Supporting Information

Characterization of imidazolium chloride ionic liquids plus trivalent chromium chloride for chromium electroplating

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Table S1(a). Temperature dependent conductivity (mS/cm) of different mixtures (1:2 $CrCl_3 \cdot xH_2O$/IL)

IL	T (°C)	10	20	25	30	40	50	60	70	80
[Ch][Cl]	x=9	0.927	1.693	2.259	2.996	5.113	8.089	12.014	16.863	23.188
	x=12	3.765	6.277	7.828	9.726	14.577	20.658	28.123	36.917	46.667
	x=15	9.459	14.357	17.164	20.501	28.447	38.060	48.922	60.829	73.703
	x=18	16.033	22.878	27.168	31.587	41.712	53.049	65.574	78.937	92.689
[emim][Cl]	x=9	0.966	1.965	2.718	3.690	6.431	10.119	10.918	14.508	19.005
	x=12	4.261	6.852	8.788	11.072	16.768	24.152	32.400	42.246	52.977
	x=15	9.246	14.790	18.174	21.857	31.183	42.578	54.651	68.600	83.283
	x=18	15.074	22.765	27.221	32.198	43.664	56.931	70.625	86.049	102.794
[bmim][Cl]	x=9	0.556	1.099	1.533	2.116	3.779	6.195	9.297	12.730	16.595
	x=12	2.216	3.745	4.939	6.377	10.113	15.142	21.274	28.505	36.611
	x=15	5.020	7.916	9.967	12.318	18.092	25.291	33.948	43.605	54.293
	x=18	10.096	15.094	18.403	22.094	30.719	41.026	52.650	65.605	79.280
[hmim][Cl]	x=9	0.484	0.942	1.296	1.775	3.114	5.040	7.692	11.066	15.221
	x=12	1.744	3.106	4.031	5.152	8.103	11.566	16.181	21.455	27.307
	x=15	4.633	7.542	9.367	11.458	16.851	22.845	30.104	38.245	46.782
	x=18	8.622	13.124	15.746	18.798	26.713	36.014	45.811	56.485	67.512

Table S1(b). Fitting parameters for Arrhenius equation (1)

1:2 $CrCl_3(xH_2O)$/ChCl	**δ_0 (Scm^{-1})**	**E_Λ(kJ/mol)**	**R^2**
x=9	3138.5 ± 1.4	34.6 ± 0.8	0.998
x=12	437.2 ± 1.3	26.8 ± 0.6	0.998
x=15	128.6± 1.2	21.8 ± 0.6	0.997
x=18	49.1 ± 1.2	18.4 ± 0.5	0.998
1:2 $CrCl_3(xH_2O)$/[emim]Cl	**δ_0 (Scm^{-1})**	**E_Λ(kJ/mol)**	**R^2**
x=9	517.9 ± 2.0	29.9 ± 1.8	0.981
x=12	430.8 ± 1.4	26.4 ± 0.9	0.996
x=15	181.3 ± 1.3	22.5 ± 0.7	0.996
x=18	82.1 ± 1.2	19.6 ± 0.5	0.997
1:2 $CrCl_3(xH_2O)$/[bmim]Cl	**δ_0 (Scm^{-1})**	**E_Λ(kJ/mol)**	**R^2**
x=9	1848.8 ± 1.9	34.0 ± 1.8	0.989
x=12	887.5 ± 1.4	29.5 ± 1.0	0.996
x=15	304.2 ± 1.3	25.3 ± 0.7	0.997
x=18	135.4 ± 1.2	21.8 ± 0.6	0.997
1:2 $CrCl_3(xH_2O)$/[hmim]Cl	**δ_0 (Scm^{-1})**	**E_Λ(kJ/mol)**	**R^2**
x=9	3921.4 ± 1.4	41.17 ± 0.97	0.997
x=12	398.6 ± 1.3	28.1 ± 0.7	0.997
x=15	146.1 ± 1.2	23.6 ± 0.6	0.997
x=18	96.1 ± 1.3	21.2 ± 0.8	0.994

Table S2(a). Temperature dependent density (g/cm^3) of different mixtures (1:2 $CrCl_3 \cdot xH_2O$/IL)

IL	T (°C)	10	20	25	30	40	50	60	70	80
[Ch][Cl]	x=9	1.33429	1.32896	1.32640	1.32380	1.31851	1.31312	1.30776	1.30204	1.29618
	x=12	1.30149	1.29652	1.29412	1.29173	1.28678	1.28161	1.27626	1.27060	1.26487
	x=15	1.27813	1.27355	1.27120	1.26884	1.26399	1.25898	1.25377	1.24827	1.24253
	x=18	1.25504	1.25054	1.24824	1.24592	1.24116	1.23623	1.23105	1.22567	1.22002
[emim][Cl]	x=9	1.34149	1.33535	1.33225	1.32913	1.32277	1.31654	1.31013	1.30347	1.29647
	x=12	1.31004	1.30418	1.30125	1.29826	1.29219	1.28597	1.27973	1.27322	1.26635
	x=15	1.28361	1.27804	1.27525	1.27238	1.26656	1.26056	1.25438	1.24783	1.24107
	x=18	1.26227	1.25688	1.25420	1.25137	1.24583	1.23990	1.23392	1.22754	1.22080
[bmim][Cl]	x=9	1.27717	1.27102	1.26791	1.26479	1.25840	1.25213	1.24570	1.23911	1.23215
	x=12	1.25916	1.25300	1.25004	1.24702	1.24086	1.23454	1.22806	1.22136	1.21427
	x=15	1.24145	1.23565	1.23266	1.22965	1.22356	1.21728	1.21082	1.20414	1.19718
	x=18	1.22546	1.21973	1.21683	1.21390	1.20792	1.20179	1.19537	1.18857	1.18167
[hmim][Cl]	x=9	1.22946	1.22269	1.21959	1.21648	1.21019	1.20381	1.19743	1.19084	1.18325
	x=12	1.21439	1.20838	1.20534	1.20227	1.19623	1.19003	1.18360	1.17691	1.17007
	x=15	1.19912	1.19317	1.19021	1.18731	1.18135	1.17525	1.16882	1.16206	1.15492
	x=18	1.18689	1.18132	1.17847	1.17559	1.16970	1.16356	1.15728	1.15061	1.14332

Table S2(b). Fitting parameters for density equation (2)

1:2 $CrCl_3 \cdot xH_2O$/[Ch][Cl]	**a(g/cm^3)**	**b·10^4(g/cm^3·K)**	**R^2**
x=9	1.488 ± 0.001	-5.415 ± 0.004	1.000
x=12	1.449 ± 0.002	-5.207 ± 0.006	0.999
x=15	1.422 ± 0.002	-5.071 ± 0.007	0.998
x=18	1.397 ± 0.002	-4.991 ± 0.007	0.998
1:2 $CrCl_3 \cdot xH_2O$/[emim][Cl]	**a(g/cm^3)**	**b·10^4(g/cm^3·K)**	**R^2**
x=9	1.523 ± 0.001	-6.403 ± 0.005	1.000
x=12	1.487 ± 0.002	-6.222 ± 0.006	0.999
x=15	1.456 ± 0.002	-6.061 ± 0.008	0.999
x=18	1.430 ± 0.003	-5.900 ± 0.008	0.998
1:2 $CrCl_3 \cdot xH_2O$/[bmim][Cl]	**a(g/cm^3)**	**b·10^4(g/cm^3·K)**	**R^2**
x=9	1.459 ± 0.001	-6.409 ± 0.004	1.000
x=12	1.440± 0.002	-6.377 ± 0.006	0.999
x=15	1.421 ± 0.002	-6.315 ± 0.007	0.999
x=18	1.403 ± 0.003	-6.241 ± 0.008	0.999
1:2 $CrCl_3 \cdot xH_2O$/[hmim][Cl]	**a(g/cm^3)**	**b·10^4(g/cm^3·K)**	**R^2**
x=9	1.413 ± 0.002	-6.496 ± 0.006	0.999
x=12	1.393 ± 0.002	-6.307 ± 0.006	0.999
x=15	1.377 ± 0.003	-6.265 ± 0.008	0.999
x=18	1.363 ± 0.003	-6.188 ± 0.009	0.998

Table S3(a). Temperature dependent viscosity (cP) of different mixtures (1:2 $CrCl_3 \cdot xH_2O$/IL)

IL	T (°C)	10	20	25	30	40	50	60	70	80
[Ch][Cl]	x=9	--	--	--	--	279.6308	172.3694	127.9245	--	--
	x=12	--	200.6017	152.1887	110.4123	71.4582	49.8529	32.1038	--	--
	x=15	116.2231	72.4722	56.3464	45.5245	29.5358	--	--	--	--
	x=18	54.5561	35.0382	28.6903	23.8420	--	--	--	--	--
[emim][Cl]	x=9	--	--	346.7171	246.8615	126.2542	71.7665	46.9587	29.9763	--
	x=12	253.9410	128.7292	98.1324	73.0374	43.0950	23.0772	--	--	--
	x=15	99.7797	57.1378	45.0118	36.0289	23.0772	--	--	--	--
	x=18	51.2273	31.8522	25.8607	--	--	--	--	--	--
[bmim][Cl]	x=9	--	--	--	343.7624	169.8667	92.6243	60.5982	37.5180	23.3160
	x=12	--	206.1237	148.4713	109.2021	60.8145	37.2877	26.6002	17.6829	--
	x=15	160.2971	87.5918	66.5630	51.5076	31.1744	20.6055	--	--	--
	x=18	82.0127	47.5047	37.1683	29.6493	19.3446	--	--	--	--
[hmim][Cl]	x=9	--	--	--	--	316.5378	165.6385	105.3387	63.5844	37.9501
	x=12	--	--	323.9428	231.84840	121.4168	69.1632	46.2215	28.8742	--
	x=15	--	214.1860	157.1574	117.1117	65.9567	40.4393	28.4090	--	--
	x=18	218.6744	117.4242	88.6892	68.0892	40.5279	26.1399	--	--	--

Table S3(b). Fitting parameters for Arrhenius equations (3)

1:2 $CrCl_3 \cdot xH_2O$/[Ch][Cl]	**$\eta_0 \cdot 10^3$ (cP)**	**E_η (kJ/mol)**	**R^2**
x=9	0.13 ± 0.07	38.3 ± 1.5	0.997
x=12	0.06± 0.03	36.5 ± 1.1	0.996
x=15	0.07 ± 0.01	33.7± 0.3	1.000
x=18	0.19 ± 0.03	29.6 ± 0.5	0.999
1:2 $CrCl_3 \cdot xH_2O$/[emim][Cl]	**$\eta_0 \cdot 10^3$ (cP)**	**E_η (kJ/mol)**	**R^2**
x=9	0.0025 ± 0.0013	46.3 ± 1.4	0.996
x=12	0.0014± 0.0005	44.8 ± 0.9	0.998
x=15	0.024 ± 0.006	35.8 ± 0.6	0.999
x=18	0.061 ± 0.015	32.1 ± 0.6	0.999
1:2 $CrCl_3 \cdot xH_2O$/[bmim][Cl]	**$\eta_0 \cdot 10^3$ (cP)**	**E_η (kJ/mol)**	**R^2**
x=9	0.0026 ± 0.0013	47.0 ± 1.3	0.996
x=12	0.0096 ± 0.0046	41.0 ± 1.3	0.994
x=15	0.0096 ± 0.0007	39.1 ± 2.1	0.999
x=18	0.023 ± 0.006	35.5 ± 0.6	0.999
1:2 $CrCl_3 \cdot xH_2O$/[hmim][Cl]	**$\eta_0 \cdot 10^3$ (cP)**	**E_η (kJ/mol)**	**R^2**
x=9	0.0032 ± 0.0014	47.8 ± 1.2	0.997
x=12	0.0032 ± 0.0015	45.6 ± 1.3	0.996
x=15	0.0078 ± 0.0036	41.7 ± 1.2	0.996
x=18	0.0074 ± 0.0016	40.4 ± 0.5	0.999

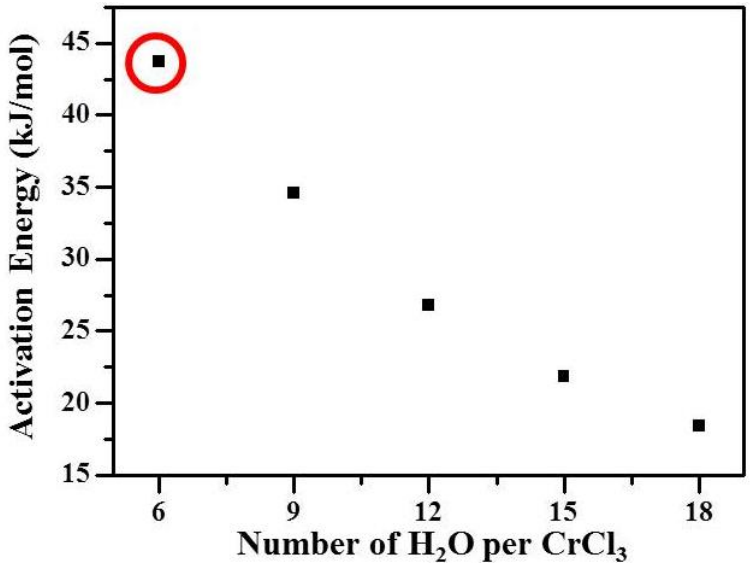

Figure S1. Activation energy for conduction as a function of the number of H_2O per number of $CrCl_3$. Reported value for 1:1 $CrCl_3 \cdot 6H_2O$/[Ch][Cl] marked with red circle.[1] Other points are 1:2 $CrCl_3 \cdot xH_2O$/[Ch][Cl] (x= 9, 12, 15, 18) mixtures studied in this work.

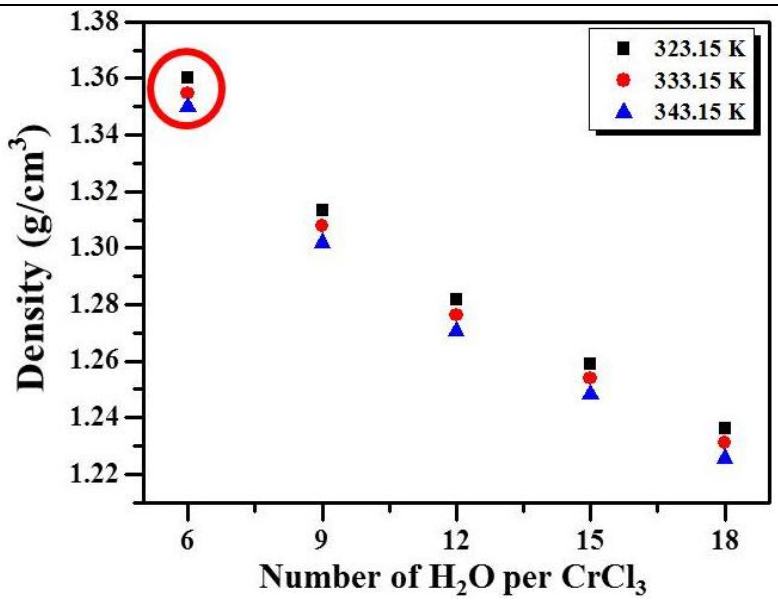

Figure S2. Density as a function of the number of H_2O per number of $CrCl_3$. Reported value for 1:2$CrCl_3 \cdot 6H_2O$/[Ch][Cl] marked with red circle.[2] Other points are 1:2 $CrCl_3 \cdot xH_2O$/ChCl (x= 9, 12, 15, 18) mixtures studied in this work.

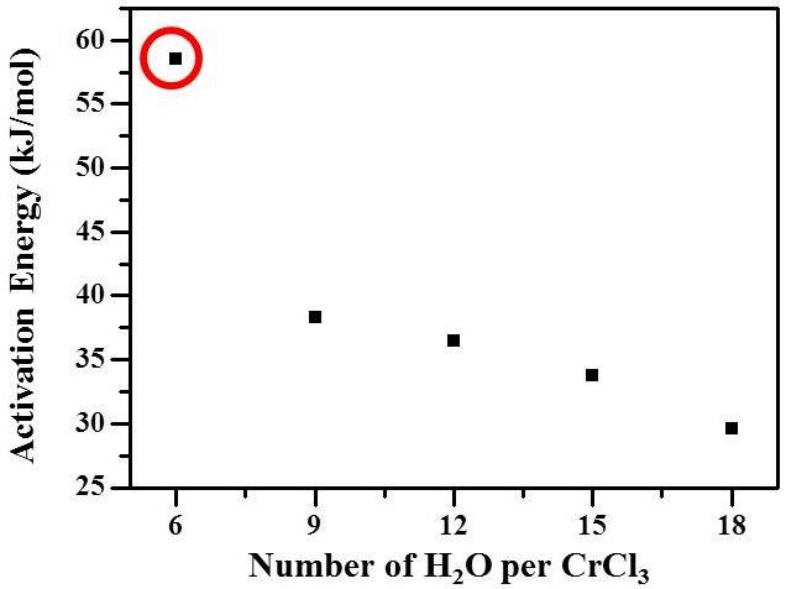

Figure S3. Activation energy for viscous flow as a function of the number of H_2O per number of $CrCl_3$. Reported value for 1:1 $CrCl_3 \cdot 6H_2O$/ChCl marked with red circle.[1] Other points are 1:2 $CrCl_3 \cdot xH_2O$/ChCl (x= 9, 12, 15, 18) mixtures studied in this work.

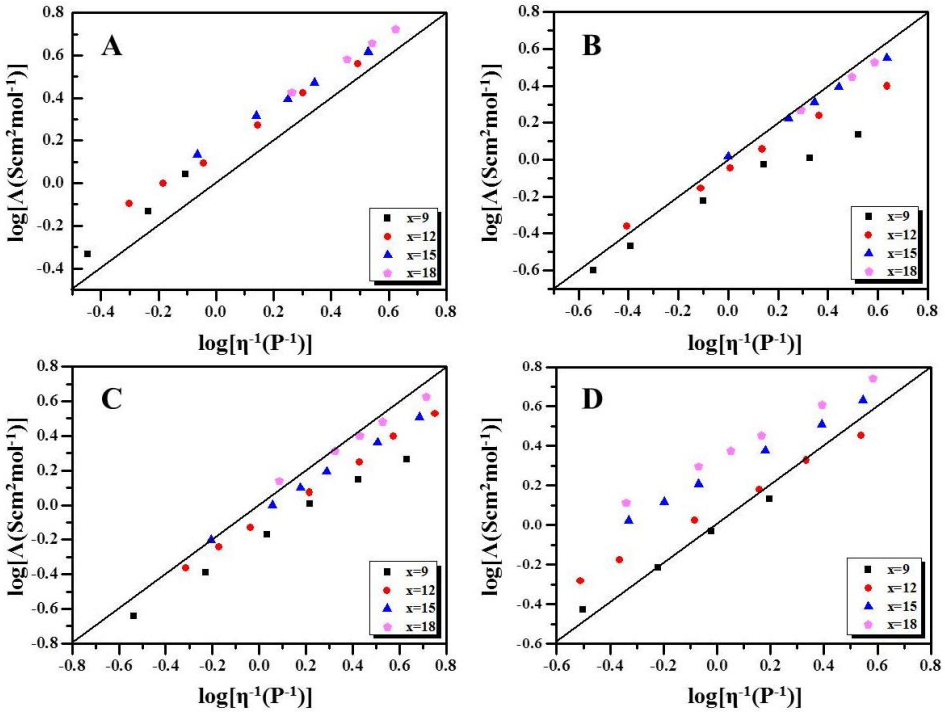

Figure S4. Walden plots of: (A) 1:2 $CrCl_3 \cdot xH_2O$/[Ch][Cl], (B) 1:2 $CrCl_3 \cdot xH_2O$/[emim][Cl], (C) 1:2 $CrCl_3 \cdot xH_2O$/[bmim][Cl], and (D) 1:2 $CrCl_3 \cdot xH_2O$/[hmim][Cl]

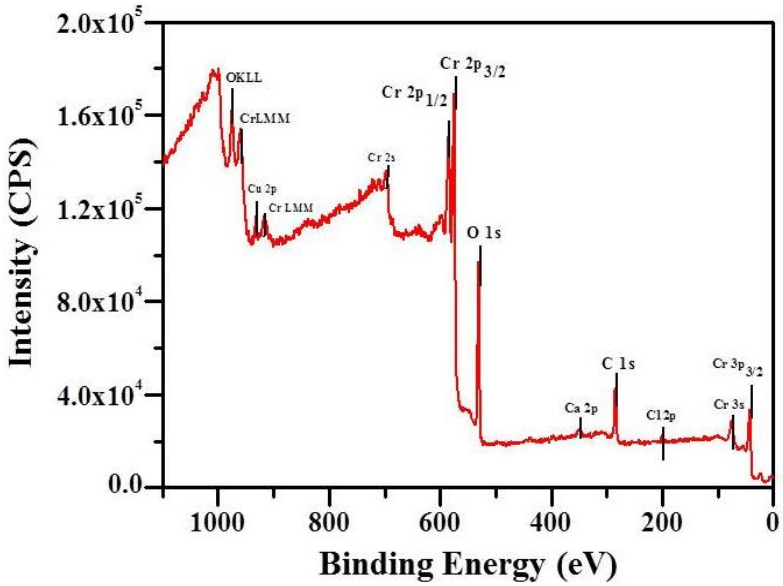

Figure S5. XPS spectra of surface coating obtained on Cu substrate from 1:2 $CrCl_3 \cdot 18H_2O$/[bmim][Cl]

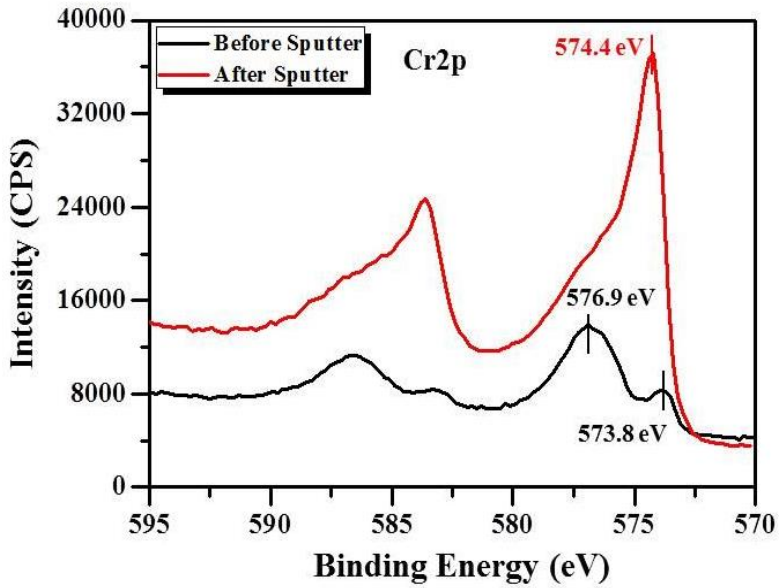

Figure S6. XPS spectra of coating obtained on Cu substrate from 1:2 $CrCl_3 \cdot 18H_2O$/[bmim][Cl] before and after Ar^+ sputtering

References

1. Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K. Ionic liquid analogues formed from hydrated metal salts. *Chemistry-a European Journal* **2004,** *10*, 3769-3774.
2. Mares, M. L.; Ciocirlan, O.; Cojocaru, A.; Anicai, L. Physico-chemical and Electrochemical Studies in Choline Chloride Based Ionic Liquid Analogues Containing Trivalent Chromium Chloride. *Rev. Chim.* **2013,** *64*, 815-824.