Ionic liquids as a neat lubricant applied to steel-steel contacts

A. García[a,]*, R. González[b,d], A. Hernández Battez[a,d], J.L. Viesca[a,d]
R. Monge[a], A. Fernández-González[c], M. Hadfield[d]

[a] Department of Construction and Manufacturing Engineering, University of Oviedo, Asturias, Spain
(*)*Email:* garciamaralberto@uniovi.es
[b] Department of Marine Science and Technology, University of Oviedo, Asturias, Spain
[c] Department of Physical and Analytical Chemistry, University of Oviedo, Asturias, Spain
[d] School of Design, Engineering and Computing, Bournemouth University, UK

Abstract

This paper studies the use of 3 ionic liquids ([(NEMM)MOE][FAP], [BMP][FAP] and [BMP][NTf_2]) as neat lubricant within steel-steel contact conditions. Tribological tests (at 40 and 100ºC) were conducted in a HFRR tribometer and hence a complementary study was developed using a MTM tribometer. The wear surface on the discs was measured after the HFRR tests by confocal microscopy and also analyzed by SEM and XPS. The [BMP][NTf_2] showed the lowest friction coefficient in the MTM and HFRR tests at 40ºC but at 100ºC its tribological behavior worsened due to its lowest viscosity. Similar results were found for wear behavior. Both antifriction and antiwear results were related to the tribofilms formation from the ECR and XPS measurements.

Keywords: ionic liquids, lubrication, wear, friction coefficient

1. Introduction

Since 2001 several papers have been published that investigate the potential use of ionic liquids (ILs) for lubrication. Most of this work has been focused on using ILs as base stock or as a pure lubricant [1]. Ionic liquids have some high performance properties for lubrication such as non-flammability, non-volatility, high ionic conductivity, high thermo-oxidative stability and miscibility with organic compounds [2- 4]. Due to the high temperature properties of the ionic liquids, they can be used as a pure lubricant under severe tribological conditions for which conventional lubricants do not perform well [5-7].

In addition, the advantages of using ILs as additives and their interaction with the wear surfaces have been studied by numerous authors [2,8,9]. Most of the early researches in the use of IL as lubricants has been focused on the use of PF_6 and BF_4 imidazolium salts [10,11]. However, the presence of these anions can produce unfavorable chemical reactions of the IL with water and lead to the formation of hydrogen fluoride, which can damage tribology systems [12]. For these reasons, several authors are focused on the research with hydrophobic ILs. Among the hydrophobic ILs can be found those based on the anions bis(trifluoromethylsulfonyl)imide [NTf_2] and tris(pentafluoroethyl)trifluorophosphate [FAP]. These ILs combine their higher hydrophobicity with their excellent hydrolytic stability [13]. Taking into account that fact, Gonzalez *et al*. studied the use of the ionic liquid 1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([BMP][FAP]) as neat lubricant and as additive in the lubrication of conventional PVD coatings (CrN, TiN and DLC) [14]. Blanco *et al*. used ethyl-dimethyl-2-methoxyethylammoniumtris(pentafluoroethyl)trifluorophosphate ([(NEMM)MOE][FAP]) as base oil additive in the lubrication of TiN and CrN PVD coatings [15,16]

The tribological behaviour of ionic liquids as neat lubricants or as additives has been evaluated for different types of contact, with steel-steel being the most studied case [17- 21]. Now, this paper studies the use of three ionic liquids based on the [FAP] and [NTf_2] anions as neat lubricant applied to steel-steel contacts.

2. Experimental details

The properties of the ionic liquids used as lubricants in this study are listed in Table 1. The viscosity of the ionic liquid at high shear rates (10^6-10^7 s^{-1}) and temperatures of 70 and 100ºC was measured using an Ultra Shear Viscometer (PCS Instruments, UK), because of typical shear rates in the boundary lubrication regime reach values greater than 10^6 s^{-1}. The tribological tests conducted using the high frequency reciprocating rig (HFRR) (PCS Instruments, UK) considered the typical specimens: AISI 52100 steel balls (with 6.0 mm diameter, 58-66 HRC of hardness and less than 0.05 μm of roughness) and softer AISI 52100 steel discs (190-210 HV_{30} and roughness of less than 0.02 μm). The HFRR is a reciprocating friction and wear test machine which provides reliable assessment of the tribological behavior of lubricants and additives under a wide range of load, stroke length, frequency and temperature values. Such experiments were developed at a normal load of 7.85 N (corresponding to a maximum contact pressure of 1.31 GPa) under fully flooded lubrication, a stroke length of 2 mm, a frequency of 25 Hz, and duration of 60 minutes (corresponding to a sliding distance of 360 m). The ionic liquid temperature was controlled and these experiments were conducted at temperatures of 40 and 100ºC. Friction force and electrical contact resistance (ECR) in order to determine the tribofilms formation on the wear surfaces were measured during the tribological tests. Each tribological test was repeated at least three times. The wear scar volume on the disc surface was measured after each test using confocal microscopy methodology. Tested surfaces were also analyzed by SEM and XPS in order to determine their chemical composition and the dominant wear mechanism.

Before the experiments using the HFRR tribometer, the ionic liquids were tested in a Mini Traction Machine (MTM) from PCS Instruments Ltd. in order to obtain their tribological behaviour under different contact conditions. The MTM is a tribometer with a ball-on-disc configuration where the antifriction and antiwear properties of lubricants and additives can be tested under variable load, speed and temperature conditions. Both the disc and the ball are driven independently providing slide-roll ratios (SRR) from 0% (pure rolling) to 200% (pure sliding). Such tests were performed at room temperatures using 0.25 ml of ionic liquid in the contact between the ball (AISI 52100, 18 mm. diameter, $R_a < 0.01$ µm) and the disc (AISI 52100, 46 mm. diameter, $R_a < 0.01$ µm), at normal load of 50 N (corresponding to a maximum contact pressure of 1.13 GPa), at sliding-rolling ratio of 50%, and rolling speed from 3 to 200 mm/s.

3. Results and discussion

The results obtained from the experiments conducted using the MTM at room temperature, Fig. 1, showed clearly that under favorable contact conditions (higher rolling speed in this case) the [BMP][NTf_2] ionic liquid performs better. However, its tribological behaviour become worse more rapidly than the FAP-based ionic liquids when the rolling speed decreases. This tribological behaviour is related not only to the balance of formation/destruction of the tribofilms on the wear scar surface but also to the rheological behavior of the ionic liquids. It is noted that [BMP][NTf_2] ionic liquid has lower viscosity than the other ionic liquids for both tested temperatures, Fig. 2.

The results of the experiments conducted at 40ºC using the HFRR machine showed that the lowest friction coefficient values was reached with the [BMP][NTf_2] ionic liquid, while the FAP-based ionic liquids presented similar friction coefficient values being slightly better the [BMP][FAP], shown as Fig. 3. Simultaneously, the electrical contact resistance (ECR) was measured during the friction and wear tests confirming the tribofilms formation in all cases.

Some tribological changes were detected during tests made at 100ºC, Fig. 4. Now, the tribofilms formation in the tests with [BMP][NTf_2] was almost null and hence the increase in the friction coefficient. The FAP-based ionic liquids with similar tribofilms formation showed close friction coefficient values. This change with temperature for the tribological behavior of the [BMP][NTf_2] was analysed more in detail using the XPS technique.

Fig. 5 shows the average friction coefficient of all testing conditions performed in the HFRR machine. In general the friction coefficient rises with temperature. It is of interest to note the sharply increase of friction coefficient showed by [BMP][NTf_2] from 40 to 100ºC.

Figs. 6, 7 and 8 show the wear behavior found in the tests at both temperatures. It can be observed that wear increase sharply with temperature. At 40ºC the wear results for ionic liquids with the same cation, [BMP][FAP] and [BMP][NTf_2] were similar (Figs. 6 and 8) and lower than the [(NEMM)MOE][FAP] values but the SEM image of the base of the wear track show identical wear behavior in all cases. At 100ºC the situation changed and the [BMP][NTf_2] ionic liquid showed poor wear behavior not only in quantity but also showing abrasive wear which can be observed in the SEM images, Figs. 7-8.

X-Ray photoelectron analysis was performed using a Phoibos hemispherical detector MDA5 from SPECS, using Mg x-ray radiation (1253.6 eV) at 13 kV and 200 W. High resolution measurements were recorded at constant pass energy 30 eV with an energy step 0.1 eV. Spatial resolution was achieved using a 2.5 mm iris between the sample and the detector. Pressure in the analysis chamber was kept below $5 \cdot 10^{-9}$ mbar during the measurements. Analysis of the spectra was recorded using CasaXPS software as well as fitting software developed by the authors. Calibration of spectra was performed using the peak of adventitious C1s at 284.6 eV.

In Fig. 9 can be seen that samples lubricated with [(NEMM)MOE][FAP] at 40ºC presents two XPS F1s bands inside the wear scar, one assignable to [FAP^-] anion at 688.6 eV (47%) and a second one at 687.5 eV (53%) related to fluoride-metal interaction due to chemical reaction between the ionic liquid and the surface [14]. When the sample is analysed outside the wear scar, only the peak corresponding to [FAP^-] can be observed, as there is no chemical reaction between the ionic liquid and the surface (tribofilm). The situation remains very similar when the test temperature increased to 100ºC both inside the wear scar with two F1s peaks at 687.5 eV (56%, fluoride-metal) and 688.6 eV (44%, [FAP^-]), and outside the wear scar with a single peak at 688.0 eV belonging to unreacted [FAP^-], see Fig. 10 and Table 2.

The sample lubricated with [BMP][FAP] behaves very similarly to that with [(NEMM)MOE][FAP]. At 40ºC, F1s photoelectron band inside the wear scar can be splitted into a [FAP^-] band at 688.5 eV (85%) and a F-metal interaction band at 686.6 eV (15%) whereas outside the wear scar only the [FAP^-] F1s photoelectron band can be observed at 688.2 eV. When temperature increased to 100ºC the situation is practically the same than at 40ºC: two bands inside the wear scar ([FAP^-] at 688.6 eV, 80%, and fluorine-metal interaction at 687.0 eV, 20%) but only [FAP^-] was found in the analysis of the outer part of the wear scar (688.4 eV) (Table 2).

Samples lubricated with [BMP][NTf_2] do not show qualitative differences at 40ºC or 100ºC in F1s photoelectron bands. F1s band appears between 689.0 eV and 689.2 eV in any case (both temperatures, inside and outside, Fig.11, Table 2), matching the F1s band of the [NTf_2^-] anion as described by Bovio et al. [22].

The presence of neat [BMP][NTf_2] can be also detected inside and outside the wear scar at both 40ºC and 100ºC analysing the N1s photoelectron band. Pyrrolidinium based ionic liquids shows two N1s bands at 399.5 eV from the [NTf_2^-] anion and at 403 eV from the pyrrolidinium cation [23] which are clearly seen in our case as reflected in Fig. 12.

Nevertheless, O1s band shows an interesting behaviour in these samples. Three different O1s bands can be detected at 40ºC inside the wear scar: 529.8 eV (assignable to Fe_2O_3, [24]), 532.8 eV (from the [NTf_2^-] anion according to [22-23]) and 531.2 eV which probably arises from the tribofilm. Only two of these bands are present in the outer part of the wear scar (530.1 eV from Fe_2O_3 and 532.7 eV from the ionic liquid), although the band at 531.9 eV due to the tribofilm is not present, as there is no tribofilm outside the wear scar (Fig. 13, Table 3).

When the test is performed at 100ºC, the situation in the outer part is very similar (O1s bands at 530.5 eV and 532.8 eV from iron oxides and neat [NTf_2^-]) although inside the wear scar only neat ionic liquid can be detected at 532.8 eV (Fig. 14, Table 3), confirming the inexistence of tribofilm as suggested by ECR measurements. According to the previously shown results, the tribofilm in the lubrication with [BMP][NTf_2] at 40ºC does not seem to involve the anion as it happened with [BMP][FAP], but the ionic liquid seems to somehow induce the formation of the tribofilm while remaining chemically unaltered. [BMP][NTf_2] at 100ºC does not create a tribofilm on the surface, thus increasing the friction coefficient.

The presence of iron oxides was confirmed by checking the Fe2p3/2 photoelectron band inside the wear scar. Every sample shows a band between 709.9 and 710.4 eV assignable to iron oxides [24] with the single exception of [BMP][NTf_2] at 100ºC.

Further XPS analysis concerning P and S elements was also carried out. As reflected in the following tables 4 and 5, [(NEMM)(MOE)][FAP] shows a clear P2p peak both at 40ºC and 100ºC around 133.6 which is a typical value for phosphates [25]. The behaviour of [BMP][FAP] is very similar, although the intensity of the P2p peaks is lower. However, the intensity of P2p in the case of [BMP][NTf_2] is negligible.

Analysis of S2p peak reveals a band at 169.3 eV (FWHM 2.8 eV) for [(NEMM)(MOE)][FAP] at 40ºC which is almost the same than for [(NEMM)(MOE)][FAP] at 100ºC (169.6 eV (FWHM 2.5 eV)) which is near the iron (III) sulfate band at 168.9 eV [24,25]. The situation is the same for [BMP][NTf_2] with peaks at 169.2eV (FWHM 2.5 eV) at 40ºC and 169.2 eV (FWHM 2.8 eV) at 100ºC suggesting also the presence of iron (III) sulfate. However, the intensity of S2p peak is very low in the case of [BMP][FAP] with a noisy peak at 169.4 eV (FWHM 2.4 eV) at 40ºC which disappears when increasing the temperature at 100ºC suggesting the disappearance of the iron (III) sulfate in the tribolayer.

4. Conclusions

This paper studied the use of ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate, 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ionic liquids as neat lubricants within steel-steel contact.

Results show that [BMP][NTf_2] ionic liquid exhibited the minimum friction coefficient for the HFRR tests conducted at 40ºC and for MTM tests. For the two ionic liquids with the same [FAP] anion, the [BMP][FAP] showed the better anti-friction performance for all the tests made, according with previous author's results related to these two ionic liquids ([BMP][FAP] and [(NEMM)MOE][FAP]) in the lubrication of PVD coatings. Nevertheless, [BMP][NTf_2] showed the highest friction coefficient in the HFRR tests made at 100ºC according with its lowest viscosity value at this temperature.

Wear results exhibited similar behavior, showing the surfaces lubricated with [BMP][NTf_2] as the lowest wear volume for the tests made at 40ºC. However with the increasing temperature this ionic liquid worsened its anti-wear performance showing the higher wear track with an important surface damage. Wear volume measured after tests made with [BMP][FAP] and [(NEMM)MOE][FAP] were similar, although the former showed a slightly higher anti-wear behavior.

XPS confirmed the presence of tribofilms in samples lubricated with [BMP][FAP] or [(NEMM)MOE][FAP] both at 40ºC and 100ºC whereas only neat ionic liquid without interaction with the surface could be detected inside the wear scar of sample lubricated with [BMP][NTf_2] at 100ºC, thus confirming the evidences obtained through ECR.

Acknowledgements

The authors are grateful to the FICYT (the Foundation for the promotion in Asturias of the Applied Scientific Research and Technology) for supporting the research stay of the first author at Imperial College London (UK) and the Spanish Ministry of Science and Innovation for also supporting this paper within the framework of the Research Project WINDTRIB (DPI2010-18166). They also thank the

Ministry of Education, Culture and Sport for funding, within the program "*José Castillejo*", the research stay of José Luis Viesca at Bournemouth University. In addition, we would like to thank the Unit for Molecular Spectroscopy and XPS from the Scientific-Technical Services of the University of Oviedo.

References

[1] Qu J, Bansal DG, Yu B, Howe, JY, Luo H, Dai S, et al. Antiwear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive. ACS Appl. Mater. Interfaces 2012;4:997−1002.

[2] Minami I. Ionic Liquids in Tribology. Molecules 2009;14:2286-305.

[3] Jimenez AE, Bermudez MD. Imidazolium ionic liquids as additives of the synthetic ester propylene glycol dioleate in aluminium–steel lubrication. Wear 2008;265:787-98.

[4] Zhou F, Liang Y, Liu W. Ionic liquid lubricants: designed chemistry for engineering applications, Chemical Society Reviews 2009;28: 2590-9.

[5] Bermúdez MD, Jiménez AE, Sanes J, Carrión, FJ. Ionic Liquids as Advanced Lubricant Fluids. Molecules 2009;14:2888-908.

[6] Yao M, Fan M, Liang Y, Zhou F, Xia Y. Imidazolium hexafluorophospate ionic liquids as high temperature lubricants for steel-steel contacts. Wear 2010;268:67-71.

[7] Jiménez AE, Bermúdez MD, Iglesias P. Lubrication of Inconel 600 with ionic liquids at high temperature. Tribol Int 2009;42:1744-51.

[8] Liu W, Liang Y, Zhou F. Ionic liquid lubricants: designed chemistry for engineering applications. Chem Soc Rev 2009;38:2590-9.

[9] Jimenez AE, Bermudez MD, Carrion FJ, Martinez-Nicolas G. Room temperature ionic liquids as lubricant additives in steel-aluminium contacts: Influence of sliding velocity, normal load and temperature. Wear 2006;261:347-59.

[10] Battez AH, González R, Viesca JL, Blanco D, Asedegbega E, Osorio A. Tribological behavior of two imidazolium ionic liquids as lubricant additives for steel/steel contacts. Wear 2009;266:1224-8.

[11] Viesca JL, Battez AH, González R, Torres Pérez A, Reddyhoff T, Spikes HA. Assesing boundary film formation of lubricant additivised with 1-hexyl-3-methylimidazolium tetrafluoroborate using ECR as qualitive indicator. Wear 2010;269:112-7.

[12] Torimoto T, Tsuda T, Okazaki K, Kuwabata S. New Frontiers in Materials Science Opened by Ionic Liquids. Adv Mater 2010; 22:1196–221.

[13] Graciño FM, Regueira T, Lugo L, Comuñas MJP, Fernández F. Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids. J Chem Eng Data 2011;56:4984–99.

[14] Gonzalez R, Hernandez Battez A, Blanco D, Viesca JL, Fernández-González A. Lubrication of TiN, CrN and DLC PVD coatings with 1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate. Tribol Lett 2010;40:269–77.

[15] Blanco D, Viesca JL, Hernandez Battez A, Gonzalez R, Fernández-González A. Lubrication of CrN Coating With Ethyl-Dimethyl-2-Methoxyethylammonium Tris(pentafluoroethyl)Trifluorophosphate Ionic Liquid as Additive to PAO 6. Tribol Lett 2011;41:295-302.

[16] Blanco D, Gonzalez R, Hernandez Battez A, Viesca JL, Fernández-González A. Use of ethyl-dimethyl-2-methoxyethylammoniumtris(pentafluoroethyl)trifluorophosphate as base oil additive in the lubrication of TiN PVD coating. Tribol Int 2011;44:645-50.

[17] Liu W, Ye C, Gong Q, Wang H, Wang P. Tribological performance of room-temperature ionic liquids as lubricant. Tribol Lett 2002;13:81-5.

[18] Lu Q, Wang H, Ye C, Liu W, Xue Q. Room temperature ionic liquid 1-ethyl-3-hexylimidazoliumbis(trifluoromethylsulfonyl)-imide as lubricant for steel/steel contact. Tribol Int 2004;37:547-52.

[19] Sanes J, Carrion FJ, Bermudez MD, Martinez-Nicolas G. Ionic liquids as lubricants of polystyrene and polyamide 6-steel contacts. Preparation and properties of new polymer-ionic liquid dispersions. Tribol Lett 2006;21:121-33.

[20] Yao M, Liang Y, Xia Y, Zhou F. Bisimidazolium Ionic Liquids as the High-Performance Antiwear Additives in Poly (ethylene glycol) for Steel-Steel Contacts. ACS Appl Mater Interfaces 2009;1:467-71.

[21] Palacio M, Bhushan B. A Review of Ionic Liquids for Green Molecular Lubrication in Nanotechnology. Tribol Lett 2010; 40:247–68.

[22] Bovio S, Podesta A, Lenardi C, Milani P. Evidence of Extended Solidlike Layering in [Bmim][NTf2] Ionic Liquid Thin Films at Room-Temperature. J Phys Chem B 2009;113:6600-3.

[23] Shuang M, Hurisso BB, Lovelock KRJ, Licence P. Does the influence of substituents impact upon the surface composition of pyrrolidinium-based ionic liquids? An angle resolved XPS study. Phys Chem Chem Phys 2012;14:5229–38.

[24] Wagner CD, Riggs WM, Davis LE, Moulder JF. Handbook of X-Ray Photoelectron Spectroscopy. 1st ed. Eden Prairie: Perkin-Elmer Corporation; 1979.

[25] Mangolini F, Rossi A, Spencer N D. Chemical Reactivity of Triphenyl Phosphorothionate (TPPT) with Iron: An ATR/FT-IR and XPS Investigation. J. Phys. Chem. C 2011;115(4):1339-54.

Figure(s)

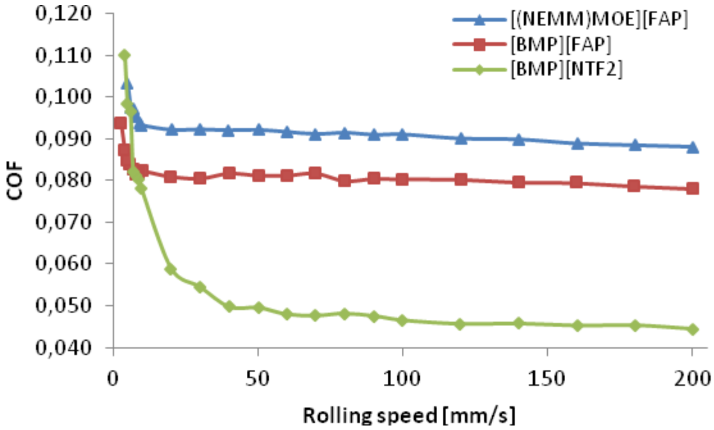


Fig. 1. Stribeck curves obtained at the MTM at normal load of 50N and 50% of SRR.

Figure(s)

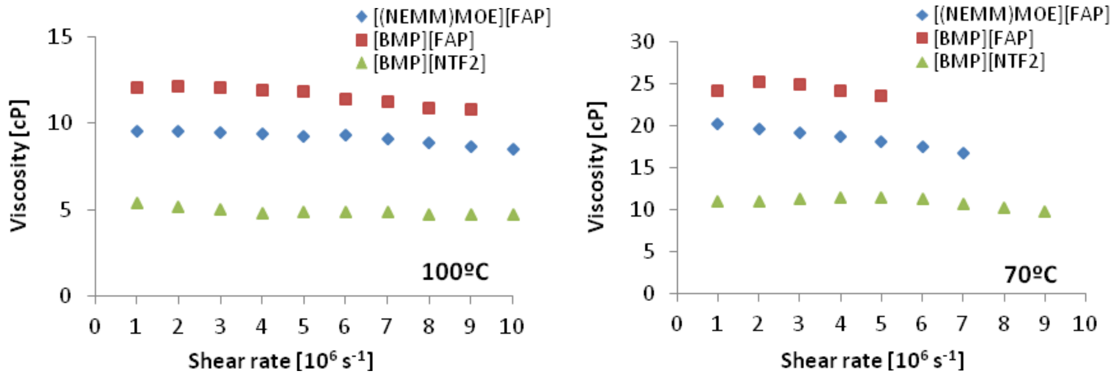


Fig. 2. Viscosity of IL's measured at high shear rates.

Figure(s)

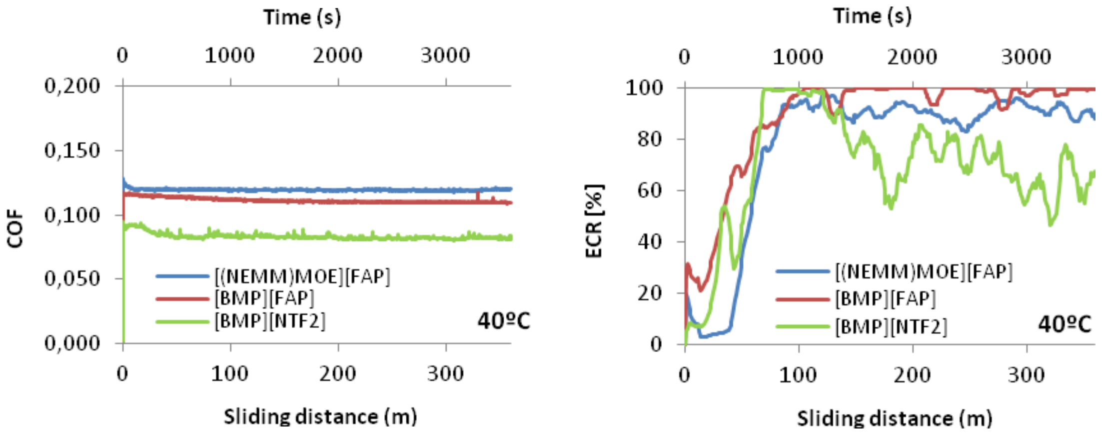


Fig. 3. Friction and ECR behavior for tests at 40ºC.

Figure(s)

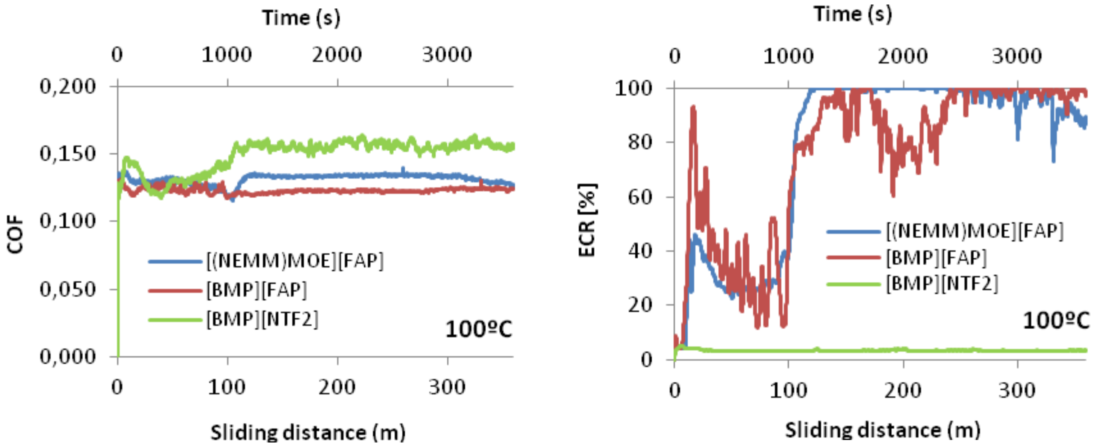


Fig. 4. Friction and ECR behavior for tests at 100ºC.

Figure(s)

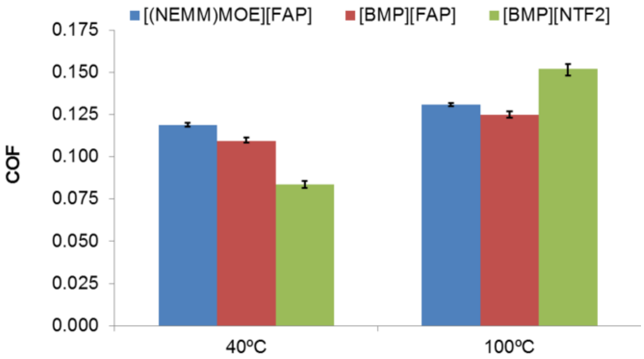


Fig. 5. Average friction coefficient from the reciprocating wear tests made in the HFRR machine.

Figure(s)

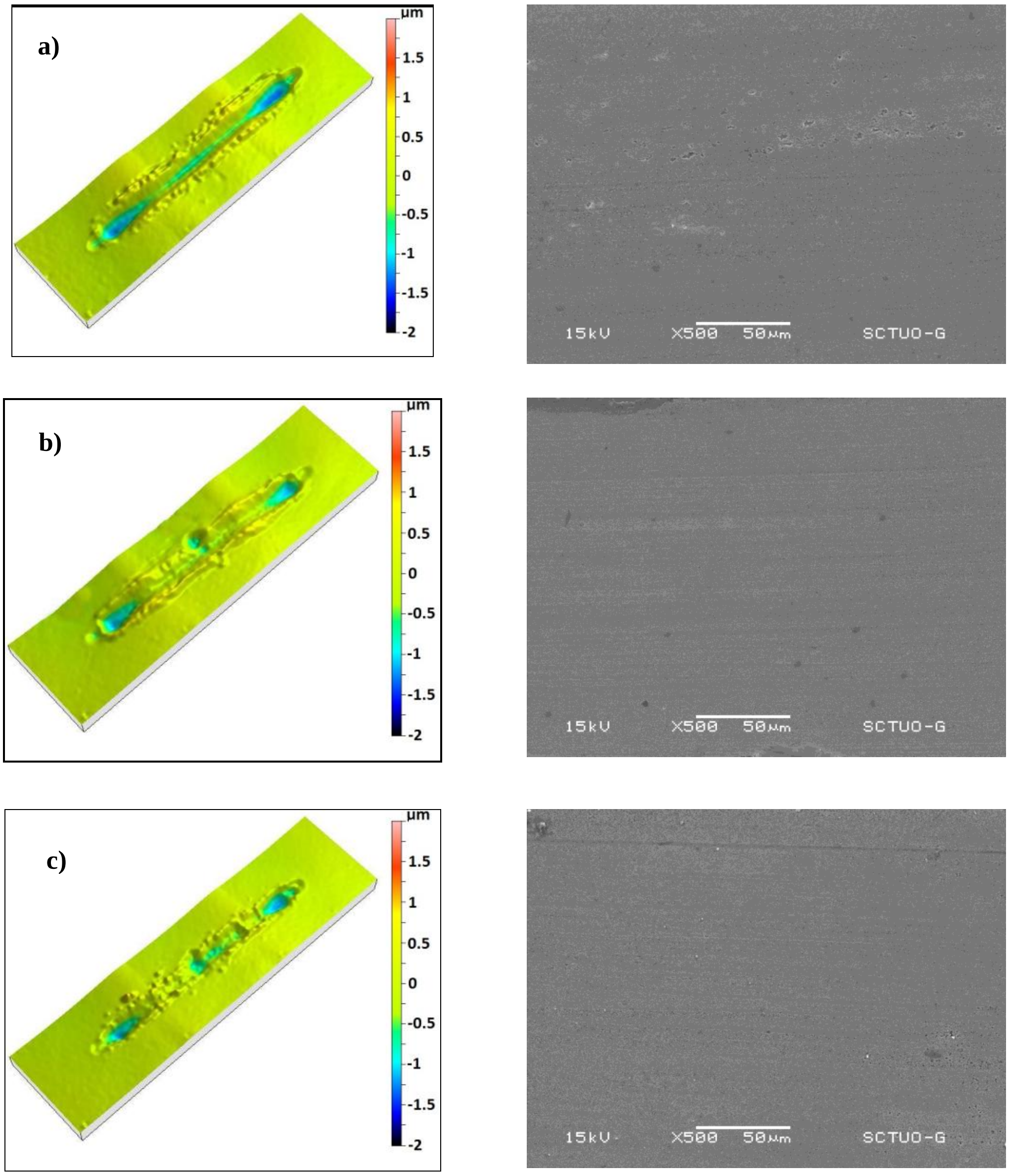


Fig. 6. 3D confocal reconstruction of wear track and SEM image of the bottom of wear track for test at 40ºC. a) [(NEMM)MOE][FAP]; b) [BMP][FAP]; c) [BMP][NTf_2]

Figure(s)

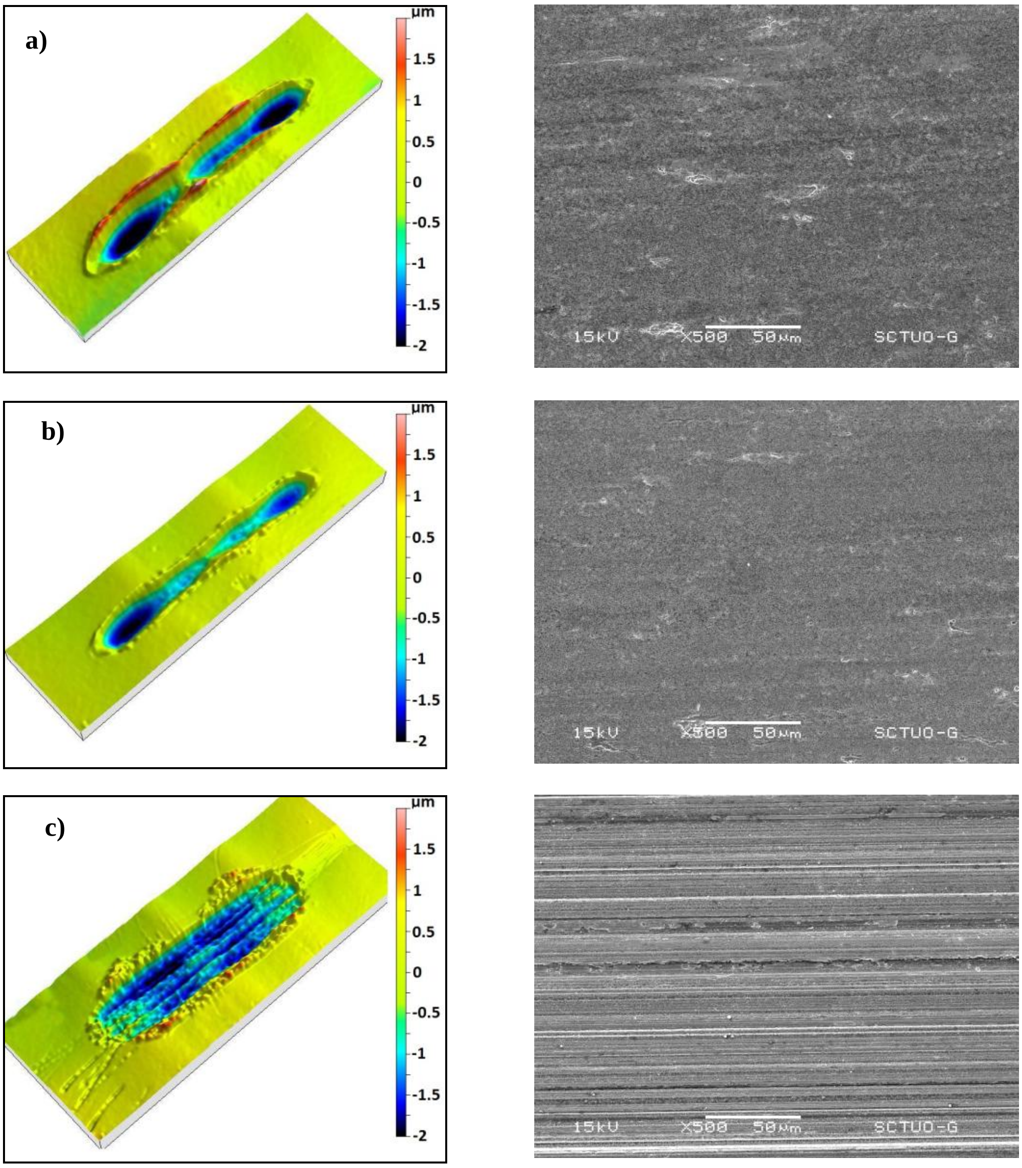


Fig. 7. 3D confocal reconstruction of wear track and SEM image of the bottom of wear track for test at 100ºC. a) [(NEMM)MOE][FAP]; b) [BMP][FAP]; c) [BMP][NTf_2]

Figure(s)

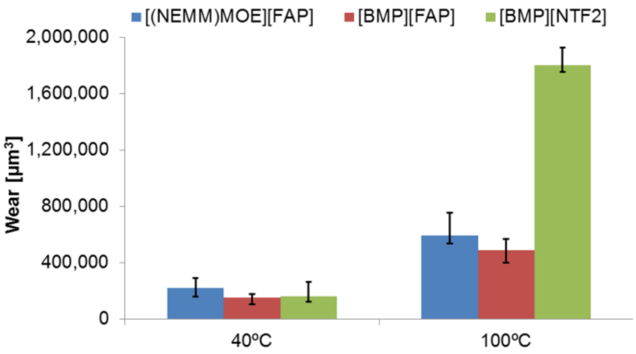


Fig. 8. Average wear volume.

Figure(s)

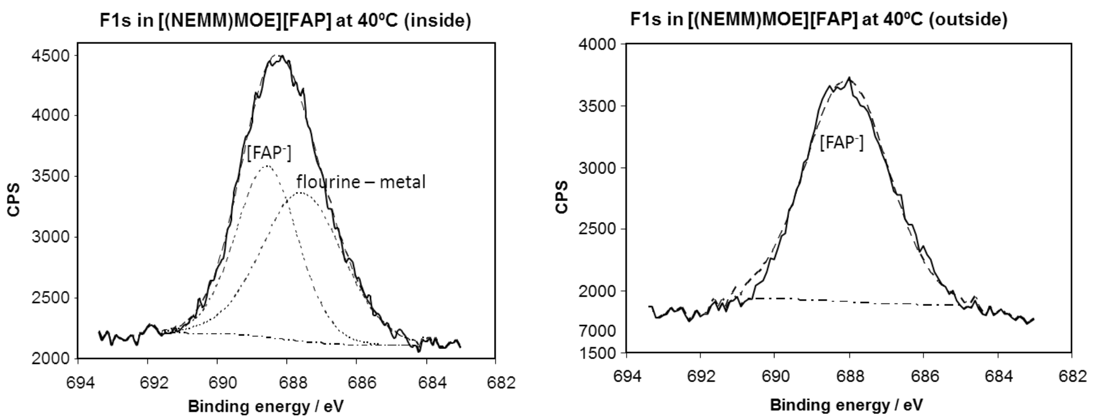


Fig. 9. F1s XPS spectra for [(NEMM)MOE][FAP] at 40ºC (inside and outside the wear scar).

Figure(s)

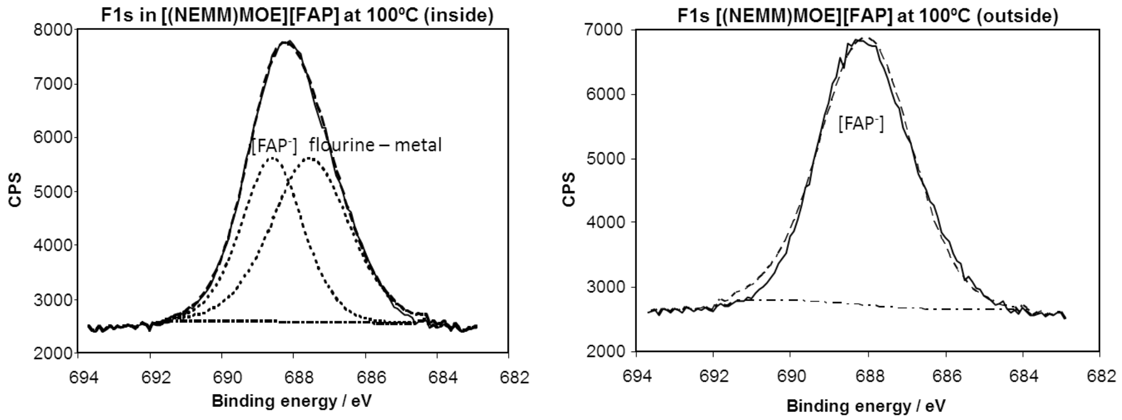


Fig. 10. F1s XPS spectra for [(NEMM)MOE][FAP] at 100ºC (inside and outside the wear scar).

Figure(s)

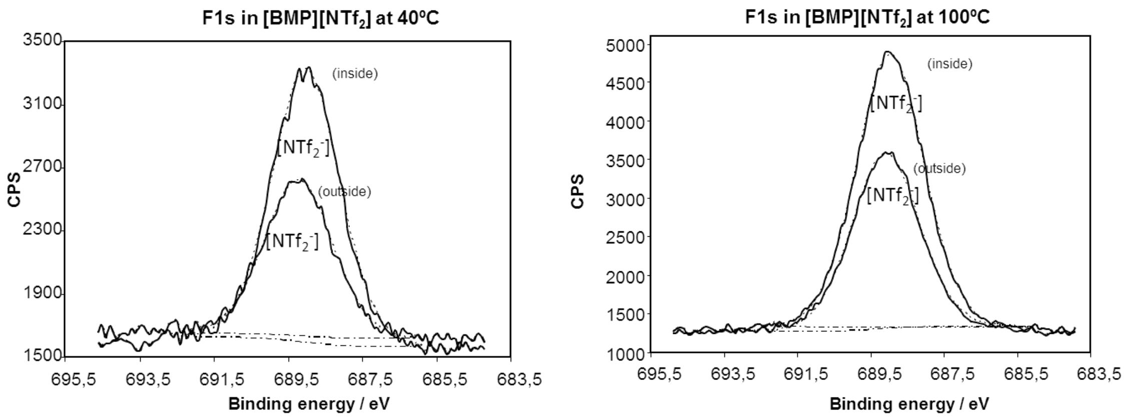


Fig. 11. F1s XPS spectra for [BMP][NTf_2] at 40ºC and 100ºC (outside and inside the wear scar).

Figure(s)

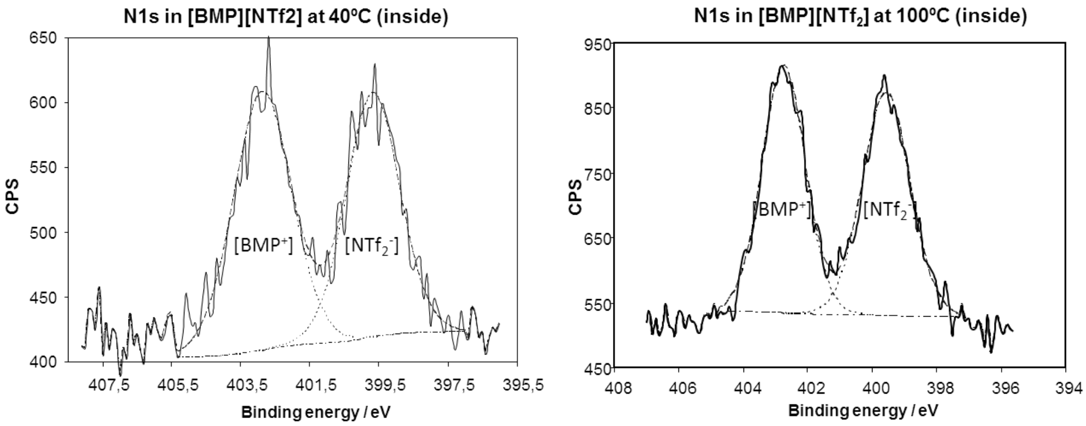


Fig. 12. N1s XPS spectra for [BMP][NTf_2] at 40ºC and 100ºC (inside the wear scar).

Figure(s)

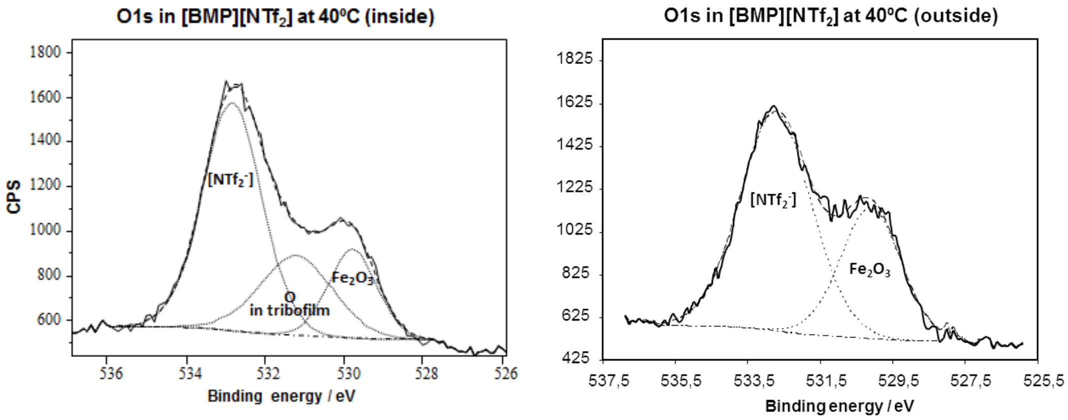


Fig. 13. O1s XPS spectra for [BMP][NTf_2] at 40ºC (inside and outside the wear scar).

Figure(s)

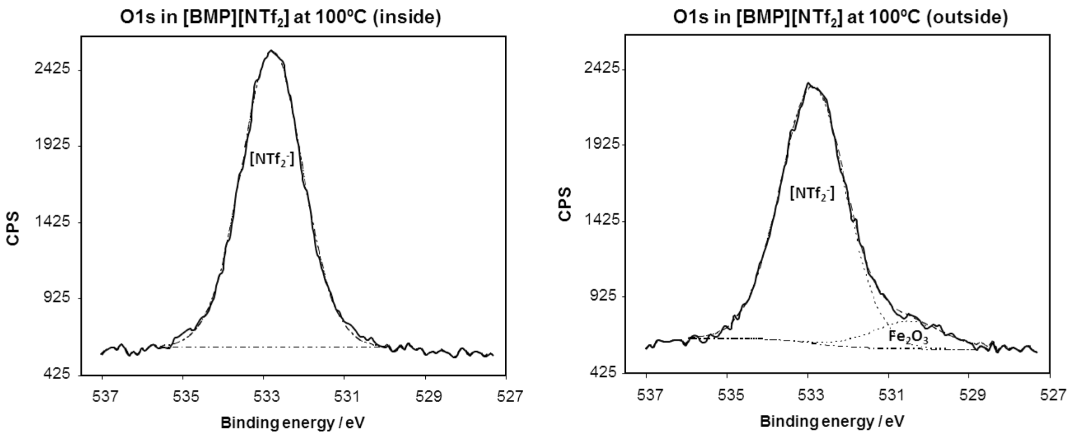


Fig. 14. O1s XPS spectra for [BMP][NTf_2] at 100^{o}C (inside and outside the wear scar).

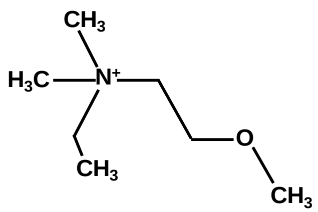
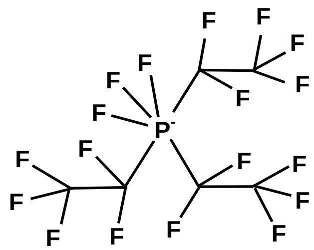
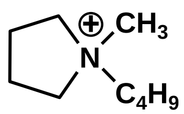
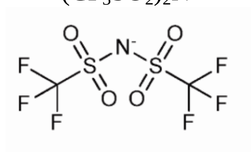
Table(s)

Table 1. Ionic liquids properties.

Ionic Liquids: Cation	Ionic Liquids: Anion	IUPAC name	Purity (%)	Water content (ppm)	Viscosity (mm^2/s)* 40ºC	Viscosity (mm^2/s)* 100ºC	Viscosity Index*
[(NEMM)MOE]	[FAP]	ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate	>99	<100 (Karl Fisher)	38.652	6.550	123
[BMP]	[FAP]	1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate	>99	<1 %	58.758	8.538	118
[BMP]	[NTf_2]	1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	>99	<100 (Karl Fisher)	28.826	6.228	174

* Measured in a SVM 3000 Stabinger Viscometer (ASTM D7042, D2270)

Chemical structure

Cations	Anions
$(CH_3)_2(CH_2CH_3)(CH_2CH_2OCH_3)N^+$	$F_3(C_2F_5)_3P^-$
	
[(NEMM)MOE]	[FAP]
$C_9H_{20}N$	$(CF_3SO_2)_2N^-$
	
[BMP]	[NTf_2]

Table(s)

Table 2. F1s photoelectron band. FWHM is given in brackets.

F1s (inside)	**[(NEMM)(MOE)][FAP]**	**[BMP][FAP]**	**[BMP][NTf_2]**
40ºC	688.6 (2.1) eV 47% 687.5 (2.7) eV 53%	688.5 (2.4) eV 85% 686.6 (2.1) eV 15%	689.0 (2.1) eV
100ºC	687.5 (2.5) eV 56% 688.6 (2.0) eV 44%	688.6 (2.2) eV 80% 687.0 (1.9) eV 20%	689.0 (2.1) eV

F1s (outside)	**[(NEMM)(MOE)][FAP]**	**[BMP][FAP]**	**[BMP][NTf_2]**
40ºC	688.0 (2.6) eV	688.2 (2.7) eV	689.2 (2.2) eV
100ºC	688.0 (2.8) eV	688.4 (2.8) eV	689.1 (2.1) eV

Table(s)

Table 3. O1s photoelectron band. FWHM is given in brackets.

O1s (inside)	**[(NEMM)(MOE)][FAP]**	**[BMP][FAP]**	**[BMP][NTf_2]**
40ºC	531.6 (2.9) eV 68% 529.8 (1.5) eV 32%	531.7 (2.7) eV 62% 529.9 (1.6) eV 38%	532.8 (1.8) eV 57% 531.2 (2.1) eV 25% 529.8 (1.4) eV 18 %
100ºC	532.4 (2.9) eV 62% 530.0 (1.8) eV 38%	531.4 (3.1) eV 75% 529.7 (1.4) eV 25%	532.8 (1.8) eV

O1s (outside)	**[(NEMM)(MOE)][FAP]**	**[BMP][FAP]**	**[BMP][NTf_2]**
40ºC	532.3 (2.3) eV 60% 530.1 (1.8) eV 40%	531.9 (2.3) eV 55% 529.9 (1.7) eV 45%	532.7 (2.2) eV 66% 530.1 (1.9) eV 34%
100ºC	532.2 (2.8) eV 60% 530.0 (1.8) eV 40%	531.9 (2.8) eV 68% 529.9 (1.6) eV 32%	532.8 (1.9) eV 90% 530.5 (2.1) eV 10%

Table(s)

Table 4. P2p photoelectron band. FWHM is given in brackets.

P2p (inside)	**[(NEMM)(MOE)][FAP]**	**[BMP][FAP]**	**[BMP][NTf_2]**
40ºC	133.5 (2.1) eV	133.8 (2.2) eV	Undetectable
100ºC	133.6 (2.1) eV	133.4 (2.3) eV	Undetectable

Table(s)

Table 5. S2p photoelectron band. FWHM is given in brackets.

S2p (inside)	**[(NEMM)(MOE)][FAP]**	**[BMP][FAP]**	**[BMP][NTf_2]**
40ºC	169.3 (2.8) eV	169.4 (2.4) eV	169.2 (2.5) eV
100ºC	169.6 (2.5) eV	Undetectable	169.2 (2.8) eV