Impurities of Ionic Liquids and their Influence on the corrosion of metals and alloys

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Ionic Liquids Technologies

Introduction

Over the past years ionic liquids (ILs) have attracted much interest, since they can be used in a broad variety of interesting applications (Fig. 1). Today, ionic liquids are not just used as solvents, but also for physico- and electrochemical applications.

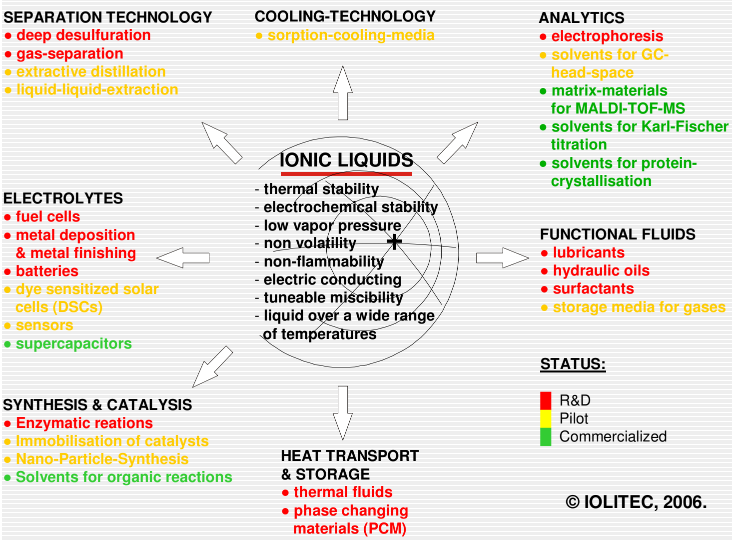


Fig. 1. Commercialization of Ionic Liquids.

The influence of impurities

Many of these properties of IL are very sensitive to impurities like halides or water. As shown elsewhere, small amounts of halides can have a strong influence on viscosities and conductivities.

Another important property of ionic liquids that is influenced very strongly by impurities is the corrosion of metal and alloys. Again halides, but also free acids or amines can be responsible for a substantial corrosion behaviour.

Experimental Results

To test the influence of halides on the corrosion against a typical alloy, we used brass together with a couple of typical neat ionic liquids (halide and water content <50 ppm, ion chromatography & Karl-Fischer) and ionic liquids, containing 1% of sodium chloride. After 24 hours at 100°C, we evaluated the samples visually and gravimetrically.

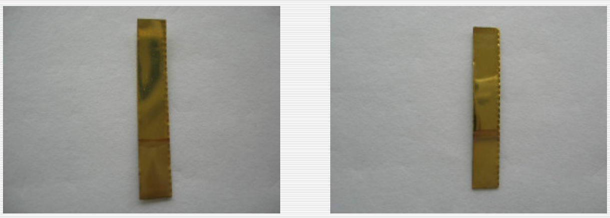


Fig 2. [BMIM] PF_6 without (left) and with addition of 1% NaCl (right).

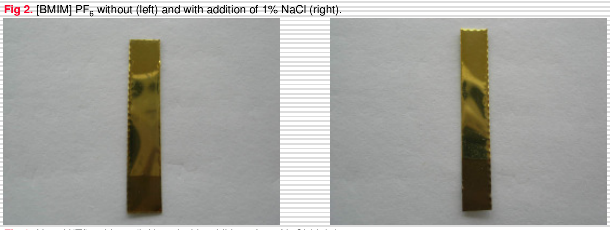


Fig 3. N_{1114} $N(Tf)_2$ without (left) and with addition of 1% NaCl (right).

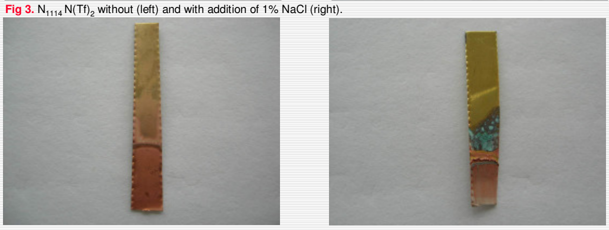
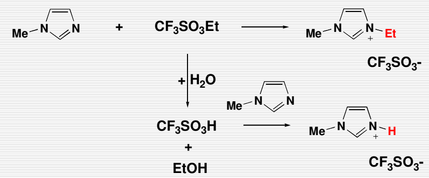


Fig 4. [EMIM] OTf without (left) and with addition of 1% NaCl (right).

To our surprise, typical ionic liquids such as BMIM PF_6 (Fig. 2 & Tab. 1, run 2) or HMIM BF_4 (Tab. 1, run 1) showed a better performance than expected (both IL are known that they can decompose under formation of HF). This trend did not even change after the addition of 1% NaCl (Tab. 2, run 1+2).

The best performances showed a commercially available product (Tab. 1+2, run 3) and the two $N(Tf)_2$-based ionic liquids (Tab. 1+2, run 4, and Tab. 1, run 10, Tab. 2, run 11). Even after the addition of 1% NaCl, no substantial corrosion was observed after 24 hours.

This was totally different for triflate-based ILs: The neat IL led to a massive corrosion, which was significantly enhanced after the addition of NaCl. We explain this aggressive behaviour with acid impurities, caused by a side-reaction:



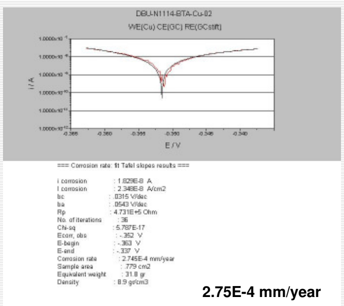
Tab. 1. Corrosion of neat IL.

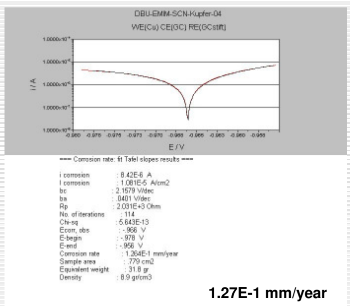
run no.	IL	mass alloy [g]	mass after 3d [g]	mass lost [g]
1	HMIM BF_4	0,4616	0,4613	0,0003
2	BMIM PF_6	0,5514	0,5507	0,0007
3	Comm. Prod.	0,5289	0,5288	0,0001
4	EMIM $N(Tf)_2$	0,6068	0,6067	0,0001
5	EMIM OTos	0,5622	0,5614	0,0008
6	EMIM $EtSO_4$	0,5552	0,5548	0,0004
7	EMIM $MeSO_3$	0,5901	0,5893	0,0008
8	EMIM OTf*	0,5850	0,5785	0,0065
9	BMIM OTf*	0,4931	0,4813	0,0029
10	N_{1114} $N(Tf)_2$	0,7874	0,7873	0,0001

Tab. 2. Corrosion of neat IL+1% NaCl.

run	IL	added NaCl [g]	Wgt.-% NaCl	IL [g]	mass [g]	mass after 3d [g]	lost mass [g]
1	HMIM BF_4	0,0011	0,05	2,3110	0,5361	0,5349	0,0012
2	BMIM PF_6	0,0015	0,08	1,9329	0,4944	0,4934	0,0010
3	Comm. Prod.	0,0018	0,12	1,4541	0,4266	0,4265	0,0001
4	EMIM BTA	0,0016	0,10	1,6335	0,4882	0,4878	0,0004
5	EMIM OTos	0,0009	0,05	1,6583	0,5269	0,5260	0,0009
6	EMIM $EtSO_4$	0,0010	0,07	1,4294	0,5067	0,5058	0,0009
7	EMIM $MeSO_3$	0,0019	0,10	1,9665	0,4072	0,4058	0,0014
8	BMIM OTf	0,0011	0,11	0,9973	0,4977	0,4948	0,0118
9	N_{1114} $N(Tf)_2$	0,0018	0,11	1,6289	0,5736	0,5734	0,0002

Finally, we determined the electrochemical noise (using a Metrohm Autolab PG STAT 30 system) to quantify the corrosion rate of EMIM SCN and N_{1114} $N(Tf)_2$ against neat copper. After evaluating the data using the so-called Tafel-plot, we found that the corrosion-rate for EMIM SCN was not negligible ($1.26 \cdot 10^{-1}$ mm/year), while the rate for N_{1114} $N(Tf)_2$ was comparable low ($2.75 \cdot 10^{-4}$ mm/year).





Summary

Whenever IL are in contact with metals and alloys, it is necessary to keep impurities as low as possible to avoid corrosion. In addition, even some pure ionic liquids can be very corrosive, while other materials are more or less corrosion-inhibitors.

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