Supplementary Material

Role of H^+ in polypyrrole and poly(3,4-ethylenedioxythiophene) formation

using FeCl₃.6H₂O in the room temperature ionic liquid, C₄mpyrTFSI

Graeme A. Snook,^a Anand I. Bhatt,^{*b} Muhammad E. Abdelhamid,^{a,c} Adam S. Best^b

^a Commonwealth Scientific Industrial Research Organisation (CSIRO), Process Science and Engineering, Box 312, Clayton South, Vic., 3169, Australia

^b Commonwealth Scientific Industrial Research Organisation (CSIRO), Energy Technology, Box 312, Clayton 3169. Victoria. Australia.

> ^c RMIT University, School of Applied Sciences, Melbourne 3001. Victoria, Australia Email: Anand.Bhatt@csiro.au

Scan rate / mV s ⁻¹	E _p ^{red} / mV	${\rm E_p}^{\rm ox}$ / mV	$\mathbf{E}_{\mathrm{mid}}$ / mV	$\Delta E_p / mV$	J_p^{red}/J_p^{ox}
20	-601	-522	-562	79	0.91
40	-604	-520	-562	84	0.85
60	-607	-520	-564	87	0.92
80	-609	-517	-563	92	0.93
100	-610	-514	-562	96	0.94
120	-612	-512	-562	100	0.97
140	-614	-508	-561	106	0.95
160	-615	-508	-562	107	0.97
180	-617	-508	-563	109	0.94
200	-620	-495	-558	125	0.86

Table SI1: Cyclic voltammetry parameters obtained for 10 mM Fe₂Cl₂.4H₂O in C₄mpyrTFSI at a Pt electrode at 22 °C.

Table SI2: Cyclic voltammetry parameters obtained for HTFSI in C₄mpyrTFSI at a Pt electrode at 22 $^{\circ}$ C.

	Concentration														
Scan		15 mM				20 mM					40 mM				
rate / mV s ⁻¹	E _p ¹ / mV	E _p ^{II} / mV	E _{mid} / mV	△E _p / mV	J_p^{red}/J_p^{ox}	E ^I /mV	E ⁿ / mV	E _{mid} / mV	ΔE / mV	J_p^{red}/J_p^{ox}	E _p ^I / mV	E _p ^{II} / mV	E _{mid} / mV	ΔE / mV	$J_p^{\ red}/J_p^{\ ox}$
20	-466	-400	-433	66	1.03	-463	-387	-425	76	1.03	-468	-378	-423	90	1.07
40	-464	-392	-428	72	0.88	-468	-380	-424	88	0.83	-476	-367	-422	109	0.88
60	-475	-383	-429	92	0.77	-473	-376	-425	97	0.79	-484	-359	-422	125	0.84
80	-477	-377	-427	100	0.78	-473	-370	-422	103	0.75	-486	-354	-420	132	0.78
100	-479	-375	-427	104	0.70	-475	-365	-420	110	0.72	-490	-348	-419	142	0.79
120	-482	-371	-427	111	0.67	-479	-365	-422	114	0.71	-496	-344	-420	152	0.75
140	-483	-365	-424	118	0.68	-482	-359	-421	123	0.69	-497	-342	-420	155	0.74
160	-485	-363	-424	122	0.65	-483	-355	-419	128	0.69	-497	-337	-417	160	0.71
180	-483	-351	-417	132	0.63	-483	-354	-419	129	0.67	-502	-335	-419	167	0.69
200	-473	-355	-414	118	0.64	-480	-354	-417	126	0.67	-506	-332	-419	174	0.69
	60 mM					80 mM					100 mM				
	E _p ^I / mV	Е _р п / mV	E _{mid} / mV	∆E / mV	J_p^{red}/J_p^{ox}	E ^I /mV	Е _р п / mV	E _{mid} / mV	ΔE / mV	J_p^{red}/J_p^{ox}	E _p ^I / mV	Е _р п / mV	E _{mid} / mV	△E / mV	$J_p^{\ red}/J_p^{\ ox}$
20	-468	-371	-420	97	1.07	-471	-360	-416	111	1.04	-476	-354	-415	122	1.08
40	-478	-361	-420	117	0.92	-484	-345	-415	139	0.95	-492	-337	-415	155	0.96
60	-487	-353	-420	134	0.89	-494	-335	-415	159	0.92	-502	-327	-415	175	0.88
80	-492	-346	-419	146	0.81	-501	-328	-415	173	0.87	-511	-318	-415	193	0.85
100	-497	-341	-419	156	0.81	-506	-321	-414	185	0.79	-517	-310	-414	207	0.82
120	-502	-334	-418	168	0.77	-515	-316	-416	199	0.83	-526	-303	-415	223	0.80
140	-507	-331	-419	176	0.78	-518	-311	-415	207	0.79	-529	-299	-414	230	0.77
160	-510	-327	-419	183	0.71	-522	-306	-414	216	0.80	-537	-293	-415	244	0.76
180	-510	-324	-417	186	0.72	-527	-302	-415	225	0.78	-542	-289	-416	253	0.75
200	-516	-322	-419	194	0.70	-536	-298	-417	238	0.73	-546	-285	-416	261	0.74

Figure SI01: Voltammograms of 10 mM FeCl₃.6H₂O in C₄mpyrTFSI recorded at a Pt rotating disk electrode. Rotation rates of 500, 800, 1000, 1200, 1400, 1600, 1800, 2000 and 2500 rpm and scant rate of 50 mV s⁻¹. All voltammograms recorded under a Ar atmosphere at 22 °C.



Potential / V vs. Ag/Ag⁺

Figure SI02: Plot of limiting current as a function of square root of rotation rate for 10 mM FeCl₃.6H₂O in C₄mpyrTFSI recorded at a Pt rotating disk electrode. Rotation rates of 500, 800, 1000, 1200, 1400, 1600, 1800, 2000 and 2500 rpm and scant rate of 50 mV s⁻¹. All voltammograms recorded under a Ar atmosphere at 22 °C.



Figure SI03: Voltammograms of 10 mM Fe(NO₃)₃.9H₂O in C₄mpyrTFSI recorded at a Pt working electrode. Scan rates of 20 to 200 mV s⁻¹ in 20 mV s⁻¹ steps. All voltammograms recorded in an Ar glovebox at 22 °C.

