Electrochemical control of lubrication by ionic liquids

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1. Friction on gold surfaces in aqueous solutions

Friction between the sliding tip of an atomic force microscope and a gold surface changes significantly upon electrochemical modification of the gold surface. Atomic-scale variations of the lateral force reveal details of the friction mechanisms. Stick-slip motion with atomic periodicity on perfect Au(111) terraces exhibits extremely low friction and almost no dependence on load. In contrast, irregular stick-slip motion and a linear increase of friction with load are observed on electrochemically oxidized surfaces of Au(111) [1] or Au(100) [2].

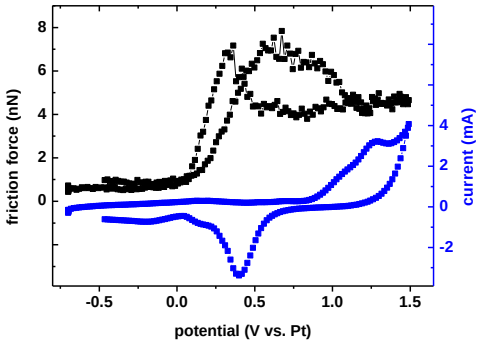
The sensitivity of friction force microscopy to atomic stick-slip motion allows also to reveal sulfate adsorption in ordered layers under the sliding tip at the respective electrochemical potentials. No ordered adsorption is found in lateral force measurements for the weakly adsorbed perchlorate anions. Correspondingly, friction increases in the anion adsorption regime for sulfate but not for perchlorate adsorption [3].

The results indicate that only chemical modification of the surface – by oxidation or by covalent adsorption of anions – will change the frictional response of gold surfaces in aqueous electrolytes.

2. Lubrication at the nanometer scale by ionic liquids under electrochemical control

A different situation is observed in atomic force microscopy experiments in ionic liquids such as 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate ([$Py_{1,4}$]FAP). Ionic liquids form a layered nanostructure in front of charged surfaces, where the last ion layer strongly resists squeeze-out [4]. The lubricating properties the of [$Py_{1,4}$]FAP ionic liquid on gold surfaces can be controlled through application of an electric potential to the sliding contact. A nanotribology approach has been used to study the frictional behavior of [$Py_{1,4}$]FAP confined between silica colloid probes or sharp silica tips and a Au(111) substrate using atomic force microscopy [5]. Friction forces vary with potential because the composition of a confined ion layer between the two surfaces changes from cation-enriched (at negative potentials) to anion-enriched (at positive potentials). This offers a new approach to tuning frictional forces reversibly at the molecular level without changing the substrates, employing a self-replenishing boundary lubricant of low vapor pressure.

The approach is now implemented for various ionic liquids. The figure below combines a cyclic voltammogram recorded for a Au(111) electrode in the ionic liquid [EMIm][OTf] with friction force results obtained by atomic force microscopy. While the microscopic mechanisms of lubrication remain to be analyzed in this case, the correlation between electrochemical modifications of the system and frictional response is obvious.



3. References

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