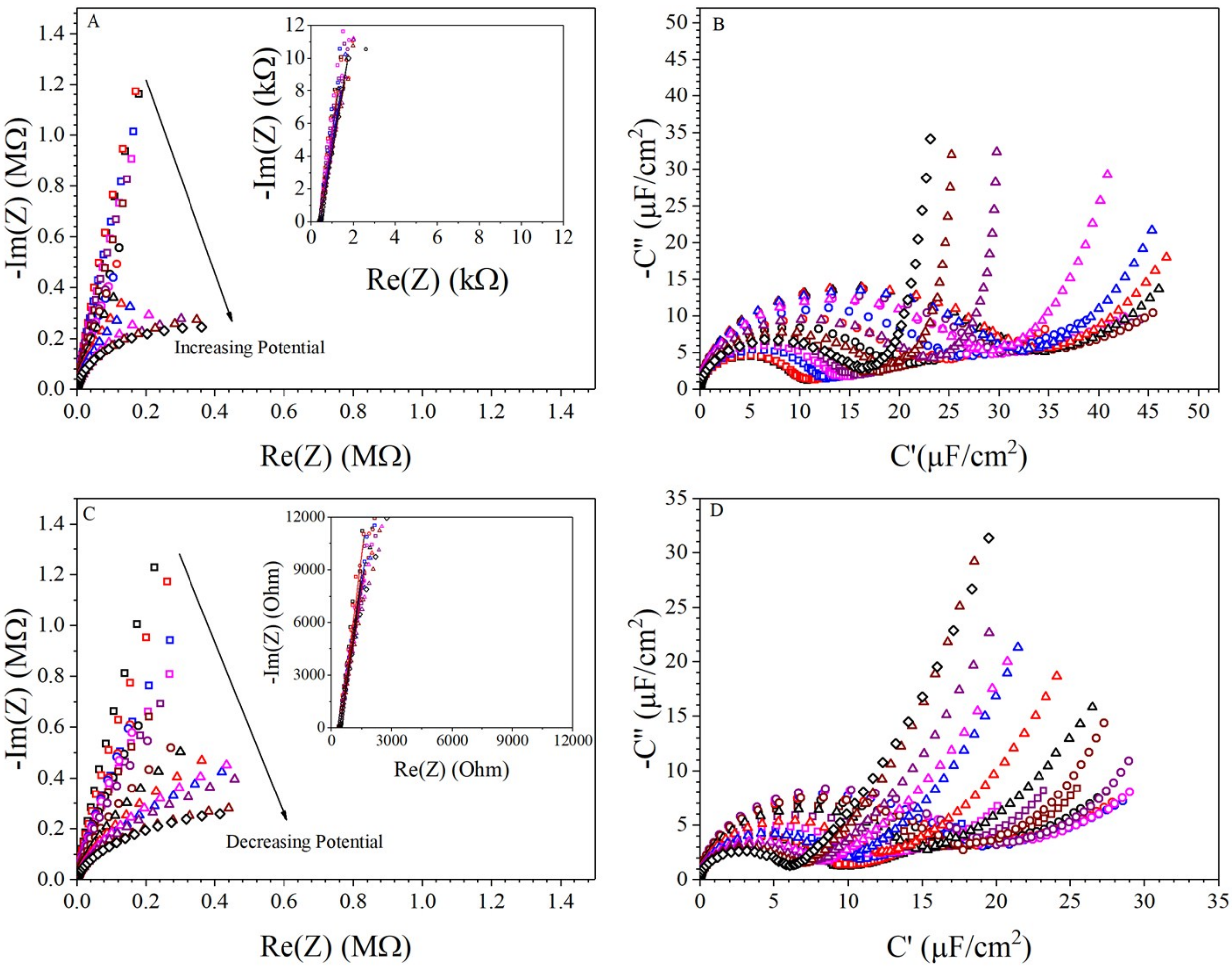

Figure S.4 Complex impedance (A and C) and complex capacitance (B and D) representations for $[PYR_{13}][TFSI]$ over the positive (A and B) and negative (C and D) potentials.

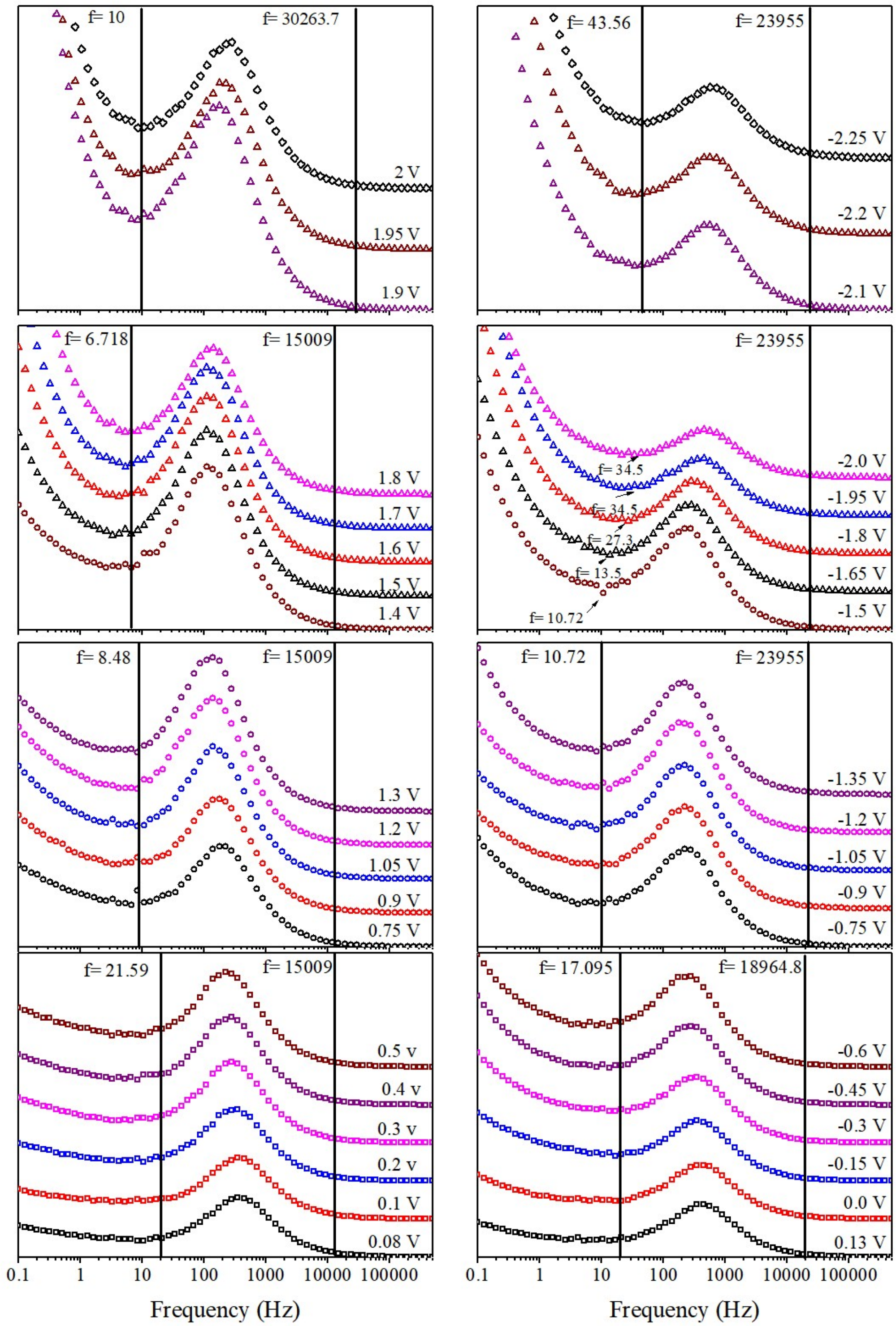

Figure S.5 Complex capacitance with respect to frequency for [PYR$_{13}$][TFSI] at all potentials. The vertical lines indicate the frequency range used for the equivalent circuit fit. Y axis is complex capacitance, but all values have been offset to show trends in the curvature. Reported potentials are with respect to Ag quasi reference. Fc|Fc$^+$ redox peak occurred at 0.30 V vs Ag in [Pyr$_{13}$][TFSI].

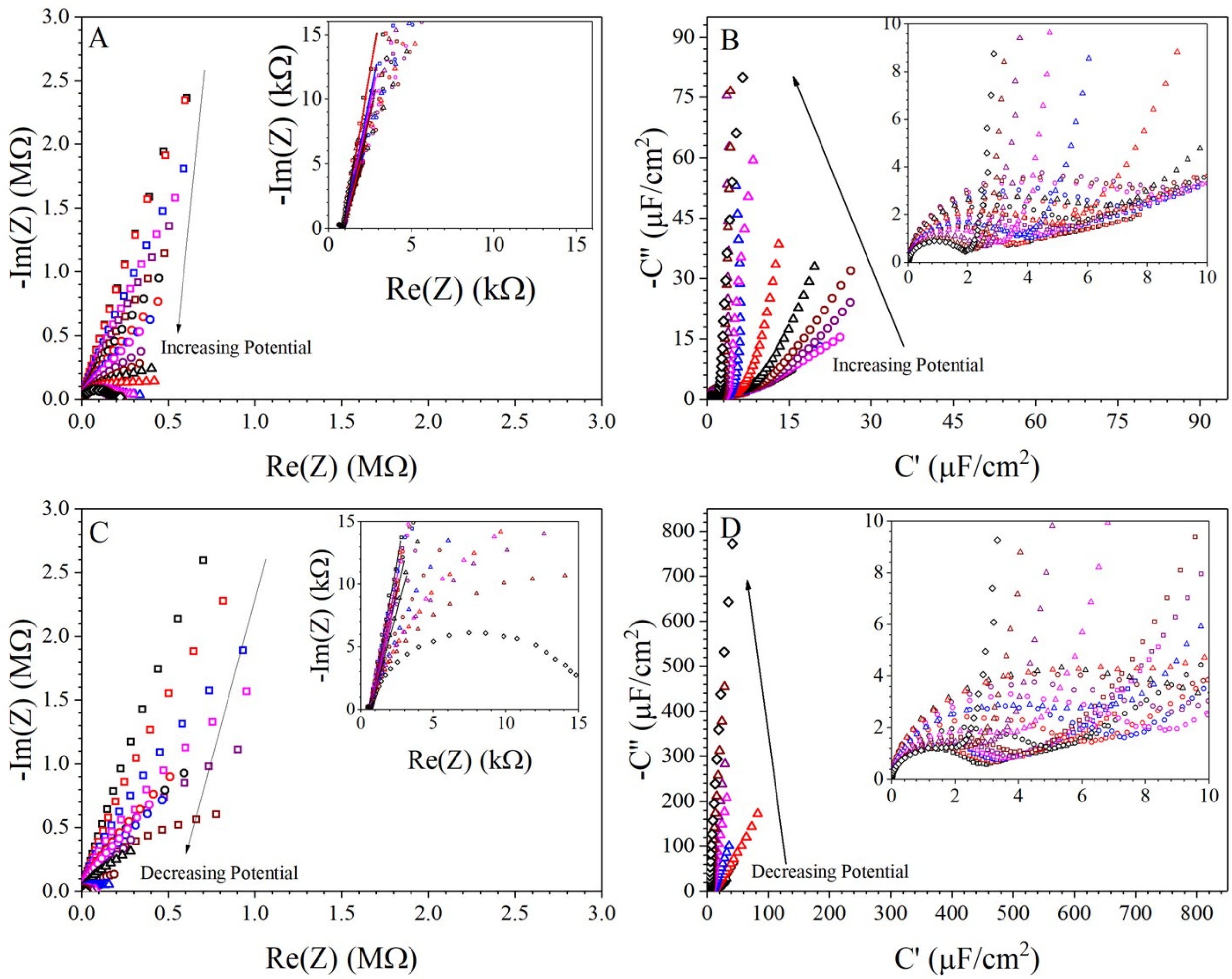

Figure S.6 Complex impedance (A and C) and complex capacitance (B and D) representations for $[N_{1114}][TFSI]$ over the positive (A and B) and negative (C and D) potentials.

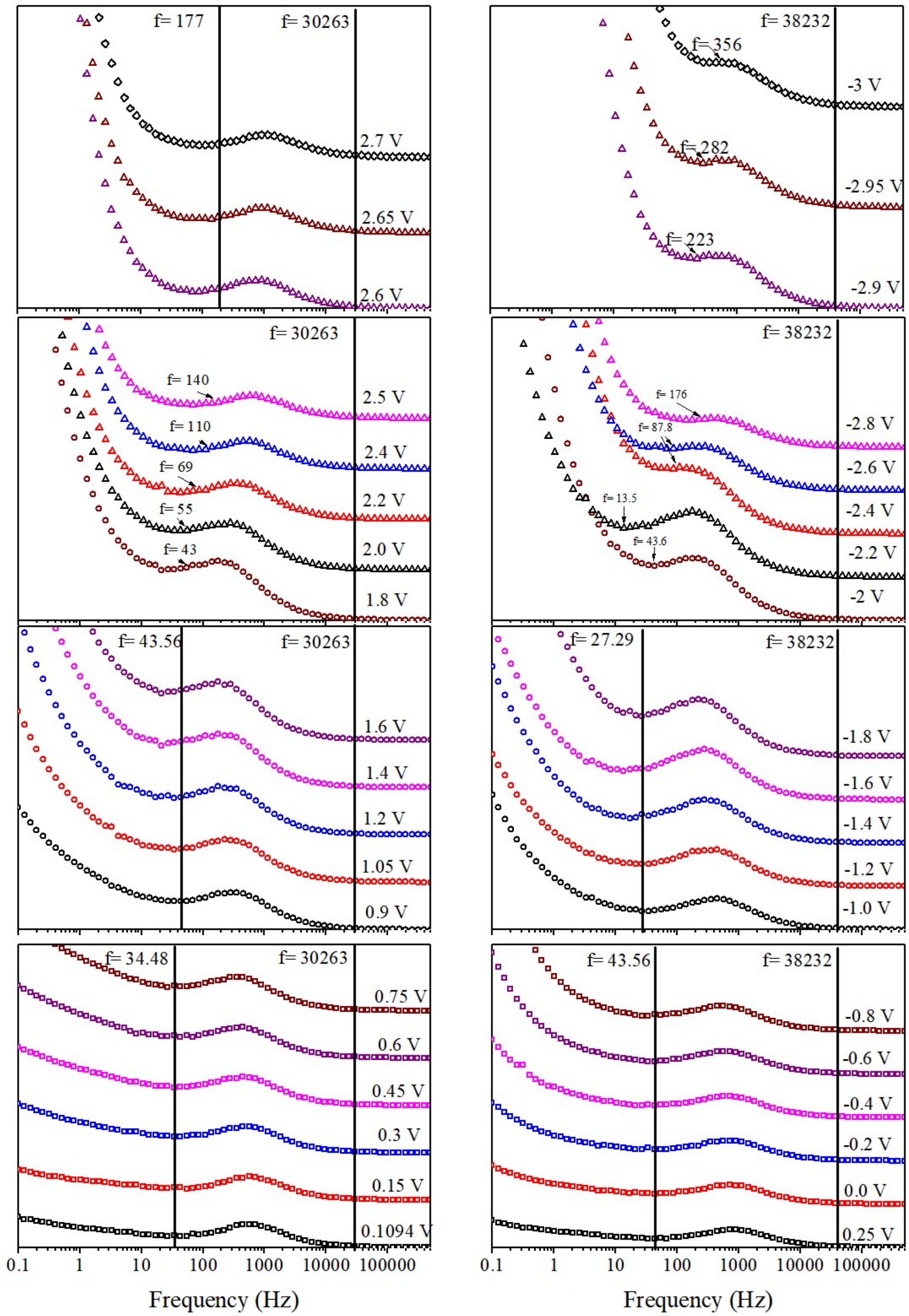

Figure S.7 Complex capacitance with respect to frequency for $[N_{1114}][TFSI]$ at all potentials. The vertical lines indicate the frequency range used for the equivalent circuit fit. Y axis is complex capacitance, but all values have been offset to show trends in the curvature. Reported potentials are with respect to Ag quasi reference. $Fc|Fc^+$ redox peak occurred at 0.24 V vs Ag in $[N_{1114}][TFSI]$.

Table S.2 Equivalent circuit fit parameters for the resistor- constant phase element (RQ) fit for $[N_{1114}][TFSI]$ at each measured potential (with respect to Fc|Fc$^+$).

Ionic Liquid	Potential (V)	R (Ohm)	Q (F.s$^{(a-1)}$)	a	Chi Squared
$[N_{1114}][TFSI]$	-0.1257	838.5	4.82E-07	0.9134	0.01439
	-0.0851	844.1	4.82E-07	0.9131	0.01422
	0.0649	839.8	6.22E-07	0.8973	0.01281
	0.2149	840.1	6.94E-07	0.8916	0.01578
	0.3649	839.9	7.89E-07	0.8834	0.01246
	0.5149	843	8.73E-07	0.8805	0.01093
	0.6649	838.8	1.01E-06	0.874	0.00878
	0.8149	841.4	1.18E-06	0.8667	0.01033
	0.9649	840.2	1.34E-06	0.8619	0.01025
	1.1649	839	1.58E-06	0.8529	0.01078
	1.3649	836.8	1.73E-06	0.8477	0.0146
	1.5649	836.7	1.69E-06	0.846	0.01052
	1.7649	838.7	1.30E-06	0.8567	0.01021
	1.9649	841.6	9.33E-07	0.8712	0.01272
	2.1649	843.7	6.36E-07	0.8915	0.01299
	2.2649	840.8	4.76E-07	0.9053	0.01398
	2.3649	841	4.02E-07	0.9073	0.01193
	2.4149	835.8	3.26E-07	0.9177	0.01366
	2.4649	834	2.92E-07	0.9183	0.0132
	0.0141	644.9	4.65E-07	0.9018	0.02214
	-0.2351	643.3	5.36E-07	0.8916	0.01986
	-0.4351	642.9	5.75E-07	0.8907	0.02191
	-0.6351	642.6	6.07E-07	0.891	0.02412
	-0.8351	645.1	6.50E-07	0.8902	0.021
	-1.0351	646.3	7.39E-07	0.8819	0.0198
	-1.2351	650.2	9.02E-07	0.8774	0.0218
	-1.4351	651	1.07E-06	0.8768	0.02477
	-1.6351	651.8	1.23E-06	0.8775	0.0192
	-1.8351	649.7	1.40E-06	0.878	0.02019
	-2.0351	647.5	1.69E-06	0.8665	0.01549
	-2.2351	645.5	2.11E-06	0.8448	0.00978
	-2.4351	649.5	2.04E-06	0.8553	0.01577
	-2.6351	642.9	2.62E-06	0.8183	0.00531
	-2.8351	646.5	1.76E-06	0.8287	0.00987
	-3.0351	646.4	1.15E-06	0.8394	0.00831

	-3.1351	646	9.03E-07	0.8464	0.0078
	-3.1851	645.9	8.06E-07	0.8482	0.01141
	-3.2351	641.9	8.72E-07	0.8312	0.0111

Table S.3 Equivalent circuit fit parameters for the resistor- constant phase element (RQ) fit for $[PYR_{13}][TFSI]$ at each measured potential (with respect to $Fc|Fc^+$).

Ionic Liquid	Potential (V)	R (Ohm)	Q ($F.s^{(a-1)}$)	*a*	Chi Squared
$[PYR_{13}][TFSI]$	-0.17875	414	1.17E-06	0.9302	0.0201
	-0.30255	413	1.21E-06	0.9303	0.0202
	-0.45255	411	1.46E-06	0.9174	0.01605
	-0.60255	409	1.67E-06	0.9114	0.01166
	-0.75255	407	2.01E-06	0.9088	0.01364
	-0.90255	408	2.23E-06	0.9118	0.01723
	-1.05255	407	2.35E-06	0.9126	0.02049
	-1.20255	407	2.43E-06	0.9132	0.01985
	-1.35255	407	2.45E-06	0.9172	0.01794
	-1.50255	407	2.50E-06	0.9202	0.02097
	-1.65255	407	2.50E-06	0.9211	0.01679
	-1.80255	407	2.26E-06	0.9231	0.01616
	-1.95255	408	2.01E-06	0.919	0.01787
	-2.10255	408	1.73E-06	0.9167	0.01626
	-2.25255	410	1.44E-06	0.9125	0.01307
	-2.30255	410	1.21E-06	0.9142	0.01347
	-2.40255	4.10	1.11E-06	0.9119	0.01045
	-2.50255	4.09	1.04E-06	0.9095	0.01062
	-2.55255	4.10	9.26E-07	0.914	0.01187
	-0.22755	4.18	1.30E-06	0.9321	0.02267
	-0.20255	419	1.29E-06	0.9352	0.02617
	-0.10255	419	1.52E-06	0.934	0.02834
	-0.00255	419	1.69E-06	0.9344	0.03134
	0.09745	416	1.87E-06	0.9316	0.02935
	0.19745	416	2.06E-06	0.9266	0.02392
	0.44745	414	2.59E-06	0.9171	0.03074
	0.59745	413	2.94E-06	0.9171	0.01772
	0.74745	412	3.25E-06	0.9202	0.01679
	0.89745	414	3.53E-06	0.9238	0.02434
	0.99745	413	3.76E-06	0.9222	0.02037
	1.09745	413	3.94E-06	0.9215	0.02366

	1.19745	415	3.98E-06	0.9224	0.01994
	1.29745	413.8	4.07E-06	0.9199	0.02009
	1.39745	413.9	3.95E-06	0.9195	0.0218
	1.49745	414	3.68E-06	0.9165	0.02456
	1.59745	415.4	3.00E-06	0.9134	0.01582
	1.64745	412.8	2.48E-06	0.9127	0.01908
	1.69745	416	2.15E-06	0.9164	0.01643

Table S.4 Equivalent circuit fit parameters for the resistor- constant phase element (RQ) fit for [EMIM][TFSI] at each measured potential (with respect to Fc|Fc$^+$).

Ionic Liquid	Potential (V)	R (Ohm)	Q (F.s$^{(a-1)}$)	a	Chi Squared
[EMIM][TFSI]	-0.02443	182.3	2.17E-06	0.9254	0.012
	0.03515	182.4	2.24E-06	0.9246	0.01186
	0.13515	182	2.48E-06	0.921	0.01075
	0.23515	182.3	2.69E-06	0.9202	0.0139
	0.33515	181.8	2.86E-06	0.9204	0.01193
	0.43515	181.4	3.00E-06	0.9208	0.01251
	0.53515	181.6	3.15E-06	0.9191	0.01184
	0.63515	181.1	3.29E-06	0.9175	0.01102
	0.73515	180.9	3.38E-06	0.9169	0.0102
	0.83515	180.8	3.49E-06	0.9137	0.01062
	0.93515	180.6	3.55E-06	0.9122	0.01059
	1.03515	180.8	3.56E-06	0.9102	0.00899
	1.13515	180.7	3.45E-06	0.9106	0.00928
	1.23515	180.4	3.19E-06	0.9124	0.01053
	1.33515	180.6	2.90E-06	0.9129	0.00975
	1.38515	179.9	2.60E-06	0.9148	0.01158
	1.43515	179.7	2.30E-06	0.9214	0.00755
	1.48515	179.6	2.09E-06	0.9222	0.00868
	1.53515	179.1	1.86E-06	0.9238	0.00939
	0.04515	163.8	2.22E-06	0.9213	0.01047
	-0.06485	163.9	2.24E-06	0.9216	0.00838
	-0.26485	164.5	2.48E-06	0.9199	0.00846
	-0.46485	164.7	2.45E-06	0.9215	0.00889
	-0.66485	165.9	2.38E-06	0.9222	0.01203
	-0.86485	166.5	2.31E-06	0.9165	0.01181
	-1.06485	166.7	2.20E-06	0.9114	0.01087
	-1.26485	166.8	2.21E-06	0.9048	0.01259

	-1.46485	167.1	2.08E-06	0.9038	0.0086
	-1.66485	167.8	1.90E-06	0.9097	0.1094
	-1.86485	167.7	1.84E-06	0.91	0.01044
	-2.06485	168.6	1.95E-06	0.9102	0.01114
	-2.26485	168.3	2.12E-06	0.9041	0.01381
	-2.36485	168.9	2.00E-06	0.9055	0.01234
	-2.46485	168.9	1.87E-06	0.9092	0.01329
	-2.56485	169.3	1.88E-06	0.9032	0.01202
	-2.66485	169.8	1.81E-06	0.9021	0.0104
	-2.71485	169.5	1.81E-06	0.8956	0.0098
	-2.76485	168.8	2.03E-06	0.8819	0.01191

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