Electronic Supplementary Information

Enhanced Stability of the HfO_2 Electrolyte and Reduced Working Voltage of a CB-RAM by an Ionic Liquid

A. Harada,[a] H. Yamaoka,[a] R. Ogata,[c] K. Watanabe,[c] K. Kinoshita,*[,c] S. Kishida,[c] T.Nokami,[a,b] and T. Itoh*[,a,b]
Department of Chemistry and Biotechnology, and Department of Information and Electronics, Graduate School of Engineering, Tottori University, 4-101 Koyama-minami, Tottori 680-8552 (Japan). E-mail: titoh@chem.tottori-u.ac.jp, kinoshita@ele.tottori-u.ac.jp

CONTENTS

The stress test of the model CB-RAM (Cu/HfO_2/Pt):

We investigated the stress test of the model Cu-probe/ HfO_2/ Pt cell as follows: a drop of ultra pure water or [bmim][Tf_2N] was added to the surface of the HfO_2 film (25 m) which was coated on the Pt electrode, then allowed to contact the Cu-probe ((a) in **Fig. S1**). Voltage was ramped up from 0 V to 10 V when water was added on the surface of HfO_2 film in steps of 0.02 V intervals with 640 μs per plot. On the other hand, voltage was ramped up from 0 V to 15 V when [bmim][Tf_2N] which included 0.5 wt% of water was added on the surface of HfO_2 film in steps of the same intervals. Then, the Cu-probe was removed ((b) in **Fig. S1**), and water or IL was removed by washing with acetone and drying under dry air conditions, and the surface of HfO_2 film on the Pt electrode was observed ((c) in **Fig. S1**).

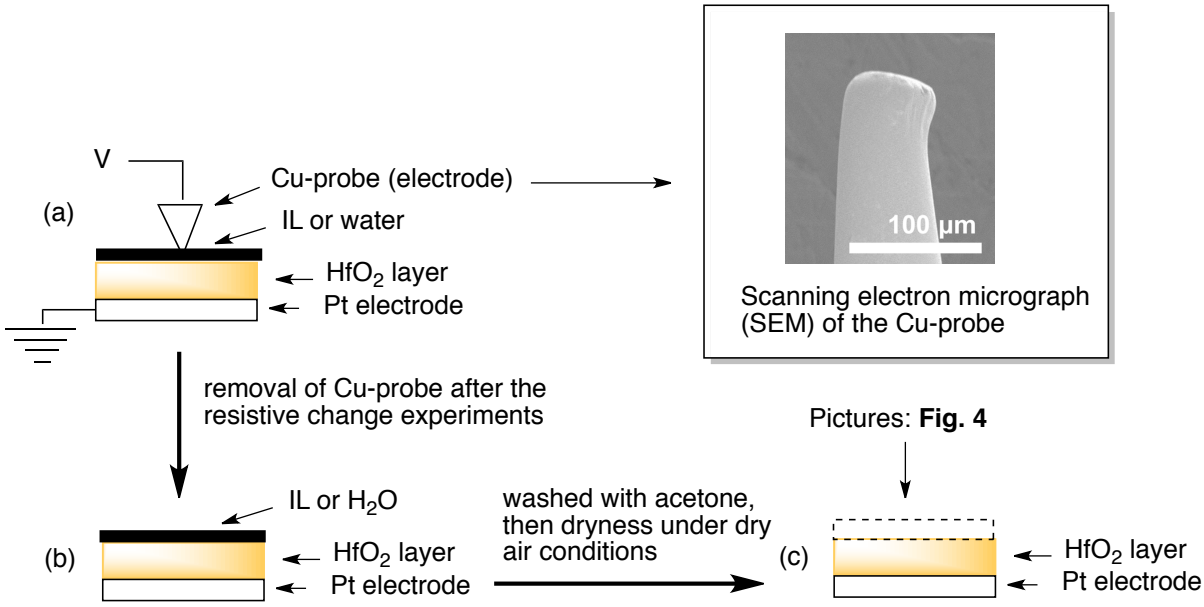
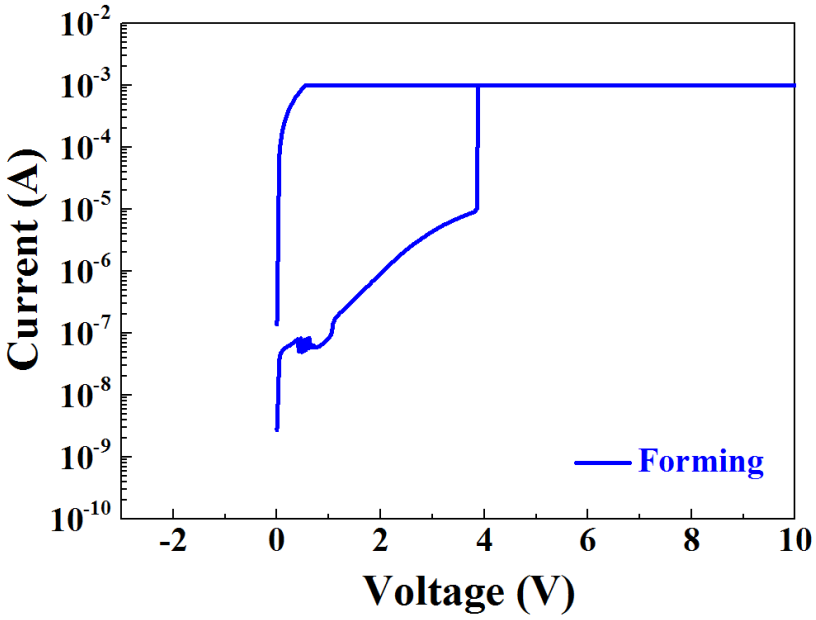


Fig. S1. Procedure of the stress test.

Photos of the surface of HfO_2 film after these experiments are shown in Fig. 4 in the main text, and *I-V* curves of these two experiments are shown in **Fig. S2.**

(a) H_2O:



(b) [bmim][Tf_2N] (0.5 wt% of H_2O):

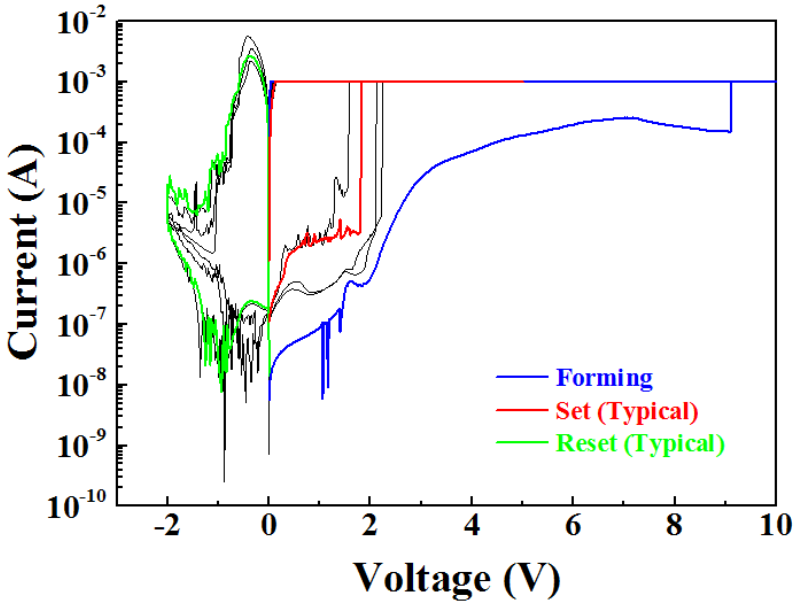


Fig. S2. *I-V* curves of two experiments.Picture (a) shows the results in the presence of water: forming occurred at 4 V. Due to the decomposition of the surface, recycling the process was unsuccessful. Picture (b) shows the *I-V* curves ofthe cell in which IL ([bmim][Tf_2N]) had been placed on the surface: forming completed at 9 V.

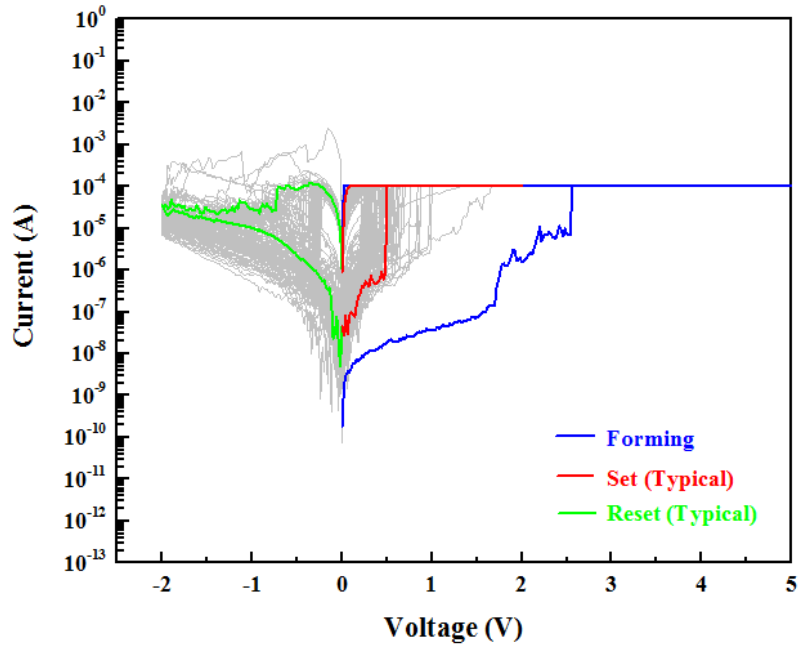


Fig. S3. Typical *I-V* curve of CB-RAM with IL (water content 100ppm) on the surface of HfO_2film (12 nm) in Fig. 3.

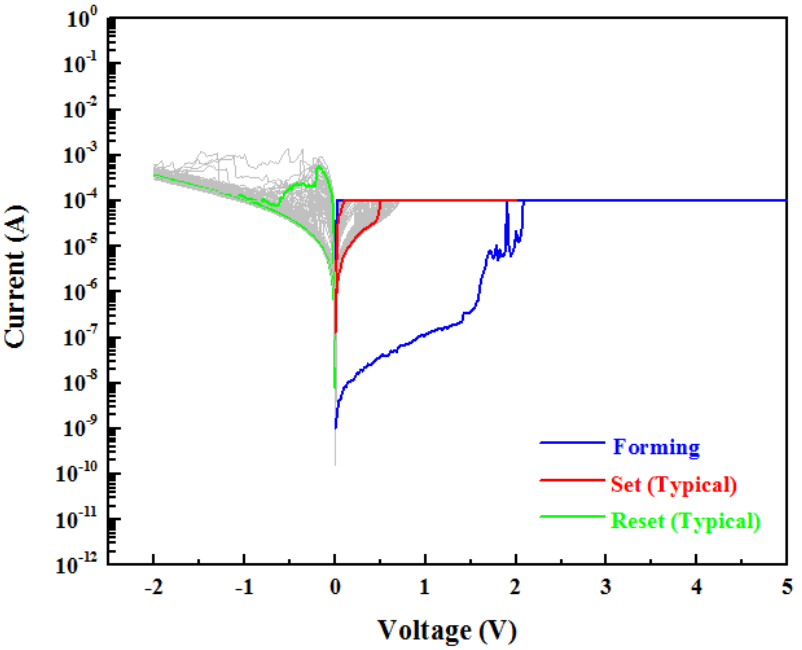


Fig. S4. Typical *I-V* curve of CB-RAM with IL (water content 800ppm) on thesurface of HfO_2film (12 nm) in Fig. 3.

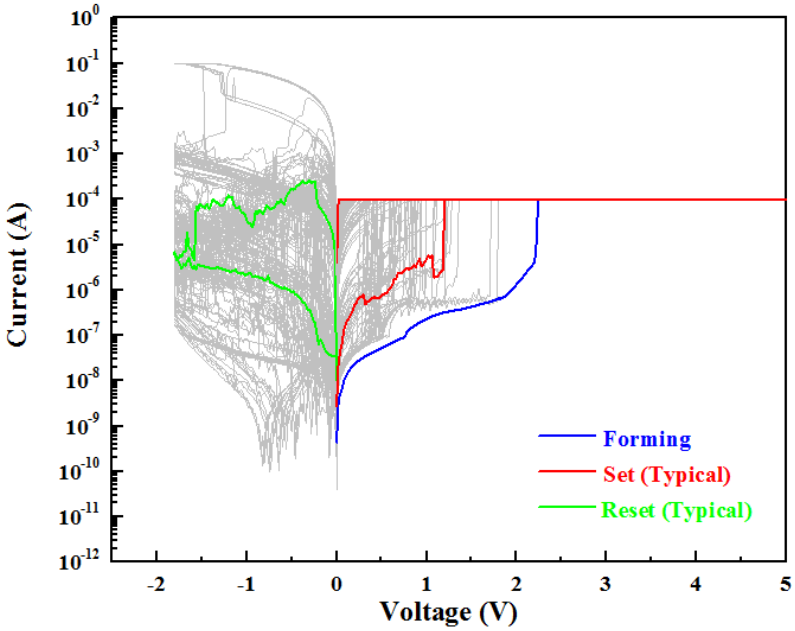


Fig. S5. Typical *I-V* curve of CB-RAM with IL (water content 5000 ppm) on thesurface of HfO_2film (12 nm) in Fig.3.

Table S1. Details of results in Fig.2.

V_{form}				V_{set}				V_{reset}			
Voltage [V]	Cumlative probabilities [%]			Voltage [V]	Cumlative probabilities [%]			Voltage [V]	Cumlative probabilities [%]		
	Ionic Liquid [a)]	H_2O	Blank		Ionic Liquid [a)]	H_2O	Blank		Ionic Liquid [a)]	H_2O	Blank
0.05	0	0	0	0.05	0	0	0	0.05	0	0	0
0.15	0	0	0	0.15	0	0	0	0.15	0	0	0
0.25	0	5	0	0.25	6	11	3	0.25	21	43	9
0.35	0	15	0	0.35	18	24	12	0.35	41	63	19
0.45	0	15	0	0.45	31	35	18	0.45	53	74	35
0.55	0	30	0	0.55	41	45	23	0.55	69	82	53
0.65	0	45	0	0.65	50	52	29	0.65	73	87	69
0.75	0	50	0	0.75	59	58	40	0.75	74	90	75
0.85	5	50	0	0.85	65	64	53	0.85	75	93	77
0.95	5	50	0	0.95	70	70	65	0.95	77	94	79
1.05	5	50	0	1.05	74	74	72	1.05	78	94	81
1.15	5	50	0	1.15	76	77	77	1.15	79	95	87
1.25	5	50	0	1.25	79	80	83	1.25	79	95	88
1.35	5	50	0	1.35	80	82	86	1.35	80	96	88
1.45	5	55	0	1.45	81	84	89	1.45	81	96	89
1.55	5	60	0	1.55	81	87	89	1.55	83	96	90
1.65	5	60	0	1.65	82	89	90	1.65	86	96	92
1.75	15	60	5	1.75	82	91	91	1.75	100	100	100
1.85	15	60	5	1.85	82	93	91	1.85	100	100	100
1.95	15	65	5	1.95	83	94	92	1.95	100	100	100
2.05	15	70	5	2.05	83	95	92	2.05	100	100	100
2.15	15	75	5	2.15	84	95	93	2.15	100	100	100
2.25	20	80	10	2.25	84	96	94	2.25	100	100	100
2.35	25	80	10	2.35	86	97	95	2.35	100	100	100
2.45	25	85	15	2.45	88	97	95	2.45	100	100	100
2.55	30	85	15	2.55	89	98	96	2.55	100	100	100
2.65	40	90	15	2.65	92	98	97	2.65	100	100	100
2.75	40	95	25	2.75	93	98	97	2.75	100	100	100
2.85	40	95	25	2.85	95	99	98	2.85	100	100	100
2.95	45	95	25	2.95	95	99	98	2.95	100	100	100
3.05	45	95	25	3.05	95	99	98	3.05	100	100	100
3.15	50	95	25	3.15	95	99	99	3.15	100	100	100
3.25	60	95	25	3.25	96	99	99	3.25	100	100	100
3.35	60	95	25	3.35	98	99	99	3.35	100	100	100
3.45	60	95	25	3.45	99	100	99	3.45	100	100	100
3.55	65	95	30	3.55	99	100	100	3.55	100	100	100
3.65	70	95	30	3.65	99	100	100	3.65	100	100	100
3.75	75	95	35	3.75	100	100	100	3.75	100	100	100
3.85	80	95	35	3.85	100	100	100	3.85	100	100	100
3.95	80	95	35	3.95	100	100	100	3.95	100	100	100
4.05	80	95	40	4.05	100	100	100	4.05	100	100	100
4.15	85	95	40	4.15	100	100	100	4.15	100	100	100
4.25	90	100	45	4.25	100	100	100	4.25	100	100	100
4.35	90	100	55	4.35	100	100	100	4.35	100	100	100
4.45	90	100	60	4.45	100	100	100	4.45	100	100	100
4.55	90	100	65	4.55	100	100	100	4.55	100	100	100
4.65	90	100	70	4.65	100	100	100	4.65	100	100	100
4.75	95	100	80	4.75	100	100	100	4.75	100	100	100
4.85	95	100	90	4.85	100	100	100	4.85	100	100	100
4.95	95	100	90	4.95	100	100	100	4.95	100	100	100
5.05	95	100	90	5.05	100	100	100	5.05	100	100	100
5.15	95	100	95	5.15	100	100	100	5.15	100	100	100
5.25	100	100	95	5.25	100	100	100	5.25	100	100	100
5.35	100	100	100	5.35	100	100	100	5.35	100	100	100

a) Water content of the IL was 5,000 ppm.

Table S2. Details of results in Fig. 3.

V_{form}				V_{set}				V_{reset}			
Voltage [V]	Cumlative probabilities [%]			Voltage [V]	Cumlative probabilities [%]			Voltage [V]	Cumlative probabilities [%]		
	Water content [a)]				Water content [a)]				Water content [a)]		
	100 ppm	800 ppm	5000 ppm		100 ppm	800 ppm	5000 ppm		100 ppm	800 ppm	5000 ppm
0.05	0	0	0	0.05	2	5	0	0.05	0	0	0
0.15	0	0	0	0.15	4	8	0	0.15	7	8	0
0.25	0	0	0	0.25	21	18	6	0.25	34	34	21
0.35	0	0	0	0.35	39	29	18	0.35	46	42	41
0.45	0	0	0	0.45	52	40	31	0.45	53	52	53
0.55	0	0	0	0.55	62	51	41	0.55	60	57	69
0.65	0	0	0	0.65	68	57	50	0.65	63	60	73
0.75	0	0	0	0.75	72	63	59	0.75	64	61	74
0.85	0	0	5	0.85	76	69	65	0.85	66	62	75
0.95	5	0	5	0.95	81	75	70	0.95	68	63	77
1.05	5	0	5	1.05	84	79	74	1.05	70	64	78
1.15	5	0	5	1.15	86	85	76	1.15	72	65	79
1.25	5	0	5	1.25	88	89	79	1.25	74	67	79
1.35	5	0	5	1.35	91	92	80	1.35	78	70	80
1.45	5	10	5	1.45	93	93	81	1.45	80	77	81
1.55	5	15	5	1.55	93	96	81	1.55	82	78	83
1.65	5	15	5	1.65	95	97	82	1.65	84	79	86
1.75	10	15	15	1.75	96	97	82	1.75	87	81	100
1.85	10	15	15	1.85	97	98	82	1.85	89	83	100
1.95	15	20	15	1.95	98	99	83	1.95	100	100	100
2.05	15	35	15	2.05	98	99	83	2.05	100	100	100
2.15	20	35	15	2.15	98	99	84	2.15	100	100	100
2.25	20	35	20	2.25	98	99	84	2.25	100	100	100
2.35	30	40	25	2.35	99	100	86	2.35	100	100	100
2.45	30	50	25	2.45	99	100	88	2.45	100	100	100
2.55	40	50	30	2.55	99	100	89	2.55	100	100	100
2.65	45	55	40	2.65	99	100	92	2.65	100	100	100
2.75	45	60	40	2.75	99	100	93	2.75	100	100	100
2.85	45	60	40	2.85	100	100	95	2.85	100	100	100
2.95	45	70	45	2.95	100	100	95	2.95	100	100	100
3.05	55	85	45	3.05	100	100	95	3.05	100	100	100
3.15	60	90	50	3.15	100	100	95	3.15	100	100	100
3.25	60	90	60	3.25	100	100	96	3.25	100	100	100
3.35	70	95	60	3.35	100	100	98	3.35	100	100	100
3.45	70	95	60	3.45	100	100	99	3.45	100	100	100
3.55	70	95	65	3.55	100	100	99	3.55	100	100	100
3.65	70	95	70	3.65	100	100	99	3.65	100	100	100
3.75	70	95	75	3.75	100	100	100	3.75	100	100	100
3.85	70	100	80	3.85	100	100	100	3.85	100	100	100
3.95	75	100	80	3.95	100	100	100	3.95	100	100	100
4.05	75	100	80	4.05	100	100	100	4.05	100	100	100
4.15	80	100	85	4.15	100	100	100	4.15	100	100	100
4.25	80	100	90	4.25	100	100	100	4.25	100	100	100
4.35	85	100	90	4.35	100	100	100	4.35	100	100	100
4.45	90	100	90	4.45	100	100	100	4.45	100	100	100
4.55	90	100	90	4.55	100	100	100	4.55	100	100	100
4.65	95	100	90	4.65	100	100	100	4.65	100	100	100
4.75	95	100	95	4.75	100	100	100	4.75	100	100	100
4.85	95	100	95	4.85	100	100	100	4.85	100	100	100
4.95	100	100	95	4.95	100	100	100	4.95	100	100	100
5.05	100	100	95	5.05	100	100	100	5.05	100	100	100
5.15	100	100	95	5.15	100	100	100	5.15	100	100	100
5.25	100	100	100	5.25	100	100	100	5.25	100	100	100

a) Water content of the IL was determined by Karl Fischer method prior to use the experiments.

Table S3. Details of results in Fig. 5.

Ionic Liquid [a)]		H_2O		Blank	
$1/R_L$ [$M\Omega^{-1}$]	I_{reset} [μA]	$1/R_L$ [$M\Omega^{-1}$]	I_{reset} [μA]	$1/R_L$ [$M\Omega^{-1}$]	I_{reset} [μA]
19370	9480	275	105	618	176
22160	10000	372	96	368	396
24550	11040	323	112	785	392
23140	11200	415	70	656	221
29820	14740	911	152	2760	460
35200	17930	440	108	300	140
21560	10360	576	108	148	165
23870	12190	304	56	1290	337
7850	2700	6160	1660	147	101
20640	9550	1660	1260	578	164
8410	2310	2150	1120	182	67
680	213	2230	947	2410	438
811	1200	1160	248	340	104
19390	6390	522	113	2080	426
1740	306	886	158	1050	182
14320	4270	590	106	1250	413
14520	4760	7640	2380	1410	316
14600	5930	5	6	3990	737
15240	5280	844	170	8440	2550
16710	5020	988	294	257	378
1140	359	1100	209	370	240
1010	168	781	197	322	239
1180	196	848	341	217	279
8530	2160	18410	3330	130	110
5470	3630	606	86	234	144
1860	522	3410	974	193	271
2060	527	3070	943	296	215
860	390	1710	372	213	268
336	430	999	576	239	318
17	716	489	322	212	223
54	735	5400	1120	217	139
7	720	13210	2240	318	220
595	217	4	14	146	3490
277	428	737	141	8060	6290
9050	2550	570	90	3880	2020
526	227	5030	1600	691	471
288	290	762	631	2800	1410
1140	246	556	329	45700	43310
35780	14450	862	270	347	404
26830	6500	5090	1220	48280	40050
1060	384	624	172	69	92
325	102	460	157	60	95
7990	3040	505	143	62	95
4790	863	599	88	68	100
457	126	556	85	69	97
822	302	546	81	60	99
3120	945	1020	202	63	91
58780	17380	7830	2320	6160	3670
2030	357	555	112	2980	1140
746	263	352	69	1900	797
11830	2390	7	2	3880	1910
761	143	679	240	1030	414
4920	1070	228	75	24450	7350
677	154	309	171	243	109
1090	940	171	128	285	144
1280	362	358	142	335	121
632	135	317	214	200	149
520	75	5910	1860	898	437
635	263	624	127	194	822
1570	922	740	141	535	755
12740	1800	572	81	453	1140
436	384	559	487	559	119
1470	452	374	80	3690	809
47	146	555	114	440	97

608	198	525	184	479	718
626	89	880	201	692	131
6660	4410	5400	1680	2340	1210
8640	2830	778	720	6310	3000
1430	495	823	141	14850	7910
1640	350	665	104	16070	7690
1520	580	697	275	8100	3470
18800	3410	1	0	14840	6850
452	65	534	478	12110	5740
138	192	7970	1880	10760	5540
8	89	562	166	427	151
275	89	2410	835	520	99
795	210	2350	509	701	139
551	168	814	228	820	145
374	142	9480	1700	637	544
194	123	183	43	964	399
404	335	756	614	732	474
366	235	5100	1390	586	666
862	290	12500	2850	1180	603
524	333	121	51	802	1200
528	482	6820	2430	1120	1490
		9100	2450	868	339
		671	182	794	294
		9300	2200	793	560
		267	70	1440	761
		11550	2490	1800	819
		2430	510	1320	1020
		354	65	2540	1010
		256	57	1020	1090
		13380	2880	11530	3270
		8550	2380	6020	2630
		2090	784	3860	1820
		917	206	236	168
		6110	1960	8290	3720
		2660	1190	2650	1530
		552	279	835	336
		1990	334	5440	2400
		618	254	3500	1460
		635	239	3970	1920
		703	133	6240	2890
		568	172	5550	2390
		707	103	3610	1670
		561	87	4210	1800
		725	104	1090	544
		468	84	37740	22690
		406	94	2020	712
		513	113	2110	797
		439	125	576	656
		656	81	2400	795
		445	134	2730	969
		608	106	2200	784
		503	157	231	585
		687	139	154	106
		508	126	356	198
		150	114	272	123
		1110	222	6970	1700
		487	201	1120	1440
		423	189	1820	706
		255	83	833	334
		338	177	2410	926
		208	51	227	112
		313	93	1770	707
		4040	1290	2700	1180
		144	180	130	109
		139	64	101	116
		3140	946	292	148
		507	144	386	265
		398	178	1530	702
		2600	507	31150	25590

		345	221	833	471
		14110	3670	2380	889
		3040	1490	1080	430
		7400	1400	1150	544
		594	151	2180	857
		584	146	176	122
		404	107	204	161
		1100	224	206	135
		132	113	183	152
		389	174	269	200
		2050	552	289	211
		958	187	262	151
		1010	197	153	183
		6760	2250	192	201
		469	97	196	137
		792	429	229	201
		1560	691	145	163
		481	110	174	151
		363	111	21640	7450
		428	130		
		229	72		
		4450	2050		
		2080	1020		
		11140	7300		
		13040	3180		
		7060	1890		
		6250	1290		
		713	355		
		315	85		
		3440	874		
		4800	980		
		676	615		
		630	202		
		579	240		
		381	458		
		666	188		
		614	261		
		628	574		
		713	398		
		13970	2570		
		8380	5800		
		1520	608		
		8440	5450		
		6790	1180		
		488	1200		
		497	106		
		3900	844		
		915	197		
		705	165		
		5040	1460		
		3080	882		
		3870	933		
		10960	2090		
		14820	2620		
		9810	2310		
		8730	2240		

a) Water content of the IL was 5,000 ppm.