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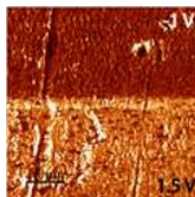
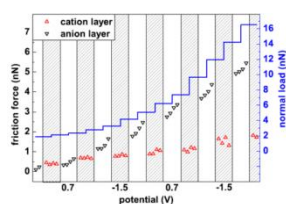
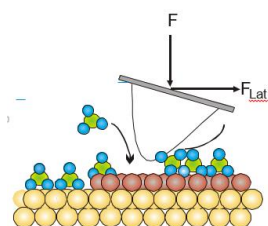
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German Research Foundation



116th AGEF symposium: Triboelectrochemistry

22.09 ~24.09.2021

Bonn, Germany



Time/ Bonn				CDT (-7)	Beijing/ Perth(+6)
Wed 22/09					
15:00			COFFEE		
15:30	0:05	H. Baltruschat	opening words/explanation of recording		
15:35	0:35	F. Hausen	Triboelectrochemistr: An introduction based on experimental results	8:35	21:35
16:10	0:35	A. Kornyshev	Ionic liquids at electrified interfaces and nanoconfinement: a road toward electrotuneable friction	9:10	22:10
16:45	0:35	F. Bresme	Impact of molecular structure on the electrotunable lubrication of ionic liquids	9:45	22:45
17:20	0:35	M. Urbakh	Effect of Hydration and Organic Solvent on Structure and Friction in Ionic Liquid Nanoscale Films	10:20	23:20
17:55	0:20		Joint DISCUSSION	10:55	23:55
18:15			Walk to Dinner	11:15	0:15

Time/ Bonn				CDT (-7)	Beijing/ Perth(+6)
Thu 23/09					
9:00	0:35	W. Schmickler	The crucial role of charge fluctuations in dendrite growth	2:00	15:00
9:35	0:35	M. Müser	Atomistic modeling of electron transfer: Toy-model studies from Thales's cat to Galvanic cells	2:35	15:35
10:10	0:20	Q. Hu	Understanding Triboelectric Charging at the Molecular Scale: an Atomic Force Microscopy based Approach	3:10	16:10
10:30	0:20	A. Bittner	AFM of wet viruses and wet virus models	3:30	16:30
10:50	0:10	Joint DISCUSSION		3:50	16:50
11:00	0:20	COFFEE		4:00	17:00
11:20	0:35	H. Li	Nanotribology of Ionic Liquids at Charged surfaces	4:20	17:20
11:55	0:20	C. Rodenbücher	Nanoscale analysis of the electrode/electrolyte interface in protic ionic liquids	4:55	17:55
12:15	0:35	M. Rutland	Ionic liquids under applied fields at interfaces and under confinement: Forces, friction and tribotronics.	5:15	18:15
12:50	0:20	I. Park	Atomic-scale friction study: Underpotential deposition (UPD) of silver on I-modified Au(111) in aprotic electrolyte	5:50	18:50
13:10	0:10	Joint DISCUSSION		6:10	19:10
13:20	1:00	LUNCH BREAK		6:20	19:20
14:20	0:20	J. Hörmann	Morphology, concentration, potential: Exploring tunable adsorption film friction with molecular dynamics	7:20	20:20
14:40	0:20	C. Seed	Tribotronic control and cyclic voltammetry of platinum interfaces with metal oxide nanofluids	7:40	20:40
15:00	0:35	R. Bennewitz	Friction force microscopy of shear planes at the electrochemical interface	8:00	21:00
15:35	0:20	H. Baltruschat	Friction at Au(111) during underpotential deposition (UPD): Effect of potential, normal load, and the ionic adsorbate I	8:35	21:35
15:55	0:10	A. Köllisch	Sulfate adsorption on Au(111) electrodes-Influence of the potential on the force distance curves	8:55	21:55
16:05	0:10	Joint DISCUSSION		9:05	22:05
16:15	0:20	COFFEE		9:15	22:15
16:35	0:35	N. Pesika	Anomalous Potential-Dependent Friction on Au(111) Measured by AFM	9:35	22:35
17:10	0:20	S. Franklin	The influence of corrosion on diamond-like carbon topography and friction at the nanoscale	10:10	23:10
17:30	0:35	P. Egberts	Tribocorrosion of Pipeline Steels used in Conventional Energy Extraction Processes	10:30	23:30
18:05	0:10	Joint DISCUSSION		11:05	0:05
18:15		Walk to Dinner		11:15	0:15

Time/ Bonn				CDT (-7)	Beijing/ Perth(+6)
Fri 24/09					
9:00	0:20	S. Lone	Triboelectrochemical study of various Nb-Ti-Zr alloys in simulated body environment.	2:00	15:00
9:20	0:10	C. Xiao	Atomic wear governed by synergic energy: the roles of tribochemistry and electrochemistry	2:20	15:20
9:30	0:20	A. Bermudez	The influence of electrochemistry on the tribocorrosion behavior of Ti6Al4V alloys	2:30	15:30
9:50	0:20	J. Laboulais	Integrodifferential equation describing the tribocorrosion phenomena. A numerical model.	2:50	15:50
10:10	0:20	Joint DISCUSSION		3:10	16:10
10:30	0:20	COFFEE		3:30	16:30
10:50	0:35	A. de Wijn	Shear Viscosity of Dense Polar Fluids	3:50	16:50
11:25	0:35	S. Perkin	Tuning surface forces using AC electric fields	4:25	17:25
12:00	0:20	M. Mariappan	Fracture of soft tissue-mimicking hydrogels during needle insertion	5:00	18:00
12:20	0:20	K. Skibinska	Synthesis of conical Co-Fe alloys structures obtained with crystal modifier in the superimposed magnetic field.	5:20	18:20
12:40	0:20	Joint DISCUSSION		5:40	18:40
13:00	1:00	LUNCH BREAK		6:00	19:00
14:00		optional:	Tour Bonn or Drachenfels		

Triboelectrochemistry:

An introduction based on experimental results

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Triboelectrochemistry is a very interdisciplinary field where chemists, physicists, materials scientists and engineers meet to better control friction and wear in sliding contacts – from the nanoscale to industrial applications. The high importance of this topic stems from the observations that friction often occurs on wet surfaces, i.e. electrodes, and that electrochemistry offers a way to control and modify friction.

Within this presentation a comprehensive introduction of friction in electrochemical environments based on experimental results is provided – from the first mention by Edison in 1875 to current investigations by dedicated instruments. Additionally, electrochemical foundations and design guidelines for electrochemical cells will be shortly discussed.

Ionic liquids at electrified interfaces and nanoconfinement: a road towards electrotuneable friction

Alexei A Kornyshev

Imperial College London

Electrotuneable friction with room temperature ionic liquid lubricants is a hot subject nowadays. What are the pertinent properties of ionic liquids that determine the electrotuning of lubricity? In this talk I will present an overview of the problem, starting from our current understanding of the structure and electric properties of ionic liquids in the bulk, at electrified interfaces, and in ultra-narrow nanoconfinement. But 'electronanotribology' deals with intermediate situations of several ionic layers between the sliding surfaces, and although the mentioned knowledge is invaluable for electrochemistry, it cannot be directly used in rationalising electrotuneable friction. I will describe the first steps towards understanding the generic effects and the physics determining electrotuneable friction, preparing the platforms for the analysis of finer effects to be covered in the talks by F.Bresme and M.Urbakh.

Impact of molecular structure on the electrotunable lubrication of ionic liquids

Friction is responsible for significant energy losses on the industrial scale and material fatigue, degradation and mechanical failure. Room Temperature Ionic liquids (RTILs) are promising lubricants due to their unique thermophysical properties: chemical and thermal stability, low vapour pressure and low melting temperature. Further, external electrostatic fields provide a route to modify their structure and tune the lubrication properties. We will discuss recent simulation studies to establish microscopic correlations between the molecular structure of imidazolium RTILs, nanoconfinement, and confining plates' surface charges. Evidence is shown for lateral structuring of the ions, leading to a significant reduction of friction. Furthermore, the lateral order can be activated or inhibited by changing the polarity of the confining surfaces, hence providing a mechanism to control friction with electric fields.

Effect of Hydration and Organic Solvent on Structure and Friction in Ionic Liquid Nanoscale Films

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Room temperature ionic liquids (RTILs) recently attracted a lot of scientific attention as the flexibility in the choice of the cation/anion molecules allows the properties of the liquid to be fine-tuned. The behavior of RTILs in confined geometries is of great interest for different fields, ranging from biological systems to super-capacitors, micro/nano-fluidic, and lubrication.

It is very difficult to ever have pristine RTIL films, as RTILs tend to sorb water from humid air, but even small amount of water (“solvent-in-salt”) can have a dramatic effect on the structure and dynamics of nanoscale films. We have found that penetration of water into the film can screen the electrostatic interactions between the ions and thus influence the response of the films to the applied electric field and shear. In particular, water adsorption changes the orientation of molecular ions and the slip conditions at the solid-liquid interfaces, resulting in a reduced resistance against squeezing-out of the film by an external load. The impact that this kind of screening has on friction involves several aspects that have been systematically analyzed and will be presented in this talk.

Despite the remarkable tribological properties of RTIL lubricants, their use has been hindered in recent years due to their high cost. Furthermore, RTILs exhibit high viscosities, which reduce mass flow slowing down the dynamic response, essential for switching technologies. The addition of organic solvents to RTILs might provide a solution, first by reducing the cost of RTIL lubricants, and second by enhancing their dynamic response. We found that under nanoscale confinement conditions, diluted RTIL solutions, of just ~10% molar fraction, still feature a remarkable variation of the friction force with the electrode surface charge density, not weaker than had been earlier shown for nanoconfined pure RTILs. Importantly, our simulations show that charged electrodes are coated with ions even at low IL concentrations. These ion-rich layers adjacent to the charged plate surfaces are not squeezed out even under very high normal pressures. Our results highlight the potential of diluted RTIL mixtures as cost-effective electrotunable lubricants for future nanotribological applications.

The crucial role of local charge fluctuations in dendrite growth

Wolfgang Schmickler and Elizabeth Santos

Department of Theoretical Chemistry, Ulm University, Germany

Dissipation and fluctuations are intimately related, so in a certain sense this talk complements the reports on dissipation and friction presented at this workshop.

The surface tension of an electrode is highest at the potential of zero charge (pzc). Therefore surface fluctuations are lowest at the pzc, and increase as the electrode is charged. On an uneven surface, charge is not distributed equally, but accumulates at the tips of protrusions. This suggests the following mechanism for the growth of dendrites during metal deposition.

Dendrites form when the metal cations are deposited on a negatively charged surface, i.e. below the pzc. In this case, any protrusion that forms during the deposition acquires a high negative charge density, which attracts more cations, and thus induces further growth at tip. Eventually, this leads to the formation of dendrites. In order to estimate the magnitude of this effect, we have performed calculations for model tips on a negatively charged electrode surface using a tight binding method based on density functional theory (DFTB). Even a small average excess charge on the electrode leads to a high accumulation of charge at a tip and a strong field, which directs the metal cations in the solution towards the tip.

When the local excess charge at a tip becomes too high, it becomes unstable and breaks off. This suggests a mechanism for the formation of dead lithium in batteries.

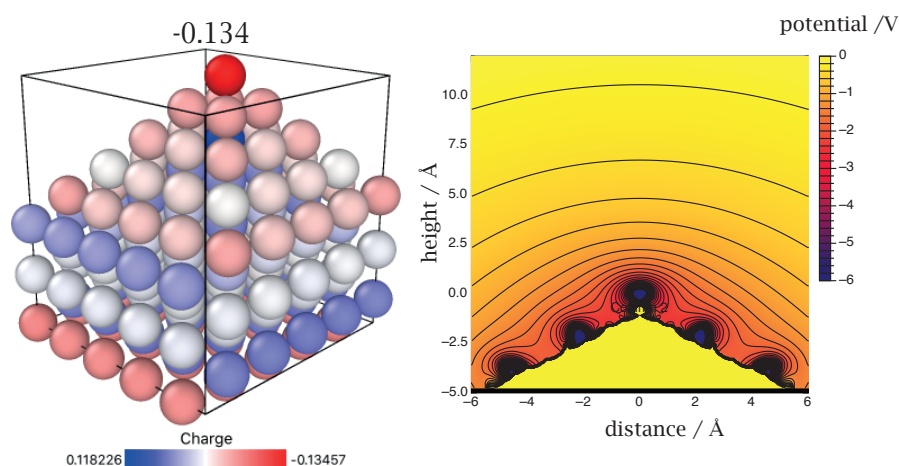


Figure 1: Charge distribution on a pyramidal tip for a Li electrode with an excess charge of $\sigma = -2.9 \times 10^{-2} \text{C m}^{-2}$ (left) and electrostatic potential contours (right) when the tip is in contact with a medium obeying the linear Poisson-Boltzmann equation with a Debye length of 10 Å.

A brief survey of experiments shows that indeed all metals whose deposition potential lies below the pzc are prone to dendrite formation; this applies particularly to the alkali metals. In contrast, metals like copper or silver, whose deposition potential lies above the pzc, generally do not form dendrites. On such metals, dendrites can form when the applied overpotential is so high that the electrode potential lies below the pzc.

Ref.: W. Schmickler and E. Santos, *Angew. Chem. Int. Ed.* 2021, **60**, 5876 - 5881.

**Atomistic modeling of electron transfer:
Toy-model studies from Thales's cat to Galvanic cells.**

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Modelling triboelectric processes from atomistic principles requires potential energy surfaces to be constructed that allow for jumps between different energy surfaces. In my talk, I will present such a model, in which each atom is assigned an integer oxidation state in addition to a partial charge. The model is shown to reproduce the characteristics of tribocharging between two metallic and between two insulating surfaces. It can also be used to simulate the discharge of a battery, which can ultimately also be seen as a process hinging on tribo electrification, since the current flown through a circuit breaker does not flow back once the switch is reopened. If time permits, it will be discussed how the compliance of a Hertzian tip adds to the work needed to be done to separate two (tribo) charges.

Understanding Triboelectric Charging at the Molecular Scale: an Atomic Force Microscopy based Approach

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The triboelectric effect is experienced many times every day and is used in macroscopic applications such as energy harvesting from ocean tides and in nanoscopic devices such as triboelectric nanogenerators (TENGs) [1, 2]. Both have in common that they harvest energy by contacting pairs of tribo-functional materials. In order to optimize and develop new triboelectric materials and devices, we need to understand the mechanism and origin of charge separation at the molecular scale. Here, we present a combination of two different AFM-based techniques study to the extent of charge separation after contacting various materials. Atomic Force Microscopy (AFM)-based force spectroscopy is used to contact the respective materials. Kelvin Probe Force Microscopy (KPFM) is performed to obtain the surface potentials before and after such contacting experiments. This combination of techniques paves the way for the characterization and understanding of the triboelectric effect at the molecular scale and will provide a platform to test new triboelectric materials for future functional polymer-based material systems.

Reference

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AFM of wet viruses and wet virus models

Alexander Bittner, Aitziber Eleta-Lopez, Maiara Iriarte-Alonso, Annalisa Calò, Thierry Ondarçuhu, Albert Verdaguer, Maria Cascajo-Castresana, Robert David, Claudia Marcolli, Jorge Melillo, Silvina Cervený, Mitsuhiro Okuda, Christina Wege*

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Biological processes are usually associated with the presence of aqueous electrolytes. However, many organisms can develop "dry" interfaces to air. This is also true for biological matter such as viruses, especially when they are transmitted by air. In analogy to solid surfaces, there are open questions about "dry surfaces", "ultrathin water layers", adsorption and absorption of water.

The tubular Tobacco Mosaic Virus has a simple helical surface structure. Although the averaged structure is known since many decades, we were able to resolve the coat proteins on a single virion by AFM. Besides recording fascinating images even on highly curved surfaces, AFM also provides new insights: The dry virion shows a complex buckling, consisting of irregularly spaced stripes of very low corrugation (<0.1 nm), while wetting gives rise to the well-known helical packing, with a pitch of only 2.3 nm. Such a purely physical surface reconstruction should occur also in many, if not all air-stable viruses, with consequences for virus transmission in general.

To address more complex mammalian viruses, specifically influenza, we have developed several model systems, which allow to characterize changes upon drying in the adsorbed state by AFM. For example, we try to model the outer virus coat, which is dominated by glycosylated proteins, by gold particles, which are covalently linked to sugar moieties.

Nanotribology of Ionic liquids at Charged Surfaces

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Tribological effects, such as friction and wear, reduce the energy efficiency and working life of machinery, and have been estimated to cost 1.5% of GDP in industrialised countries.¹ Lubricants play an important role in minimising friction and wear by acting as a barrier between moving surfaces.

Ionic liquids (ILs), which are pure salts that have melting points below 100 °C, are promising lubricant candidates for nanodevices on account of their selective affinity for solid surfaces, high temperature stability, thermal and electrical conductivity. As ILs are composed solely of cations and anions, lubricity can be externally controlled *in situ* by application of a potential to an electrode surface, i.e. gold and highly ordered pyrolytic graphite (HOPG). The ion composition in the boundary layer responds with the applied potential, and thus alters lubricity. Recently, for ILs containing hydroxy-functionalized cations, we have detected a cation bilayer structure at the IL-mica interface due to the formation of H-bonds between the hydroxy-functionalized cations ((c-c) H-bonds), which enhances the ordering of the ions in the boundary layer and improves the lubrication. The strength of the cation bilayer structure is controlled by altering the strength of (c-c) H-bonding via changes in the hydroxyalkyl chain length, cation charge polarizability and the coordination strength of the anions. This reveals a new means of controlling IL boundary nanostructure via H-bonding between ions of the same charge, which can impact diverse applications including surface catalysis, particle stability and electrochemistry, etc.

Polymeric ionic liquids (PILs) are a new class of ILs which comprise a polymer backbone containing tethered cations (or anions) and associated counterions. They combine the attractive properties of ionic liquids (ILs) with the sequence complexity and the mechanical characteristics of macromolecules. However, to date the interfacial properties of PILs at electrode interfaces, including interfacial nanostructure and nanofriction have not been investigated despite their importance for electrochemical and lubrication applications. Recently, we have found in a mixture composed of 5% PIL and 95% conventional IL, polymeric cations adsorb strongly to the Au(111) electrode and form a polymeric cation-enriched boundary layer at negative potentials. This boundary layer binds less strongly to the electrode surface at open circuit potential (OCP) and weakly at positive potentials. The lateral forces of the 5 wt% PIL/IL mixture at negative potentials and OCP are obviously higher than at positive potentials and pure conventional IL of the same potentials as the polymeric cation-enriched boundary layer is rougher and has stronger interactions with the AFM probe compared to the convention cation-enriched boundary layer; at positive potentials, the lateral force is low and comparable to pure conventional IL due to the displacement of polymeric cations with conventional anions in the boundary layer. The outcomes help to elucidate the interfacial adsorption mechanisms of PIL electrolytes at the Au(111) electrode towards bridging the gap between conventional liquid electrolytes and flexible solid state electrochemical devices.

Nanoscale analysis of the electrode/electrolyte interface in protic ionic liquids

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In order to limit the emission of greenhouse gases, fossil fuels have to be replaced by renewable resources such as wind and solar energy. Until now, their intermittency is one of the biggest challenges for a complete transition of the energy system. Therefore, a storage system, which relies on electrochemical energy converters and employs the chemical reaction between hydrogen, oxygen and water, could serve as an efficient solution for this problem. In particular for automotive application, the use of polymer membrane electrolyte fuel cells (PEMFCs) is thought as an efficient alternative to combustion engines. However, the overall efficiency of fuel cell cars is still lower in comparison to battery cars, which demands for an improvement of the employed technology.

Today's fuel cell cars operate at temperatures of about 80 °C, which requires a complicated heat and water management system. Hence, it is expected that a significant efficiency improvement can be achieved by increasing the operation temperature above 100 °C. In order to reach this goal, novel electrolytes, which are stable in this temperature range and still allow an efficient proton transport, have to be developed. Hence, we evaluate the usability of protic ionic liquids (PILs) as fuel cell electrolytes. As ionic liquids are matter composed entirely of ions, their electrochemical behavior is fundamentally different from that of aqueous solutions. In particular, the formation of the electrical double layer at the interface between electrode and electrolyte cannot be explained by the classical theories of Helmholtz, Guy, Chapman, and Stern. Instead, one has to take into account that alternating anion and cation layers will form at a charged interface, which will also influence the reactions taking place at the electrode surface and the proton transport in the membrane.

In order to investigate the nature of the double layer experimentally, we employ infrared spectroscopy and atomic force spectroscopy. These experiments confirm that a dense layered structure at the interface is present that not only depends on the electrode potential, but is furthermore influenced by the presence of water in the ionic liquid, which is unavoidable during fuel cell operation. Based on these experimental results, we aim on developing a model for the interface formation by means of density functional theory (DFT) in combination with molecular dynamics simulations, which will be used to select and develop promising material combinations of electrode, ionic liquid and membrane.

Ionic liquids under applied fields at interfaces and under confinement: Forces, friction and tribotronics.

Mark Rutland

Ionic liquids have received much attention as tribological additives and lubricants, due to their tuneability but also due to the possibility of controlling the surface composition using an applied field. Nonetheless, much work remains to understand the interfacial properties of these liquids and their corresponding frictional behavior. Of particular interest are ionic liquids with orthoborate based anions, which avoid the issue of fluorination – however relatively little is known about their properties otherwise.

Quartz crystal microbalance, Vibrational sum frequency spectroscopy and neutron reflectance have been applied at isolated interfaces, whereas confined properties have been studied using AFM and Surface Forces (ATLAS). In both cases applied electric fields are applied and the electroresponsiveness measured. The role of water is also addressed, and found to be important in this context. A brief summary of conclusions will be presented.

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Pilkington, G.A., K. Harris, E. Bergendal, A.B. Reddy, G.K. Pålsson, A. Vorobiev, O.N. Antzutkin, S. Glavatskih, and M.W. Rutland, *Electro-responsivity of ionic liquid boundary layers in a polar solvent revealed by neutron reflectance*. Journal of Chemical Physics, 2018. **148**(19).

Atomic-scale friction study: Underpotential deposition (UPD) of silver on I-modified Au(111) in aprotic electrolyte

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Friction in general is one of the main sources of energy loss, and therefore finding ways for better controlling friction is of uttermost importance. Atomic-scale friction is measured using electrochemical lateral force microscopy (EC-LFM) where the AFM tip slides on the surface of electrode under electrochemical control. It helps us to understand interfacial and tribological behavior on nanoscale. In ionic liquids (ILs) including solvate ILs, the friction as function of normal load has been studied on HOPG and Au(111), which shows that the structure of ions is a decisive factor for the friction behavior [1-4]. Our interest was focused on the adsorption of foreign metals, ranging from (sub)monolayer (underpotential deposition (UPD)) to multilayer (bulk) deposition and the adsorption of organic adsorbates, and its influence on friction as function of potential on single crystal electrodes in aqueous electrolyte[5-7].

The underpotential deposition (UPD) of silver had often been studied on gold in aqueous electrolyte since the lattice constants of silver and gold are fairly identical ($a_{Ag} = 4.09 \text{ \AA}$, $a_{Au} = 4.08 \text{ \AA}$) [8-12]. Previous results clearly show that the Ag UPD process is very sensitive to the presence of other adsorbates (e.g. SO_4^{2-} , ClO_4^-). Especially, the Ag UPD on iodine covered surface of Au(111) shows completely different atomic structures after the 1st, 2nd, and 3rd Ag UPD compared to the results on Au(111) [9, 13].

In this study, we investigate the interfacial properties on I-modified Au(111) during the Ag UPD in aprotic electrolyte. We observed two sets of Ag UPD peaks in cyclic voltammetry (CV). The charge density for these peaks is about $216 \mu\text{C}/\text{cm}^2$ close to the theoretical charge density for the monolayer ($222 \mu\text{C}/\text{cm}^2$). We observed the iodine structure at low normal load ($F_N < 20\text{nN}$), which shows that the iodine adlayer on Au(111) and Ag monolayer forms a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$. It indicates that the iodine adlayer is stable during the Ag UPD. At high normal load, the AFM tip penetrates into iodine layer and reveals the structure of Au(111) or Ag monolayer depending on the potential. It is remarkable that there is no irreversible wear during the penetration of AFM tip meaning that the iodine structure appears again with decreasing normal loads. At high normal load where the tip penetrates into iodine layer and interacts with substrates (Au and Ag), the friction on Ag monolayer is higher than on Au(111). Interestingly, even though the cyclic voltammetry (CV) shows that the amount of water in the electrolyte has minor influence, the friction increases with an increase in water content on the I/Ag/Au(111).

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Morphology, concentration, potential: Exploring tunable adsorption film friction with molecular dynamics

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Ionic solutes in aqueous solution aggregate on immersed surfaces. The composition and structure of compact adsorption films and the complementing diffuse layers influence interfacial friction. Active friction control is possible by tuning this adsorption behavior. We focus on three parametric dimensions governing film composition and morphology, namely the involved ions themselves, ion concentrations, and electrostatic potential, and show their impact on friction mechanisms on the molecular level by means of probe-on-flat and flat-on-flat shear simulations via molecular dynamics.

1. Introduction

Surfactant adsorption films at the solid-liquid interface undergo phase transitions controlled by various environmental parameters. The anionic model surfactant sodium dodecyl sulfate (SDS) forms flat-lying monolayers at low concentrations at the aqueous solution–gold interface. With increasing surface coverage, stripe-like aggregates of hemicylindrical nature assemble. Sufficiently strong attractive electrostatic potential induces another transition towards densely packed bilayers. Active tuning of concentrations and electrostatic potential allows for precise friction control at the nanoscale by navigating the adsorption film’s phase diagram [1]. Moreover, the background electrolyte’s nature and concentration is known to alter surfactant aggregation behavior as well. We explore the molecular mechanisms behind concentration- and potential-dependent friction response in the model.

2. Methods

By means of all-atom molecular dynamics simulations, we slide an atomic force microscope (AFM) tip model laterally across SDS films at the H₂O–Au(111) interface. Thereby, we shine a light upon the molecular mechanics behind distinct friction force responses of different film phases under shear [2]. Figure 1, for instance, compares sliding on a dense monolayer (a) with sliding across hemicylinders (b) on the basis of friction and load evolutions at the onset of lateral motion. In another batch of simulations, we use a constant potential approach by dynamic charge optimization to investigate potential-dependent friction of sodium chloride, a commonly encountered background electrolyte, in aqueous solutions confined within a nanogap [3].

3. Discussion

In the particular comparison between sliding on different aggregates shown in Figure 1, the hemicylindrical configuration exhibits less resistance under comparable load. The model allows us to attribute changes in tribological response directly to structural properties, such as molecular alignment within the surfactant film or potential-induced alteration of the saline solution’s electrochemical double layer. Automated screening of the parametric space spanned by concentrations and electrostatic potentials enables us to identify parameter-dependent friction trends.

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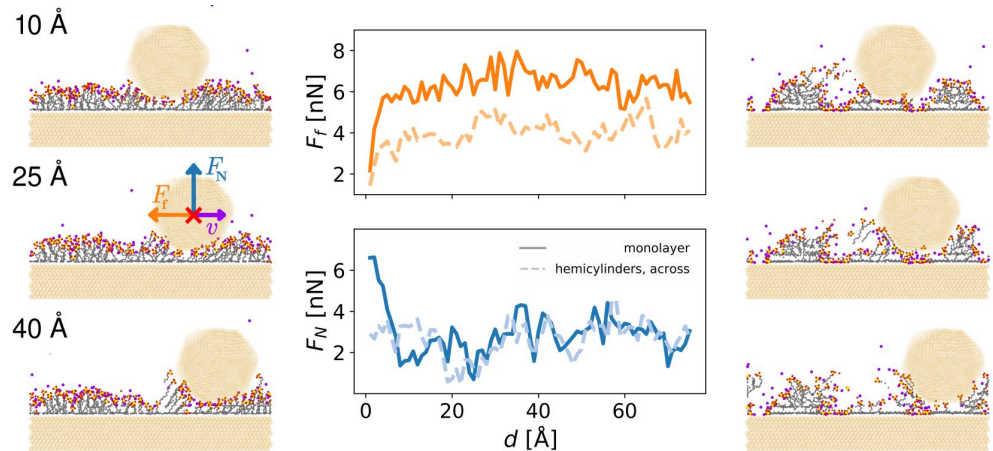


Figure 1: Friction F_f (top, center) and load F_N (bottom) felt by AFM tip (radius $r = 25 \text{ Å}$) during initial sliding phase on SDS monolayer (solid lines in plot and conceptual sketch on the left) and across hemicylinders (dashed lines, right sketch) at surface packing density $n = 3 \text{ nm}^{-2}$, fixed surface–surface distance $a = 10 \text{ Å}$ and velocity $v = 10 \text{ m s}^{-1}$. Labels in left hand side conceptual sketch indicate laterally travelled distance d for each snapshot.

Tribotronic control and energy storage attributes of metal-oxide nanofluid interfaces

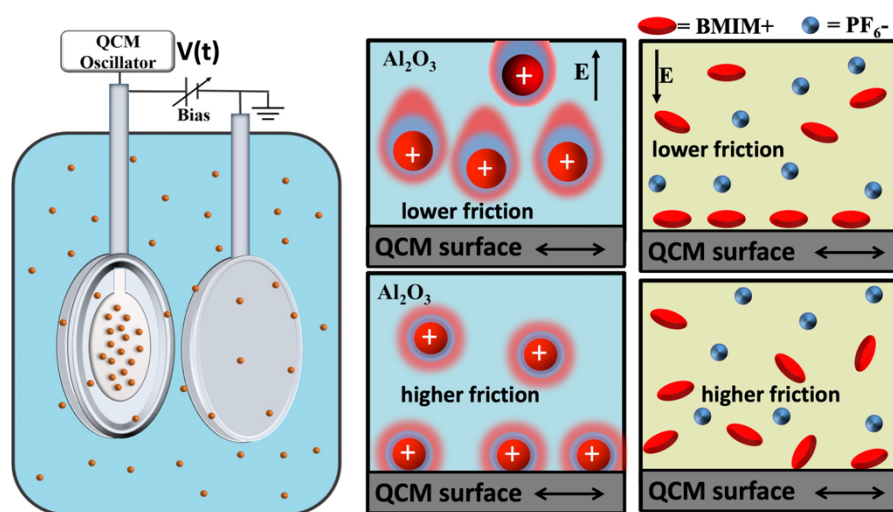
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A Quartz Crystal Microbalance (QCM) technique has been employed to tune friction at liquid-solid interfaces with tribotronic methods, employing externally applied electric fields in nanoparticle suspension and ionic liquid systems [1-3]. The setup consists of a QCM immersed in liquid containing electrically charged constituents whose sensing electrode is parallel to a nearby counter electrode. An electric field perpendicular to the QCM surface is created when a potential is applied between the two electrodes, which allows the charged constituents in the surrounding liquid to be repositioned [1,2]. For the case of nanosuspensions, the solid-suspension interfaces were also explored using cyclic voltammetry (CV) techniques [3]. Both CV and QCM measurements were able to detect differences under various field conditions, allowing detectable tuning of the friction and electrochemical attributes. Interfacial friction levels in all cases were observed to change as the charged constituents' positions were adjusted with electric fields. For electric fields of sufficient amplitude and duration, the TiO_2 nanosuspension exhibited properties consistent with reversible electrophoretic deposition of the nanoparticles, accompanied by changes in the electrochemical attributes of the electrode itself [1-3]

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Friction force microscopy of shear planes at the electrochemical interface

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Friction force microscopy offers the opportunity to study molecular mechanisms of shear at electrochemically active solid-liquid interfaces. One of the key questions in understanding and controlling friction is the identification of the actual shear plane. We will discuss results of two experimental studies which demonstrate how the shear plane may vary within one experiment. In the first system, an ionic liquid on a crystalline gold electrode, the number of layers of ionic liquid between sliding tip and surface depends on the applied potential.¹ In the second system, a metallic glass surface corroded in a phosphate buffer, the sliding tip removes a precipitated layer of corrosion products even at lowest forces. This removal process intermittently contributes to the measured friction force.²

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Friction at Au(111) during underpotential deposition (UPD): Effect of potential, normal load and the ionic adsorbate I

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Friction between a sliding AFM tip and the surface of the electrode help us to understand interfacial and tribological behavior on a nanoscale. The measurement of friction in an electrochemical cell allows controlling the interfacial interactions in situ easily. Our interest has focused on the adsorption of foreign metals, ranging from (sub)monolayer (underpotential deposition(UPD)) to multilayer (bulk deposition) and the adsorption of organic adsorbate depending on a potential on single crystal electrodes in aqueous electrolyte[1-3].

In this study, we investigate the interfacial properties on Au(111) in aqueous electrolyte. The structure of Ag UPD layers is extremely sensitive to co-adsorbed anions such as I⁻ and SO₄²⁻. We found that the iodine adlayer on Au(111) forms a ($\sqrt{3}\times\sqrt{3}$)R30° structure using the results of atomic stick-slip. It changes to a p(3×3) and ($\sqrt{3}\times\sqrt{3}$)R30° structure after 1st Ag UPD and 3rd Ag UPD, respectively. The results of the friction on potential shows that the incomplete Ag UPD layer on Au(111) leads to relatively high friction. It is in good agreement that for low and moderate coverages, the tip drags the adsorbates along the surface resulting in high friction, whereas for higher coverages the tip slides above the adsorbates resulting in low friction[4]. The results of the friction on load on I-modified Au(111) shows three apparent regimes. Under the low normal load ($F_N < 30\text{ nN}$), the friction force is independent on Ag UPD, meaning that the tip is interacting with iodine layer. Under critical normal load, the friction shows a rapid increase, which indicates that the tip penetrates into the iodine layer. Under the high normal load ($F_N > 100$), the friction shows moderate increase, which represents that the tip is interacting with Ag UPD layer.

Important is the dependence of the structure as revealed by the LFM images: whereas at low normal load the structure of the anionic adlayer is visible, at higher load the images change to the structure of either the Au substrate or the Ag upd layer. In the case of Cu upd, at higher loads multiple slips occur instead.

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Sulfate adsorption on Au(111) electrodes - Influence of the potential on the force distance curves

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As earlier studies showed a dependence of friction on the electrode^[1, 2] potential applied to a Au(111) electrode in sulfuric acid solution, we herein investigated approach curves (force vs. distance) at several electrode potentials. Utilizing atomic force microscopy (AFM) under electrochemical conditions, we expect to obtain further insights into the sulfate adsorption on Au(111) electrodes.

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Anomalous Potential-Dependent Friction on Au(111) Measured by AFM

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Abstract: We present an exploratory study of the tribological properties between an AFM probe and a Au(111) surface in an aqueous environment while subjected to applied surface potentials. Using a three-electrode setup, the electrical potential and interfacial electric field on a Au(111) working electrode are controlled. Lateral force microscopy is used to measure the friction forces between the AFM probe and the Au surface. As the AFM probe approaches the surface, normal forces are also measured to gain insight into the interfacial forces. When a positive potential is applied to the Au surface, the friction is found to rise sharply at a critical potential and levels off at a relatively high value. However, when a negative potential is applied, the friction is low, even lower compared to the open circuit potential case. These changes in friction, by a factor of approximately 35, as a function of the applied potential are found to be reversible over multiple cycles. We attribute the origin of the high friction at positive potentials to the formation of a highly confined, ordered icelike water layer at the Au/electrolyte interface that results in effective hydrogen bonding with the AFM probe. At negative potentials, the icelike water layer is disrupted, resulting in the water molecules acting as boundary lubricants and providing low friction. Such friction experiments can provide valuable insight into the structure and properties of water at charged surfaces under various conditions and can potentially impact a variety of technologies relying on molecular-level friction.

The influence of corrosion on diamond-like carbon topography and friction at the nanoscale

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Abstract

The influence of corrosion upon the nanoscale topography and friction response of a hydrogenated amorphous carbon film (a-C:H) was investigated. Electrochemical atomic force microscopy was used to characterise topographical changes to the coating at two oxidative potentials. Corrosion of the coating at 1.5 V (corrosion rate 0.5 nm hr⁻¹) resulted in no changes to the nanoscale topography; whereas corrosion at 2.5 V (corrosion rate 26.4 nm hr⁻¹) caused the root mean square roughness of the a-C:H film topography to decrease, but the local fine-scale irregularity or ‘jaggedness’ of the surface to increase. X-ray photoelectron spectroscopy revealed that corrosion at both potentials oxidised the a-C:H surface to form alcohol, carbonyl and carboxyl groups. Lateral force microscopy and adhesion force measurements showed that both the friction force and surface adhesion of the coating increased upon corrosion. The outcome was attributed to the surface oxidation that had occurred at both oxidative potentials, resulting in several potential mechanisms including increased attractive intermolecular interactions and capillary forces. The highest friction coefficient was observed for the a-C:H film corroded at 2.5 V, and identified as a consequence of the jagged surface topography promoting an interlocking friction mechanism.

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Friction and Wear Issues in Conventional Energy Extraction Infrastructure

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Conventional energy extraction represents a significant portion of the Albertian and Canadian economies. While often not a primary focus of the industry, there are several factors impacting the lifetimes of the infrastructure used in energy extraction. Often the focus on low-cost steels, the ease of manufacturing and other factors out-weigh the short lifetimes of the infrastructure. Recent efforts to modernize, increase the lifetime of the infrastructure and reduce overall costs have highlighted some systematic friction and wear issues that are impacting this sector. Focusing on hydraulic fracturing, the constant recycling of the water used in the process results in high salt concentrations in the fracturing fluid as well as the entrapment of hard, irregularly-shaped debris in the fracturing fluid. The combination of the salinity and the particles in the water causes excessive corrosion issues for the steel pipes carrying the fluid to and from the fracturing site. There are several mitigation standards that can be implemented to improve the lifetimes of these pipes, including applying wear and corrosion resistant coatings to the inner walls of the steel pipes and/or injection of wear and corrosion inhibiting chemicals into the fluid to protect the infrastructure. In this talk, we will discuss how tribocorrosion (tribology + corrosion) can be used to find solutions to optimizing the performance of the systems. While this data only begins to tackle the larger issues relevant to the industry, it demonstrates a systematic approach that we have taken that can support the industry in reducing costs and environmental impact during energy harvesting.

Triboelectrochemical study of various Nb-Ti-Zr alloys in simulated body environment

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The β phase Ti alloys are under intensive research focus due to their tunable young modulus, excellent tribocorrosion resistance and biocompatibility^[1]. Pure Ti has a hexagonal structure (α) and possess a young modulus 4 to 5 times higher than a human bone (20 - 30 MPa). Several elements i.e. Nb, Mo and V can be used to stabilize the β phase of Ti^[2]. However, in addition to the β phase, a critical ω phase can also form during quenching which strongly affects the mechanical properties. It is reported that addition of Zr (5-10 wt.%) can significantly discourage the formation of ω phase^[3]. Therefore, in this work ternary NbTiZr alloys containing the Nb wt.% (7, 12, 17, 22, 27 and 45) were produce, while the amount of Zr was kept only 5 wt.% in each.

The NbTiZr alloys were prepared by vacuum arc melting and subsequently heat treated at 1000 °C in a Bridgman furnace for 12 h. The composition of each alloy was examined with Energy dispersive X-ray analysis. To analyze the crystal structure of alloys, X-ray diffraction was undertaken and the suppression of ω phase was clearly observed following the Nb content higher than 22 wt.% in Ti5Zr. All samples were mirror polished and electrochemically tested by mean of open circuit potential, electrochemical impedance spectroscopy and linear sweep voltammetry. To study the semiconducting behavior of the passive oxide, the alloys were anodized via cyclic voltammetry up to 7 V with an incremental step of 1 V. The oxide growth factor, capacitance, permittivity coefficient (ϵ_r) were evaluated for oxide films grown on various alloys. Finally with the help of Mott Schottky plots the defect concentration in each oxide was determined.

Moreover, it is equally important for an implant material to be tested under tribocorrosion conditions. For this purpose the samples were tested with the techniques namely electrochemical noise method and chronoamperometry under sliding conditions. During the triboexperiments the coefficient of friction (COF) was also recorded. A rise of COF value from (0.1 ± 0.02 to 0.2 ± 0.04) was noted with the increase in Nb content from 7 to 45 wt.%. The microscopic images and wear track profiles were assessed by mean of the light microscope and the profilometer respectively. It was revealed that the wear track volume gets significantly smaller as the Nb content increases. Based on these investigations, it can be concluded that, the ternary TiNbZr alloys containing a percentage of 22 wt.% Nb (or more) and 5 wt.% Zr showed excellent tribocorrosion properties, thus may be considered as potential candidate for further biomedical investigation.

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Atomic wear governed by synergic energy: the roles of tribochemistry and electrochemistry

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In this study, the role of tribochemistry and electrochemistry in the nanowear behavior on silicon substrate against SiO₂ microsphere were studied by using an EC-AFM. By introducing tribochemical reactions at the tribological interfaces, the threshold dissipated energy for material removal reduces significantly to 5.6% ($\sim 4 \times 10^4$ kcal/mol) of that in purely mechanical wear case ($\sim 7 \times 10^5$ kcal/mol). And the value can be further reduced with the assistance of electrochemical corrosion. The findings provide a new paradigm to regulate atomic wear process through utilizing the synergy of multi-source energy.

Keywords: Material removal; Multi-source energies; Tribochemistry; Electrochemistry;

1. Introduction

Tribochemical wear that causes atomic attrition before material yield has attracted lots of attention due to its critical role in ultra-precision manufacturing, micro-electromechanical system (MEMS) and reliable microscopy.¹ As a chemical means or processes initiated from contact interface, the potentiality of tribochemical reactions must be determined by the states of treated surface and the external energy (such as mechanical energy and electric energy).¹ Further understanding of regulating tribochemical reactions could provide insights into reducing friction and wear (in MEMS applications) or improving machining efficiency (in nanomanufacturing).

2. Methods

By using an atomic force microscope with an electrochemical cell (EC-AFM, Bruker, Icon), the tribochemical removal between SiO₂ microsphere and silicon surface was conducted in electrolyte solution (3% wt.% sodium chloride solution), as shown in Figure 1. During the tests, the displacement amplitude was set as 500 nm, the sliding velocity was 2 $\mu\text{m/s}$, and the applied voltage was constant at 1.5 V.

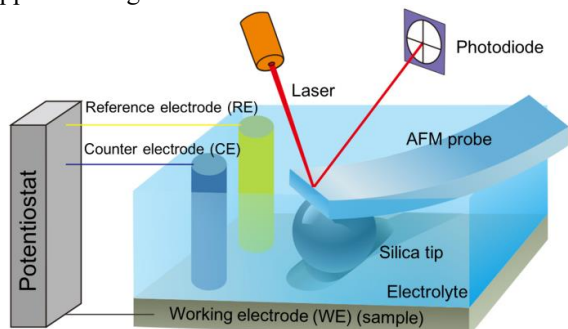


Figure 1: Schematic illustration of the tribochemical removal on silicon surface against a silica microsphere ($R \sim 1 \mu\text{m}$) attached to an AFM cantilever in EC-AFM system.

3. Discussion

Different from mechanical removal processes involving abrasion, fracture, or plastic deformation, the tribochemical wear relies on the shear-induced

hydrolysis reaction of Si substrate with existing water molecules in the sliding environment. Quantified wear results on silicon surface indicates that tribochemical removal rate follows the Arrhenius kinetics law depended on the stress-assisted chemical reactions which is described as a thermally activated atom-by-atom removal process with the lower energy barrier reduced by external mechanical energy. Tribochemical wear ($\sim 4 \times 10^4$ kcal/mol) consumes only 5.6% dissipated energy of mechanical wear case ($\sim 7 \times 10^5$ kcal/mol), which is attributed to the reduced energy barrier of Si-Si bond breakage and no lattice distortion underneath the machined area. And this value is further reduced by introducing electrochemistry. Figure 2 shows the simplified energy coordinate along the dissociation of Si-Si bond at silicon substrate. Tribo/Electrochemical reactions induced by applied mechanical/electrical energy promote the wear rate by reducing the energy barrier: $E_a = E_{\text{Thermal}} - E_{\text{Tribochemistry}} - E_{\text{Electrochemistry}}$, through lowering the activated energy and increasing the initial energy, respectively.

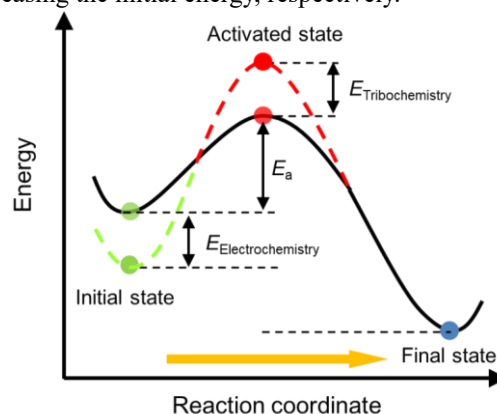


Figure 2: Schematic energy diagram along the reaction coordinate leading to the dissociation of Si-Si bond at silicon surface with the assistant of tribochemical and electrochemical reactions.

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The influence of electrochemistry on tribocorrosion of Titanium alloys

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Titanium alloys are widely used for medical devices as knee and hip prosthesis, because of its mechanical, chemical and electrochemical properties, as well as its biocompatibility. Flexibility, mobility, materials combination, among others, are some of the advantages that modular artificial joints brought to patients and medical. However, several problems have been associated to this modularity, and in turn, to its tribo-corrosion properties, which are strongly influenced by the electrochemical conditions. Indeed, most of the revision procedures could be attributed to the tribochemical degradation suffered by prosthesis made of titanium alloys.

This work presents the influence of the electrochemical condition on Ti6Al4V alloys under fretting regime. A Ti6Al4V/Al₂O₃ couple were evaluated under a rig configuration, where the same load, movement and stiffness were applied under different electrochemical condition. As the electrochemical conditions inside the human body are unclear, tribocorrosion test were done under anodic and cathodic condition. In addition, a comparison of the morphological in-vitro findings is done respect to retrievals prosthesis, seeking to establish a plausible electrochemical condition within the body.

Towards a macroscopic integro-differential equation accounting for triboelectrochemical phenomena.

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The triboelectrochemical phenomena is a dynamical process where the electrode kinetics and the mechanical interaction must be included in a general equation for the interpretation of experimental observations. The objective of the present work is the mathematical description of the time evolution of the indentation and the electrical current in a pin-on-disk tribometer.

In our model we consider that the metal mass (M_m) loss rate in a triboelectrochemical system can be expressed as the contribution of a wear term with an exclusive mechanical origin (Φ_{mech}) and the contribution of the electrochemical term caused by the tribocorrosion phenomenon (Φ_{chem}):

$$\frac{dM_m}{dt} = \Phi_{mech} + \Phi_{chem} \quad (1)$$

No synergy term has been included in this expression because it could be demonstrated that it is not necessary to describe the mechanical-electrochemical non-linear interaction. The model has been developed assuming the following hypothesis:

- a) the pure mechanical wear is described by Archard's Law
- b) the Faraday's Law describes the metal mass loss by repassivation of the bared metal surface
- c) the dynamics of repassivation is described by the impulse response of Randles-like equivalent circuit
- d) the wear track profile matches the radius of the ball indenter

Under these considerations, the wear track depth (x), an experimental observable magnitude, can be evaluated solving the equation:

$$\frac{dx}{dt} = \left[2 \rho_m L R(x(2-x))^{1/2} \right]^{-1} \left\{ \rho_m k \frac{F_N}{H} v_s + \frac{Mr}{n_e F} \frac{\rho_m}{\rho_{ox}} \int_0^L j(t, \tau) \cdot \lambda(x) \cdot |v_s(\tau)| d\tau \right\} \quad (2)$$

Where the integral is a convolution integral where considers the pin movement (v_s) and the wear track profile ($\lambda(x)$). The equation has been tested with a numerical 1D model for a tribometer. Indentation and current dynamics are provided.

Shear Viscosity of Dense Polar Fluids

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Transport properties of fluids with electrostatic interactions are theoretically challenging, even just for bulk fluids, because the long-range interactions preclude the use of a simple effective-diameter approach based solely on hard spheres. We develop an analytical approach to the viscosity of a polar fluid that incorporates electrostatic interactions. We develop a kinetic theory for dipolar hard-sphere fluids that is valid up to high density and use it to obtain the shear viscosity. We also perform molecular-dynamics simulations of this system and extract the shear viscosity numerically. The theoretical results compare favorably to the simulations. I will also show some preliminary simulation results for viscosity in external fields.

References: Phys. Rev. Lett. 124, 218004 (2020)

Tuning surface forces using AC electric fields

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A basic tenet of tribology is that the adhesion and friction between two materials is fully determined by the properties of the surface material and of any added lubricant. Recently, a series of pioneering experiments challenged this view: friction and adhesion may be controlled by means of external stimuli such as mechanical excitation or photo-switching, without need for altering the material components. An alternative route to external control of surface interactions is through electrical polarisation of one or both surfaces; a few pioneering cases of friction and adhesion control with electric fields have been reported.

In this talk, I will describe electric field control of adhesion using a different mechanism. By applying an alternating (AC) electric field perpendicular to two surfaces with a liquid film between, we introduce a force which can be used to drive the surfaces in and out of adhesive contact. Taking advantage of the oscillatory interaction potential between the surfaces across the liquid, the AC actuation allows us to choose between the available adhesive states and thus provides exquisite control of the adhesion strength. Our measurements, carried out with a surface force balance (SFB), have resolution in surface separation of ~ 0.1 nm and therefore provide insight into the adhesion process at the level of individual liquid layers between the surfaces.

Fracture of soft matter during needle insertion

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Soft matter is extensively used in the biomedical field due to its biocompatibility and tunability of tissue-mimicking properties. This talk is mainly about the in-situ fracture characteristics of soft matter (hydrogel) during needle insertion and the role of water content, and identify the stresses cause various cracks. In the process of needle insertion into the PAA hydrogel, a complex stress field is generated and causes various cracks due to contact between the needle and hydrogel. The results facilitate in better understanding of friction, fracture and damages of tissues, particularly liver, brain during needle insertion; opens a promising perspective in control of tissue damages during surgical operations.

Keywords: Cone crack, fracture, friction, soft matter, needle insertion, tissue damage

Synthesis of conical Co-Fe alloys structures obtained with crystal modifier in the superimposed magnetic field

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INTRODUCTION

The issue of renewable energy sources is more and more important these days, due to the increase in energy demand. One of the idea is using shaped structures, especially in nanoscale, as a catalyst characterized by greater electrocatalytic activity connected with their large active surface area [1]. The one-step method connects the advantages of the electrodeposition process with the control of the structure shapes caused by the presence of a crystal modifier. It promotes specific directions of growth during a single electrodeposition process. The use of an external magnetic field during the electrodeposition process allows the properties of the obtained coatings to be modified. This phenomenon is known as the magnetohydrodynamic effect (MHD) [2].

RESULTS AND DISCUSSION

In this work, the Co-Fe alloy cones were successfully synthesized using the one-step method from an electrolyte containing NH_4Cl as a crystal modifier. The influence of the external superimposed magnetic field on the sample surface development and their electrocatalytic properties were measured. The real, active surface area of samples was determined by various methods and compared. Co-Fe cones were synthesized from the electrolyte containing: 6.5 mM CoSO_4 , 6.5 mM FeSO_4 , 93.5 mM Na_2SO_4 and 0.4 M H_3BO_3 . In order to produce the conical structures, NH_4Cl was added to the solution as the crystal modifier. The electrodeposition process was carried out in galvanostatic mode at two-electrodes cell. Pt foil was an anode and Cu foil was a cathode. Due to the ferromagnetic properties of alloy components, the influence of the external superimposed magnetic field on the sample surface development and therefore their electrocatalytic properties were checked. The magnetic field was applied in two different directions by the electromagnet LakeShore (Model 642). The intensity value was 500 mT.

Produced coatings were analyzed using a Scanning Electron Microscope SEM (Figure). Their electrocatalytic properties were determined using the linear scan voltammetry (LSV) and chronopotentiometry (CP) measurements in 1 M NaOH. Due to the significant influence of the sample's active area, it was determined by various methods using: Brunauer-Emmett-Teller (BET) analysis, and the double-layer capacitance measurements during the CV's scans, Atomic Force Microscope AFM, and a Confocal Microscope.

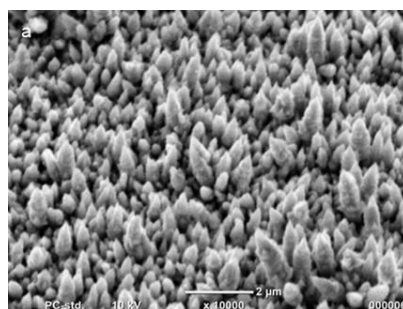


Fig. Sample obtained from the electrolyte without the magnetic field.

Performed experiments and obtained results confirm that the synthesis of conical Co-Fe alloy structures by one-step method is possible. Measurements of the electrocatalytic properties showed that the sample synthesized in the parallel magnetic field is characterized by the best electrocatalytic activity. It is probably connected with the largest development of its surface corroborated by BET, the double-layer capacitance measurements during the CV's scans, and the sample roughness value (Table).

Table. Comparison of the sample surface development determined by various methods.

Sample	Average value of R_a [μm] measured by Confocal Microscope	BET [m^2/m^2]	Ratio of double layer capacities. [$\text{mF}/\text{mF}_{\text{Cu}}$]
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Without magnetic field	0.360	36.11	84.47
With perpendicular magnetic field	0.415	19.74	54.03
With parallel magnetic field	0.345	73.50	97.22

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