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

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Tribological investigations on the macroscopic scale revealed that friction can be influenced in situ by applying electric potentials, if electrical conductive fluids such as an Ionic Liquid is used as a lubricant. An enrichment of charged ions at a steel interface occurs by applying electric surface potentials in a three-electrode setup. As a consequence, the lubrication conditions change. It is supposed that electrically influenced surface adsorption and electrokinetic effects are the main mechanisms by which friction is varied.

Ionic Liquids (ILs) are salts with melting points below 100 °C.[1] Due to their benefits compared to conventional lubricants, i.e. extremely low vapor pressure,[2] electrochemical properties,[3] chemical and thermal stability,[4] resistance to ‘squeeze out’ of the lubrication gap[5] and the ability to form well ordered structures at solid interface,[6–9] they attracted recent attention.[10–12] So far, the electric conductivity has not attracted major attention for tribological applications, though there may be a possibility to use ILs as ”smart fluids” by which friction can be switched electrically.[13]

Since Sweeney et al.[14] published electric potential controlled friction on the asperity level for non-aqueous media, the scientific interest is growing continuously. But most of the efforts are focused on the microscopic length scale. For aqueous media results on the macroscopic scale have already been published.[15,16]

In this communication we show the first macroscopic attempt for non-aqueous media with an ultrapure IL in frictional contact influenced by applying electric potentials.

The tribological characterization of an IL-lubricated 100Cr6-steel interface ($R_a = 15.8$ nm) was performed by using a modified tribological cell for a rheo-tribometer.[17] The setup allows very accurate measurement of friction coefficients over a wide velocity range including static friction. Detailed information about the electro-tribological cell are shown in the ESI†. A rotating 12.7 mm diameter 100Cr6 steel ball was loaded 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-DAWSON-model[18] an average film thickness of 30 nm was calculated. Due to the used steel sample with a certain roughness of $R_a = 15.8$ nm a partial significantly lower film thickness is therefore likely. The IL used in this study is an ultrapure (UP), air and water stable 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_2C_1IM][Tf_2N]_{UP}$, which was purchased from Iolitec GmbH (Germany) (Fig.1). To measure the water content, Karl-Fischer analysis were performed with a resulting water content of 35.7 ± 0.31 ppm, to avoid artifacts during the electrochemical and tribological investigation.

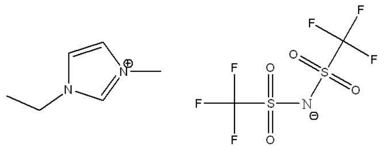

Fig. 1 Chemical structure of $[C_2C_1IM][Tf_2N]_{UP}$

The experiments were carried out at 25 ± 0.1 °C in a three-electrode configuration within the electro-tribological cell (Fig.2). Two polycrystalline platinum (Pt) wires were used, one acting as a pseudo-reference electrode (RE) and the other as a counter electrode (CE). The steel pins were set as a working electrode (WE).

For the basic characterization of the electrochemical behaviour of the IL, cyclic voltammetry (CV) as well as linear scan voltammetry (LSV) were performed in order to figure out the interactions of the IL with the steel-interface. The CV reveals an electrochemical window (ECW) between -2.2 V to +2.4 V.

The friction tests were performed within this ECW. The corrosion potential (E_{corr}), measured at a scanning speed of 1 mV/s, was -831.1 mV. Detailed information about the electrochemical characterization is included in the ESI†.

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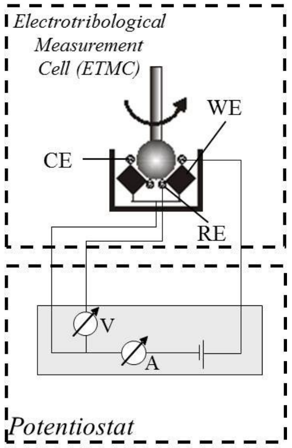

Fig. 2 Illustration of the electro-tribological cell: the modified tribological cell within a three-electrode configuration (working electrode - WE, reference electrode - RE and counter electrode - CE).

The static as well as the sliding friction at varying sliding speeds were conducted at potentials of ± 500 mV vs. the open circuit potential (OCP) and ± 250 mV vs. OCP where OCP is about -350 mV to study the influence of anodic and cathodic electric potentials on friction (Fig. 3). Further information of the experimental procedure cf. ESI†.

The results obviously show the influence of electric potentials on both static and dynamic friction. The static coefficient of friction (COF) is 0.24 ± 0.01 for an open circuit (OC) mode. Compared to the friction coefficient at OC, the static friction increases, at the cathodic as well as for the anodic potential. As shown in Figure 3a, a cathodic potential leads to an increase of the static friction coefficient to 0.23 ± 0.005 and 0.29 ± 0.01, whereas for the anodic potential values of 0.30 ± 0.001 and 0.33 ± 0.005 were measured. These changes of the static friction coefficient corresponds to an influence of up to 20 % for a cathodic polarization and 35 % for anodic polarization.

The velocity-dependent friction behaviour reveals, that the friction coefficient is clearly influenced by electric potentials. These results are well reproducible as each test was verified in 3 repetitions. As shown in Figure 3b the use of an electric potential lowers systematically the friction coefficient compared to the OC mode. At a cathodic potential of -500 mV vs. OCP, the COF decreased from initially high values at low velocities to considerably lower values (compared to reference state) at high velocities > 0.1 m/s (Fig 3b). The final COF at 1 m/s is 0.04, which corresponds to a reduction of the friction coefficient by 35 %, compared to the reference test (OC). As a result of an anodic polarization +500 mV vs. OCP, reduced friction values were already attained at low sliding velocities > 0.01 m/s. The final COF was about 0.025 which is one third of the friction value obtained at OC.

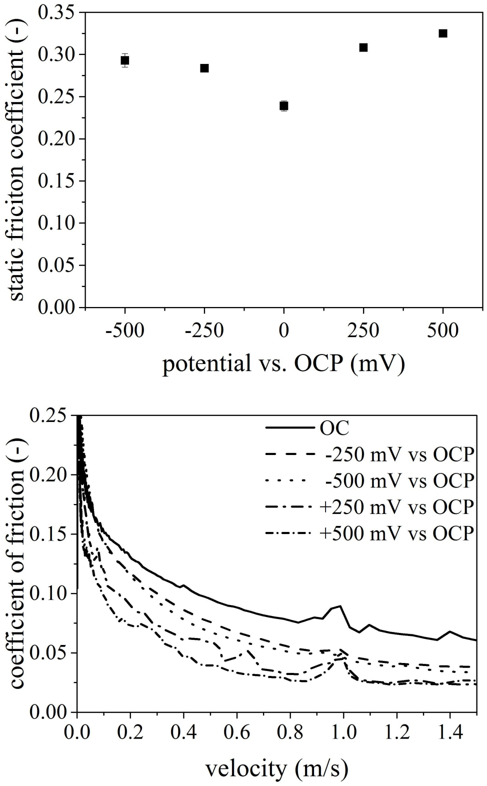

Fig. 3 a) Static friction coefficient for various potentials; b) Stribeck-curves at different potentials

Regarding the possible mechanisms that might influence the tribological results, three aspects should be taken into consideration:

1. Adsorption of ions by physisorption that form protective layers.
2. Chemical effects, that lead to a reaction of the ILs with the steel surface to form friction-reducing layers.
3. Electrokinetic effects that support hydrodynamic lubrication.

By applying an electric potential, the interaction of IL ions with the solid-liquid interface is affected.[12,19–22] Since orientation effects of ILs greatly depend on impurities it is important to use ultrapure ILs.[23,24] If the system operates in the OC mode, the interfacial adsorption layer is expected to be composed of cations and anions. The composition of the interfacial layer changes if an electric potential is applied. Depending on the polarity of the WE it is expected that the innermost layer is dominated by anions or cations. The magnitude of the applied potential determines the extent of the amount of the ions at the interfacial layer.[6] As recently reported by Li et al., the application of an electric potential leads to a smoother interfacial sliding layer.[13] This effect may also occur at surfaces that are not atomically smooth. The considerable influence of electric potentials on static friction may be explained by the coverage of the interface with charged ions which is different for anodic or cathodic electric polarization. As shown by Li et al., electrically enhanced adsorption of ions at the interface leads to the formation of solvation layers that are highly ordered.[13,25,26] In cases of mechanical contacts, these layers act as surface protection that prevent direct solid-solid contacts. Moreover, Cremer et al. proved that imidazolium-based cations with short alkyl chains show the ability to orientate at interfaces and form well-ordered layers.[7] These well-ordered structures modify the intermolecular interactions which may cause the alteration of the static friction behaviour (Fig.3a). Due to the applied electric potentials the dynamic (velocity-depended) friction behaviour is clearly influence over the entire velocity range (Fig.3b). This behaviour cannot only be attributed to orientational effects at the interfacial layer.[27] In a fundamental manner the contact conditions in sliding contacts change, and therefore the interfacial interactions, while the sliding velocity alters. The changes of the contact conditions can be further explained by the influence of the interfacial film physics. Referring to Spikes at al.[28] interfacial films that are formed by adsorption of ions are destroyed and reformed by ionic diffusion processes. This approach is based on the model of Albertson.[29]

For low velocities including static friction (Fig.3a), the covering of the interface by ions and orientational effects will dominate the frictional behaviour. Energy dissipation in the frictional contact changes due to the different order of composition and stability of the ions, which seems also plausible in view of the findings in literature.[8,30,31] This applies in particular also to surfaces that are not atomically smooth. Thus, a contact of the surfaces takes place at the asperities. This reduced contact points and especially their interfacial composition play a significant role in the tribological properties. In addition to the orientation of the ions at the interfaces, in dependence of the potential, the forming solvate layers are of particular importance. Hayes et al. were able to identify for [C_2C_1IM][Tf_2N] a structuring up to four layers, corresponding to a total layer thickness of 4 nm.[21] In terms of the expected film thickness of 30 nm for this maximum Hertzian contact pressure ($p_{max} = 0.9$ GPa), a suggestibility of layer thickness variation due to the different potentials can be assumed. In addition at mixed lubrication conditions solid-solid contacts occur.[8] Thus, changes of the adhesion layer are very likely to influence the tribological behaviour. Already in the nanometer range influences on the tribological behaviour could be detected.[32]

At higher sliding speeds, at which the lubricating film thickness increases, bulk effects became more apparent. Because the effect of polarization on the frictional behaviour still exists (Fig. 3b), there is also a need to consider electrokinetic repulsion of ions.[16,33,34] From literature it is known that with increasing film thickness the orientational effect of the ions becomes less.[27] Hence, most likely effects as electrokinetic repulsion of ions takes place under these conditions.[16] As a consequence, the viscosity of the interfacial region changes. As it is shown in the ESI† a clear influence of the dynamic viscosity by applying an electric potential was achieved. Comparing the cathodic and the anodic polarization a difference of up to 15 % could be achieved. The electro-rheological results provide principle insights into the suggestibility of the flow properties at the interface by using electrical potentials. However, it must be taken into account, that film thicknesses of the two experiments (electro-rheology and electro-tribology) are more than an order of magnitude apart which results in extremely different shear rates. Moreover, surface effects like structure formation, adhesion and electric double layer properties will affect the lubricant behaviour in tribological contacts much stronger than in the rheological experiment. To describe it in terms of tribological lubrication conditions: one would expect that within the velocity range <1.5 m/s, mixed lubrication conditions are usual.[35]

A direct comparison between the already above described static and dynamic friction (Fig 3), shows substantially differences. As a consequence of the different friction regimes various effects arise at the interfaces. For low velocities and static friction physisorption and orientational effects dominate. Due to the small relative motions only low energy inputs into the system can be expected. Tribochemical effects cannot be excluded entirely, but they can be considered as inferior. For higher relative motions the energy input into the system increases and tribochemical effects appear. In addition to the tribochemical effects, diffusion processes of the ions at the interface and electrokinetic effects might be able to explain this behaviour

Chemical effects that are caused by tribological[36,37] or electrochemical[38,39] loads are known from literature. For tribological loads there are explanatory approaches but for the electro-tribological application the influence of the combined loads are not yet fully understood. XPS measurements showed that different electrical potentials lead to different chemical compositions of the surface. In dependence of the potentials an enrichment of the elements of the ions can be detected. Comparing the experiment in open circuit with the experiments in the anodic or cathodic case, there was an increased element number of ions or compounds of these with the substrate, shown in the ESI†. As mentioned above, iron fluorine or iron sulfate are known as layers which may affect beneficial the tribological behaviour. Exactly these compounds can be obtained by the XPS analysis (depth profile). In particular, the different appearance of oxygen are instructions on tribological different behaviour due to the different electrical potentials. The presence of elements of the ions shows that the IL is partially decomposed. Due to the fact that the used potentials within the electrochemical window, it may be assumed that the decomposition is a result of combined effects of electrochemistry and tribology.

The results of electro-tribological measurements revealed that $[C_2C_1IM][Tf_2N]$ is an efficient lubricant for steel interfaces. Because of the fact that ILs are electrically conductive, the interface lubricity can be affected in situ by applying electric potentials. Different electric potentials lead to certain solvation layers of different order and stability. Hence, static as well as dynamic friction coefficients are influenced strongly. As a consequence, the mechanisms of interaction of the electrochemical double layer and the surface interactions alter. Adhesion and orientation effects are expected to dominate at low sliding velocities. At enhanced velocities diffusion processes at the interface and electrokinetic repulsion will influence the lubricity.

In our previous paper we showed that potential controlled friction is also connected with wear of the surfaces.[36] An additional work will be focused on the wear behaviour in conjunction with biased surfaces. Furthermore, the chemical composition of the interface is of high interest, since it is known that the $[Tf_2N]^-$-anion can decompose.[40,41] Because of the tribological as well as of the electrochemical loads, there is a need to examine these two effects separately, in order to interpret better the different influences on the result. Already for atomically smooth surfaces a change in the coefficient of friction behaviour could be proved due to different surface structures.[42] This proof is also interesting for fractal surfaces.

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