# Influence of electric potentials on friction of sliding contacts lubricated by an ionic liquid

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# **Electronic Supplementary Information**

## **Material and Methods**

In this work an ultra-pure (UP), air and water stable ionic liquid (IL), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide  $[C_2C_1IM][Tf_2N]_{UP}$ , which is commercially available from Iolitec, was investigated. The IL contains  $35.7 \pm 0.31$  ppm water. The basic and the counter bodies consist of 100Cr6-steel. To determine the influence of potential controlled friction (PCF) within a rheo-tribometer, an electrically modified tribological cell is required. Thus, an electro-tribological cell (three-electrode configuration) has been modeled to the principles of the cell described by Heyer et al.<sup>1</sup> Two polycrystalline Pt wires were used, one acting as pseudo-reference electrode (RE) and the other as counter electrode (CE). Steel pins were used as working electrode (WE), cf. Fig. 1. A rotating 12.7 mm diameter 100Cr6 steel ball was loaded



Figure 1 Illustration of the homemade electro-tribological cell: a) schematic representation; b) technical representation. The modified tribological cell within a three-electrode configuration (working electrode - WE, reference electrode - RE and counter electrode - CE)

against three pins of 100Cr6. Ball and Pins were both through-hardened to 62 HRC and the applied load was 10 N, giving a mean Hertzian contact pressure of 0.6 GPa and a maximum Hertzian contact pressure of 0.9 GPa. By using the HAMROCK-DOWSON-model<sup>2</sup> an average film thickness of 30 nm was calculated. Certainly the calculated film thickness would be partially lower due to the fact that the steel surface exhibits a certain roughness of  $R_a = 15.7$  nm.

Prior to the electrochemical measurements, the pretreatment of the Pt electrodes was conducted as described by Roling et al.<sup>3</sup>. The WE was cleaned with Ticopur TR3 and isopropanol with ultrasonic and then dried

at elevated temperatures. Afterwards, the specimens were cooled to ambient temperature under Ar flow. The electrochemical windows (the difference between the cathodic and anodic limits) of the IL was obtained by cyclic voltammetry measurement (CV) (Fig. 2a) and the corrosion potential (equilibrium of cathodic and anodic reactions) by linear scan voltammetry (LSV) (Fig. 2b). The knowledge of the corrosion rate is of



**Figure 2** Electrochemical basic characterization: a) CV of ultra-pure  $[C_2C_1IM][Tf_2N]$  ionic liquid on steel at a scan rate of 100 mV/s. The electrochemical window is about 4.6 V, limited by the reduction of the organic cation and by steel oxidation; b) Tafel plot at a scan rate of 1 mV/s, that implies a corrosion potential of -831.1 mV

high interest, since corrosion is known to affect the usability of ILs as lubricants.<sup>4,5</sup> The use of the Faraday equation<sup>6</sup> enables to calculate the corrosion rate,

$$\Delta m_{corr} = \frac{Mi}{zF} \int t \, dt \tag{1}$$

where *m* is the corrosion rate, *M* the molar mass, *j* the current density, *t* the time, *z* the valence of the species and *F* the Faraday constant. The results of the LSV leads to a corrosion rate of  $m = 27 \,\mu m/\text{year}$ , which is in good agreement with the findings of Uerdingen et al.<sup>4</sup>.

#### **Description of the tribological test execution**

For the tribological characterization of the potential controlled friction static friction and velocity depended experiments were conducted. To identify the influence of surface interactions through a tribological experiment - static friction experiment - was used. The execution of the static friction experiment is shown in Fig. 3.



Figure 3 Illustration of the test execution for the tribological characterization of the ultra-pure IL. a) the torque curve; b) displacement of the contact points during the experiment duration.

Due to the fact that frictional systems require a contact, it is not possible just to increase the deflection amplitude in order to define the transition from stick to slip. If one would proceed like described before, the determination of the transition point would be impossible. The control of the deflection within a contact is hardly possible, because the torque increase to reach a preset deflection would be to fast due to the contact. Therefore the experiment is proceeded by means of moment control, on the other hand to detect the transition point of microscopic motion a deflection in the sub micrometer range is important. This means that the experiment was interrupted when a sliding distance in the micrometer range was reached, cf. Fig. 3b. To determine the velocity depended friction behavior in conjunction with the different electric potentials, Stribeck curves<sup>7</sup> with a certain velocity curve were measured, cf. Fig. 4.



Figure 4 Sliding velocity by time for the measured Stribeck curves (velocity dependent friction)

#### Description of the rheological test execution

In order to identify if the electric potentials influence the flow behavior of the IL, rheological experiments were conducted. Thus, a electro-rheological cell was build. For the electrode configuration a three-electrode arrangement was chosen as already for the electrochemical and electro-tribological investigations (Fig. 5).



Figure 5 Schematic representation of the homemade electro-rheological cell: (working electrode - WE, reference electrode - RE and counter electrode - CE)

Here the rotating plate is the working electrode. Both two rings are copper rings which are coated with platinum. The rings in the lower assembly act as counter electrode and a reference electrode.

Rheological experiments were performed using a modular rotating rheometer (MCR501, Co. Anton-Paar). The EC motor (electrically commutated) was equipped with a high-precision air bearing system for minimal friction losses. Rheological tests were conducted in the rotational mode. The standard viscosity measurements were carried out in the rotational mode using a plate-plate system with a diameter of 25 mm and a gap

of 0.8 mm. The temperature is maintained by a Peltier temperature control and held constant at  $25 \pm 0.1$  °C. Viscosity was measured to characterize the flow behavior with respect to the different electric potentials. The test procedure was performed with a shear rate of  $\dot{\gamma} = 50 s^{-1}$  (Fig. 6).



Figure 6 electro-rheological characterization. Investigation of the influence of electric potentials on the flow behavior for a parameter set in the cathodic area of -250 mv vs. OCP  $\rightarrow -500 \text{ mV}$  vs. OCP and in the anodic area +250 mv vs. OCP  $\rightarrow +500 \text{ mV}$  vs. OCP

By applying different potentials a clear influence of the flow behavior was achieved. Compared to the anodic potentials higher viscosities are recognizable on average for the cathodic potentials. There can be accomplished a maximum difference of the viscosity of up to 20 % by using different potentials. This is due to the phase differences in the organization of the ions in the bulk.<sup>8–10</sup>

#### **Description of the XPS results**

To understand if the electric potentials influence the tribological behavior X-ray photoelectron spectroscopy (XPS) were conducted after performing a tribological test (Fig. 7). Particularly the depth profile made for a better understanding how does the decomposition products of the IL react with the tribologically as well as electrochemically loaded surface.

The comparison of the different spectra reveal that the different potentials influence the chemical surface composition. For an anodic polarization the highest oxygen peak was achieved. Furthermore, an increase in the elements from which the IL consist of can be identified as well as compounds of the substrate with the IL. This shows that by the potential in combination with the tribological stress there is an increased decomposition of the IL. In addition, an increase in the oxygen peak is observed, which indicates a change of the tribological properties. For the cathodic potential (Fig. 7c) the elements nitrogen and sulphur are both lower. The oxygen peak has comparatively the lowest maximum value. In particular, as tribo-layer known iron fluorine compound is most pronounced for the anodic potential.

## References

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Figure 7 XPS-Analysis of the wear track after tribological tests; a) At open circuit potential, b) +500 mV vs. OCP, c) -500 mV OCP

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