

Electrochemical study of corrosion of copper
in 1-alkyl-3-methylimidazolium tetrafluoroborates

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Copper is resistive to corrosion in dry and chloride-free 1-alkyl-3-methylimidazolium tetrafluoroborates at room temperature, and the corrosion rate decreases with the chain length of the substituent in imidazolium ring and increases with the temperature. The activation energies of corrosion are on the order of 50 kJ/mole. The corrosion is enhanced in the presence of traces of chlorides.

1. INTRODUCTION

Low temperature ionic liquids are considered as an attractive alternative to other solvents in organic synthesis, heat transfer and batteries [1-5]. Low volatility at temperatures <100 °C is their unique property, and it is much desired in different applications [6-8]. It can very well be that indeed low temperature ionic liquids will soon replace traditional solvents in certain applications. In spite of high publication activity in the field of low temperature ionic liquids, corrosion of metals, which may be a problem in certain practical applications, was seldom visited by scientists. Any industrial installation involving low temperature ionic liquids may require their contact with metals, and enhanced corrosion is possible. Not necessarily metals, which are corrosion-resisting in traditional solvents will also be corrosion-resisting in low temperature ionic liquids. Corrosion is a complex phenomenon, and it depends on many factors. Full analogy between corrosion in water on one hand and in other solvents on the other is not expected, but application of standard methods and concepts used to study corrosion in aqueous media is a good starting point.

Perissi et al. [9,10] studied corrosion of metals in 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide containing traces of chloride. At room temperature the rate of corrosion was negligible (j_{corr} of $1.11 \mu\text{A}/\text{cm}^2$ for Cu), and the rate of corrosion (pitting corrosion) increased with temperature. Interestingly the studied temperature range (150-325 °C) exceeded the range of thermal stability of the ionic liquid [11]. The products of high-temperature corrosion contained Cl and F. Uerdingen studied corrosion of various metals in ionic liquids containing air and water at 90 °C under stirring. Water was found as a factor enhancing the corrosion [12].

The results of our preliminary study of corrosion of copper in 1-alkyl-3-methylimidazolium tetrafluoroborates are presented in this paper.

2. EXPERIMENTAL

2.1. Ionic liquids

The 1-alkyl-3-methylimidazolium chlorides were obtained from methylimidazole and alkyl chlorides by means of standard method. The 1-alkyl-3-methylimidazolium tetrafluoroborates were obtained by metathesis from 1-alkyl-3-methylimidazolium chlorides and NH_4BF_4 in acetonitrile. Stoichiometric proportions of the reagents lead to chloride-containing tetrafluoroborates. Chloride-free tetrafluoroborates are obtained in the presence of excess of NH_4BF_4 when the equilibration time is long enough. By analogy with aqueous systems we expect that the presence of traces of chlorides can enhance the corrosion. Thus in our preparations we paid special attention to the chloride-impurities in the ionic liquids. In addition to chloride-free tetrafluoroborates, we studied 1-butyl-3-methylimidazolium tetrafluoroborate containing 0.02 % Cl by mass. The concentration of chlorides in the ionic liquids was controlled by Vollhard method.

The ionic liquids were dried prior to electrochemical experiments, and no attempts to determine the water concentration were made. Yet the experience of the others suggests that tetrafluoroborates are hygroscopic, and even carefully dried ionic liquids contain traces of water.

2.2. Corrosion studies

The electrochemical study was carried out in a 3 - electrode system. A piece of copper rod, 99.9 % pure and 2.5 mm in diameter was the working electrode. The rod was mounted in a Teflon housing, and the exposed area was 0.196 cm^2 . The electrode was polished by means of #1200 abrasive paper, washed in water and in acetone, and dried. Platinum plate, exposed area of 1.5 cm^2 was a counter electrode, and platinum wire, 0.5 mm in diameter in a glass capillary filled with the ionic liquid of interest (chloride-free) was the reference electrode. The

electrodes were mounted in a specially designed thermostated vessel containing 10 cm³ of ionic liquid, which assured reproducible geometry of the system. Each measurement was carried out with a fresh portion of ionic liquid. The ionic liquids were dried and outgassed in a vacuum dryer just before the measurements, and the measurements were carried out in a dry box filled with a drying agent.

Electrochemical analyzer Atlas (Poland) was used in the polarization measurements of Cu electrode. The density of corrosion current was determined from voltammetric curves in non-Tafel range, which corresponds to low polarization conditions, ± 20 mV from the stationary potential. The stationary potential was measured 30 min. after the immersion. The scan range was 10 mV/min, and the data points were recorded every 1 mV. The polarization curves were interpreted in terms of the following Stern-Geary equation [13]

$$R_p = \Delta E / \Delta j_{\text{corr}} = b_k b_a / [2.3 j_{\text{corr}} (b_a + b_k)] \quad (1)$$

where R_p is the polarization resistance, b_a and b_k are Tafel coefficients for anodic and cathodic reaction, and j_{corr} is the density of corrosion current.

The voltammetric curves were also obtained in the range ± 1 V at a scan rate of 100 mV/min and the data points were recorded every 10 mV. The activation energy of corrosion was calculated from the following Arrhenius equation

$$E_a = \frac{(\log j_1 - \log j_2) 2.303 R T_1 T_2}{T_1 - T_2} \quad (2)$$

where j_1 and j_2 are current densities at $T_1=25$ °C and $T_2=50$ °C, respectively, over the potential range of the anode of 0 to 1000 mV.

Similar measurements as with ionic liquids were carried out in 3 % aqueous NaCl at 25 °C without stirring. No attempts were made to remove dissolved gases from the solution.

Morphology of Cu stored for 2 d at 50 °C in BMIBF₄ (with or without admixture of chloride) under open-circuit-conditions was studied by means of BS-304 scanning electron microscope (Tesla) with a X-ray probe.

3. RESULTS AND DISCUSSION

3.1. Physical properties of the ionic liquids

Physical properties of the ionic liquids are summarized in Table 1. Similar results were reported in other publications [4,6,7,14].

Tab. 1. Physical properties of 1-alkyl-3-methylimidazolium tetrafluoroborates.

Liquid	d [gcm ⁻³]	η [mPas]	κ [mScm ⁻¹] 25°C	κ [mScm ⁻¹] 35°C	κ [mScm ⁻¹] 50°C
BMIBF ₄	1.210	98.28	3.214	3.821	4.902
BMIBF ₄ + 0.02 % Cl	1.205	100.57	3.177	3.767	4.829
HMIBF ₄	1.149	205.29	1.395	1.714	2.394
MOIBF ₄	1.042	316.01	0.714	0.897	1.324

3.2. Corrosion in aqueous medium

The density of corrosion current in 3 % aqueous NaCl at 25 °C was 11.5 $\mu\text{A}/\text{cm}^2$. Similar results are reported in literature [15,16].

3.3. Reproducibility of results

The density of corrosion current depends of parameters, which may be difficult to control. Therefore the significance of single measurement is limited. Table 2 reports results of a series of 5 measurements carried out at apparently identical conditions.

Tab. 2. Reproducibility of polarization curves of Cu in BMIBF₄ at 25 °C.

number of measurement	E_{corr} mV	j_{corr} $\mu\text{A cm}^{-2}$	b_a mV	b_k mV	R_p k Ω
1	- 175	0.74	58.4	51.9	16.1
2	- 225	0.58	53.2	68.6	22.3
3	- 193	0.68	84.4	72.3	24.9
4	- 202	0.49	60.9	54.5	25.5
5	- 191	0.47	64.0	60.8	28.8
average	- 197	0.59	64.2	61.6	23.5
standard deviation	18.3	0.12	11.9	8.7	6.7

The densities of corrosion current relate to the geometric surface area, that is, surface roughness was ignored. The last 3 columns in Table 2 are parameters calculated from Stern-Geary equation. Most likely the differences in j_{corr} by 50 % between the highest and the lowest value in Table 2 are due to a difference in surface roughness. The parameters reported in Table 2 show a standard deviation on the order of 20 % of the measured (calculated) quantity, and we assume that similar scatter will be observed with other ionic liquids. Thus only one decimal digit is significant, but we report our results with 3 decimal digits.

The value j_{corr} , obtained for BMIBF₄ is lower by an order of magnitude that j_{corr} observed in aqueous medium, and it is similar to the j_{corr} of Cu in 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide containing traces of chloride [9].

3.4. Corrosion in ionic liquids

Table 3 reports analogous results as Table 2 obtained for BMIBF₄, BMIBF₄ containing 0.02 mass % of Cl, HMIBF₄ and MOIBF₄ at 25, 35 and 50 °C.

Tab. 3. Parameters of polarization curves of Cu in 1-alkyl-3-methylimidazolium tetrafluoroborates.

Liquid	Temp. °C	E_{corr} mV	j_{corr} $\mu\text{A cm}^{-2}$	b_a mV	b_k mV	R_p^* k Ω	$E_a \pm$ standard deviation kJ/mol
BMIBF ₄	25	-197	0.59	64.2	61.6	23.5	43.9 \pm 5.9
	35	-246	1.38	83.7	71.5	12.1	
	50	-265	1.88	88.2	31.5	5.3	
BMIBF ₄ /Cl	25	-392	1.13	54.2	46.6	9.6	38.4 \pm 3.8
	35	-457	2.06	59.7	36.9	4.8	
	50	-448	3.99	88.6	28.3	3.1	
HMIBF ₄	25	-63	0.57	98.6	70.4	31.3	48.7 \pm 1.1
	35	-104	1.29	73.3	51.8	10.2	
	50	-154	1.65	54.6	41.1	6.17	
MOIBF ₄	25	-43	0.41	83.3	47.5	32.1	52.5 \pm 1.6
	35	-74	0.98	62.9	46.7	11.9	
	50	-103	1.43	74.4	38.5	7.71	

* calculated from Stern-Geary equation

Results of single measurements are reported except for BMIBF₄, at 25 °C for which an average of 5 measurements is reported. The j_{corr} in particular ionic liquids is plotted as the function of temperature in Figure 1, and the entire voltammetric curves are presented in Figures 2-5. In spite of limited significance of single measurements discussed in Section 3.3, the above results are significant enough to draw a few general conclusions. First, j_{corr} decreases as the chain length of the substituent in imidazolium ring increases and increases with the temperature. This result is consistent with the effect of the chain length and of temperature on the conductivity (Table 1). The temperature coefficient of the viscosity of ionic liquids of about 5.3 % K⁻¹ [8] was used to estimate the temperature effect on j_{corr} . The estimated increase in j_{corr} induced by increase in temperature by 25 °C is by a factor of 3.6, which overestimates the experimental value of <3 (Table 2). The polarization resistance calculated from Stern-Geary equation increases with the chain length of the substituent in imidazolium ring and decreases with the temperature. The Tafel coefficients characterizing corrosion of Cu in ionic liquids suggest anodic or mixed control. Traces of chloride, which have rather insignificant effect in physical properties of ionic liquids enhanced j_{corr} and depressed R_p by a factor of 2. Complexation of Cu by chloride is probably responsible for enhanced corrosion [17-19].

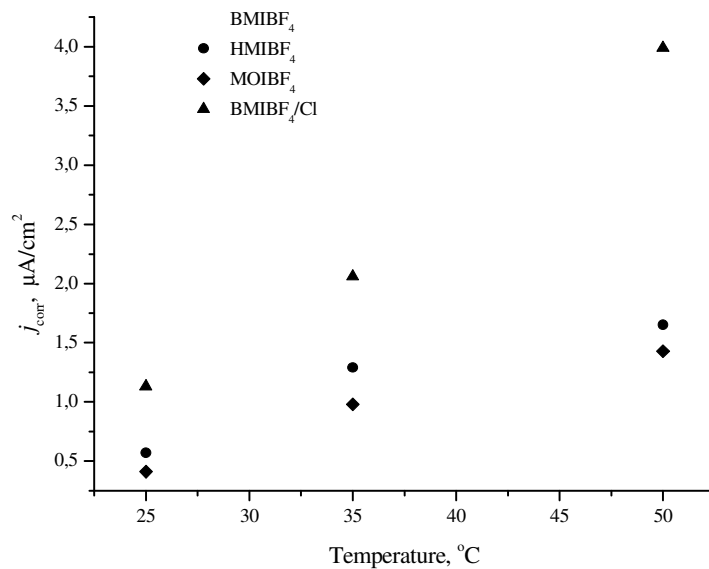


Fig. 1 Corrosion current of Cu in 1-alkyl-3-methylimidazolium tetrafluoroborates as the function of temperature.

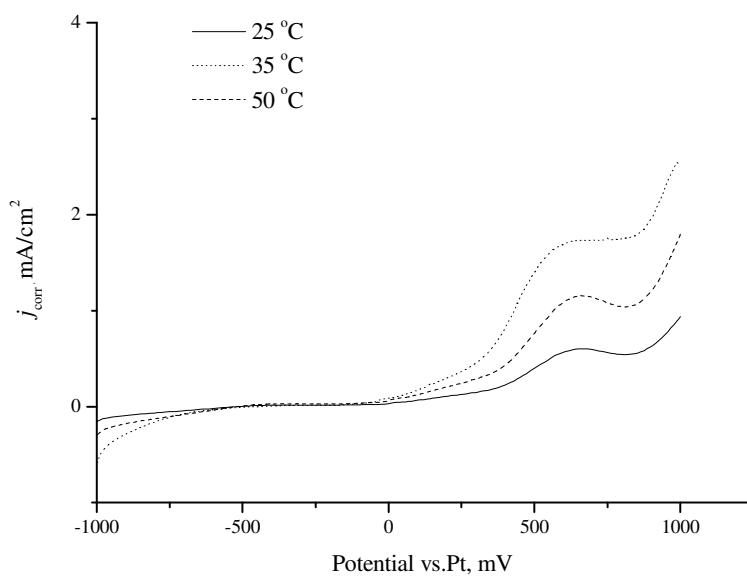


Fig. 2. Voltammetric curves of Cu in chloride-free BMIBF₄.

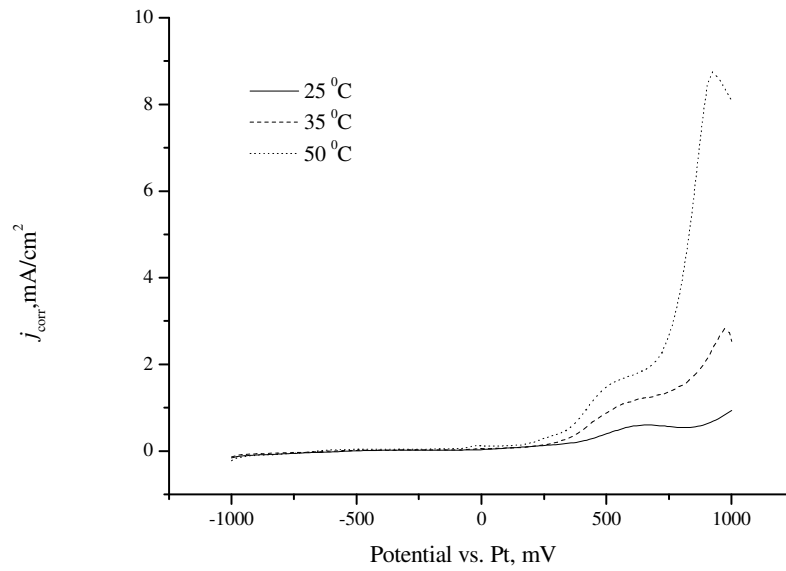


Fig. 3. Voltammetric curves of Cu in BMIBF₄ containing 0.02 mass % of Cl.

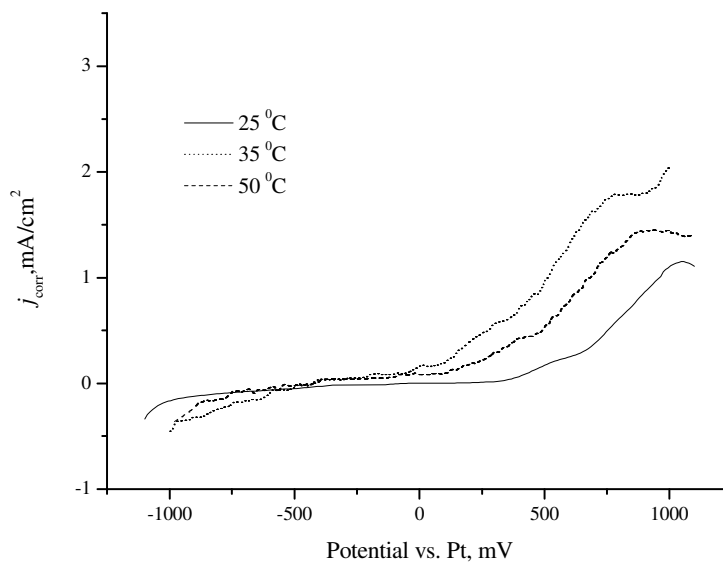


Fig. 4. Voltammetric curves of Cu in HMIBF₄.

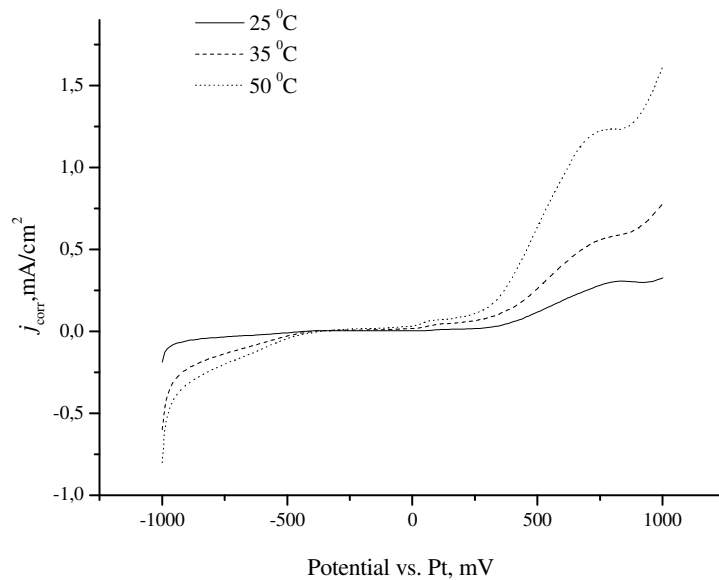


Fig. 5. Voltammetric curves of Cu in MOIBF₄.

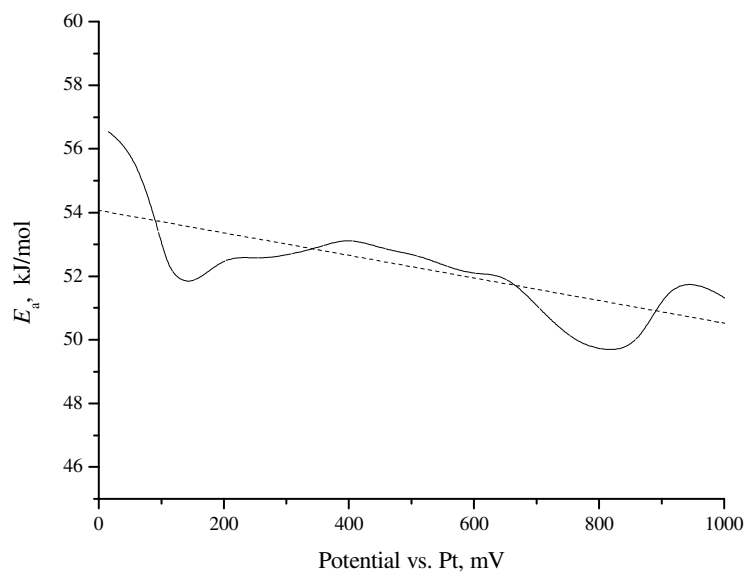


Fig. 6. Activation energy of corrosion of Cu in MOIBF₄. Solid line represents the results. Dashed line represents linear interpolation.

The activation energies calculated by means of Eq.(2) over a potential range 0–1000 mV are plotted in Figure 6. The effect of potential on E_a is rather insignificant, thus the average values reported in Table 2 are representative for a broad potential range. The magnitude of E_a and limited effect of potential suggest that the corrosion rate is controlled by diffusion. E_a slightly increases with the chain length of the substituent in imidazolium ring, and it drops substantially in the presence of traces of chloride.

3.5. Surface morphology

The morphology of Cu stored for 2 days at 50 °C in BMIBF₄ (with or without admixture of chloride) is illustrated in Figures 7 and 8.

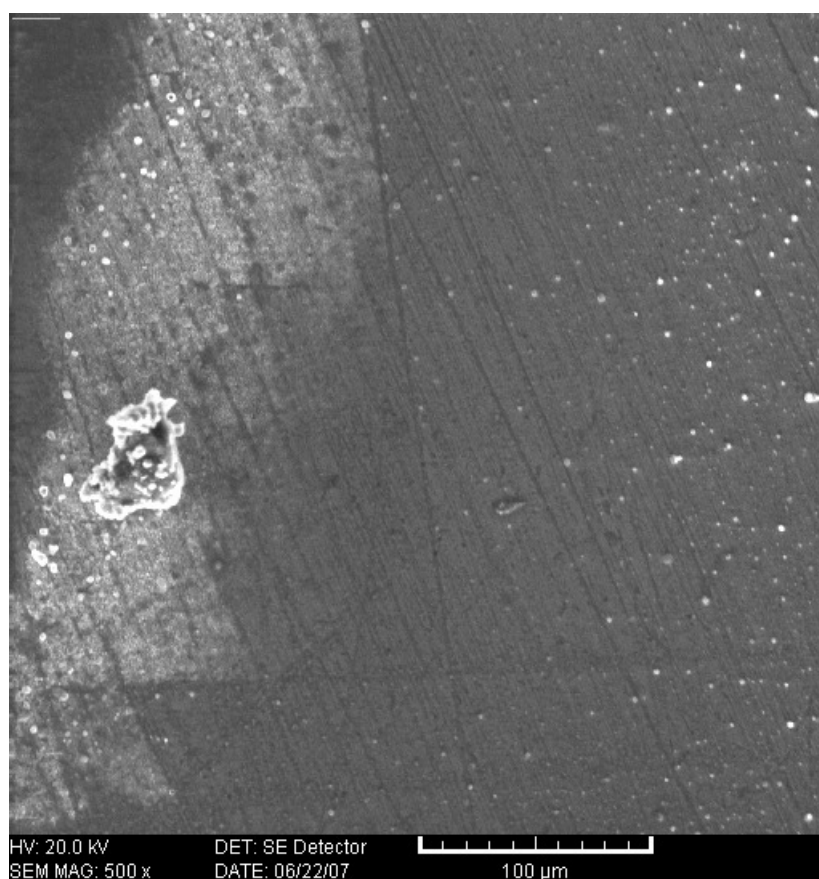


Fig. 7. Surface of Cu after 2 d in chloride-free BMIBF₄ at 50 °C.

The specimen corroded in chloride-free BMIBF₄ (Fig. 7) shows irregularly distributed small pits and a few larger pits. The specimen corroded in chloride-containing BMIBF₄ (Figure 8) shows etches and large pits, but also large flat areas affected by uniform corrosion.

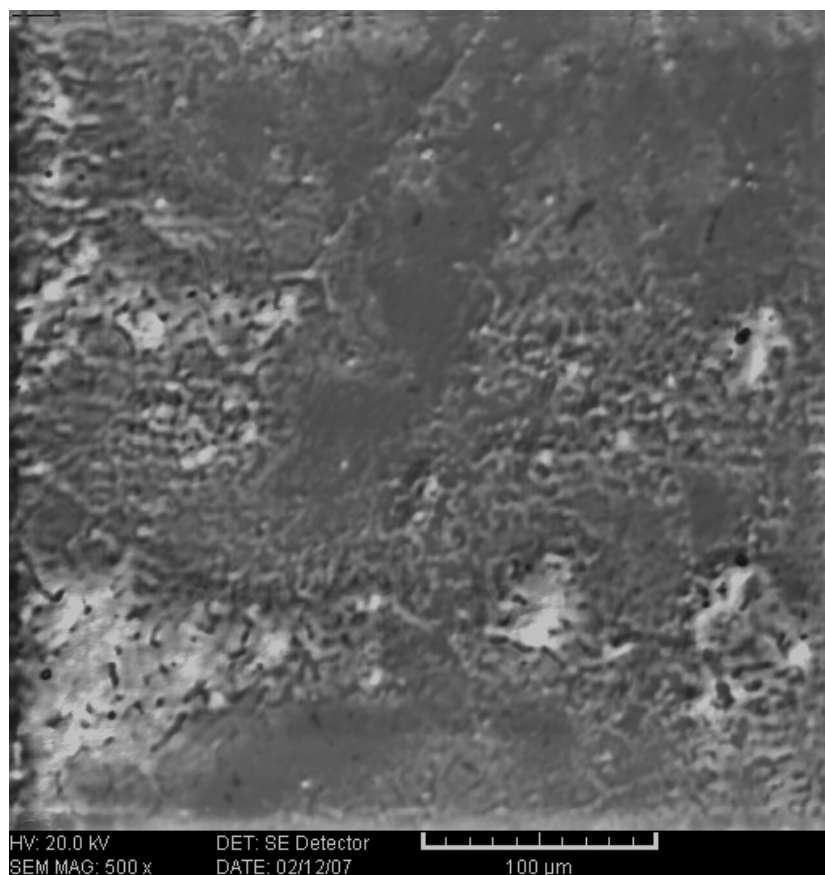


Fig. 8. Surface of Cu after 2 d in BMIBF₄ containing 0.02 mass % of Cl at 50 °C.

The analysis of corrosion products, performed by microanalyser EDS (Thermo electron Co. USA) with NORAN 300 system, products indicated presence of F, B, N, C, Cl and O in both samples. An example of quantitative analysis is presented in Table 4.

Tab. 4. Composition of corrosion products (in mass %, from K-line).

Element	Cu aged for 2 days at 50 °C in	
	BMIBF ₄	BMIBF ₄ /Cl
B	0.5	0.89
C	17.35	18.74
N	7.35	5.85
O	18.94	15.41
F	1.73	3.11
Cl	0.42	1.64
Cu	53.71	54.36

The presence of Cl in corrosion products obtained in apparently chloride-free ionic liquid indicate that even traces of Cl not detectable by Vollhard method may significantly affect the corrosion process. It can very well be that the effect of the chain length of the substituent in imidazolium ring observed in the present study was distorted by the presence of Cl not detectable by Vollhard method in apparently chloride-free ionic liquids.

4. CONCLUSION

Apparently chlorides play a key role in the corrosion process of Cu in dry ionic liquids, and removal of every trace of Cl from ionic liquids, which have to contact with copper can be suggested as a measure against corrosion.

5. REFERENCES

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