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An Ionic Liquid lubricant enables Superlubricity to be “Switched On”

in situ using an Electrical Potential

Hua Li,^a Ross J. Wood,^a Mark W. Rutland,^b and Rob Atkin^{a,*}

Atomic force microscopy measurements reveal that superlubricity can be “switched” on and off *in situ* when an ionic liquid is used to lubricate the silica-graphite interface. Applying a potential to the graphite surface changes the ion composition of the boundary layer and thus the lubricity. At positive potentials, when the interfacial ion layer is anion rich, friction falls to ultra-low levels.

Ionic liquids (ILs), which are pure salts that have melting points below 100 °C, are promising candidate lubricants on account of their selective affinity for solid surfaces,¹ high temperature stability and thermal conductivity. ILs interact strongly with solid interfaces¹⁻⁴ and resist ‘squeeze out’ as surfaces are compressed, meaning the ion boundary layer remains in place at higher forces than for a comparable molecular lubricant.⁵ A lubricant that reduces friction to very low levels, such that the friction coefficient is less than 0.01 is “superlubricating”. (The friction coefficient is the gradient of the relationship between friction force and applied load). “Super-lubricity” has been previously reported for a variety of interfaces.⁶⁻¹² In this article we show that the use of an IL lubricant allows the lubricity of a graphite surface to be controlled *in situ* by applying a potential to the surface. At positive potentials, the anion rich boundary layer is “superlubricating”.

The nanotribology of the silica – highly ordered pyrolytic graphite (HOPG) interface is investigated using atomic force microscopy (AFM). The IL lubricant used was 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate ([HMIm] FAP) which is chemically stable to both air and water. The cyclic voltammetry of [HMIm] FAP on HOPG was measured *in situ*, within the AFM electrochemical cell, shown in the supporting information Figure S1. The cyclic voltammogram reveals the IL is electrochemically inert between -2.3 V and +2.6 V, and friction measurements were performed within this potential range.

Friction force microscopy (FFM) images and line traces of the lateral force obtained using a sharp AFM tip ($r \approx 5$ nm) and an HOPG surface, are shown in Figure 1. Data is shown for air, and when the tip is immersed in [HMIm] FAP as a function of potential. Scans were conducted at a sliding speed of $58.6 \text{ nm}\cdot\text{s}^{-1}$ at surface potentials of 0 V, ± 1.0 V, and ± 1.5 V (vs. Pt quasi reference electrode). Normal force curves for these systems are shown in the supporting information (Figure S2). When the “apparent separation” is equal to 0, the AFM tip presses against a counter-ion rich interfacial layer strongly bound to the HOPG surface.^{2, 13-15} Figure S2 shows that, for all potentials, this “interfacial layer” condition (apparent separation equal to zero) is met when the normal force is greater than 10 nN. Thus, to probe the properties of the interfacial ion layer, the normal load was kept constant at approximately 20 ± 1 nN.

For HOPG in air, the line trace shows that the tip undergoes stick-slip motion, as observed previously.¹⁶ The appearance of the friction image in air is also consistent with prior work.¹⁶ The distance between each peak in the line trace corresponds to the diameter of the graphite hexagonal ring. The approximate position of the carbon atoms in a ring is indicated in the friction image by the white dots. The area enclosed by the line trace corresponds to the magnitude of energy dissipated due to stick-slip events and provides a quantitative measure of the energy lost by the system during a friction loop. For the silica tip sliding on the HOPG surface in air at this normal load and speed, the energy dissipated is 85 eV.¹⁶

When [HMIm] FAP is present, the magnitude and regularity of stick-slip events in the line traces are reduced for all potentials, and the appearance of the friction images becomes “blurred”, c.f Figure 1. The line trace for [HMIm] FAP at 0 V is more irregular than for HOPG in air, with jumps ranging in size from ~ 0.1 nm to ~ 1.0 nm, consistent with the AFM tip moving over an interfacial layer of mixed ion composition. The friction image is correspondingly which is less well-defined than for HOPG in air, consistent with lower friction; the energy dissipation at 0 V is 39 eV, which is about half that in air.

The jumps in the line trace become smaller at more negative potentials compared to 0 V, and the FFM images are less well defined. The energy dissipated is consequently lower: 27 eV and 19 eV for -1.0 V and -1.5 V, respectively. At positive potentials, the line traces have the smallest jumps. At +1.5 V jumps can hardly be discerned and the FFM images are almost featureless. The energy dissipated at +1.0 V is 17 eV and the value for +1.5 V is 10 eV. However, the highest lateral forces measured (~ 0.5 nN) at +1.5 V are close to the instrumental detection limit, so this value should be interpreted as being between 0 and 10 eV.

Friction (energy dissipation) changes with potential because, when the potential is changed, the composition of the IL interfacial layer on HOPG responds;¹⁷ i.e. the boundary layer the AFM slides against changes. The sign of the potential determines whether the layer is cation rich, or anion rich, and the magnitude determines the extent of the ion enrichment.¹⁷ Ion enrichment creates a smoother sliding surface compared to 0V. This decreases the magnitude of stick-slip events, and reduces energy dissipation. Pertinent questions are why friction is higher at negative potentials than (the same) positive ones, and what is the origin of ultra-low friction at +1.5 V?

Both experimental and simulation studies confirm that silica is negatively charged in ILs.^{18,19} At negative potentials, the cation rich interfacial layer must satisfy the potential of the HOPG substrate and the charge of the silica tip. Cations in the interfacial layer are attracted to the HOPG surface electrostatically via their charged group and through van der Waals interactions with the hydrocarbon tail, and as such are orientated relatively flat across the surface.¹⁷ As the AFM tip slides across the interfacial layer, cationic groups are attracted to negative charge sites on the silica tip and re-orientate to maintain electroneutrality. This reorientation results in energy dissipation and friction.

For a positively biased surface, the interfacial layer is anion rich, but there is still an appreciable concentration of cations. Cation alkyl chains are attracted to the HOPG surface by van der Waals interactions,¹⁸ but the charged groups are electrostatically repelled

and thus further from the HOPG surface.¹⁷ This means that little change in the cation orientation is required to satisfy the charge of the tip as it slides over the interfacial layer, so the energy dissipated is lower than at negative potentials. At +1.5 V, most of the cations have been expelled from the interfacial layer, meaning the interfacial layer is highly enriched in anions and very smooth. The energy loss due to local stick-slip events is minimal, as is the energy dissipated by cation re-orientation. The lateral force is consistent with superlubrication.

The next set of experiments tested whether these trends hold when the tip is scanned faster over larger distances, and the effect of changing the normal load. Measurements were performed using a scan size of 100 nm and scan speed of $6.5 \mu\text{m}\cdot\text{s}^{-1}$ as the load was increased from 0 to 40 nN. Representative data obtained at surface potentials of 0 V, ± 1.0 V, and ± 1.5 V are shown in Figure 2, as well as the control experiments obtained in air (no potential). These experiments were repeated on more than 10 occasions. Data with the same form, but with small variations in the lateral force was obtained. The order of the potential change was varied between experiments to rule out tip wear induced hysteresis as a factor.

Fig. 1. Representative lateral force images (forward) and lateral force versus AFM tip displacement while sliding over an HOPG surface with an amplitude of 3 nm at $58.6 \text{ nm}\cdot\text{s}^{-1}$ in air, and immersed in [HMI]m FAP at 0 V, -1.0 V, -1.5 V, +1.0 V, and +1.5 V (versus Pt quasi reference electrode). The scale bars in the image are 0.5 nm. The energy dissipation is calculated from the area enclosed by the curve; the value listed is an average of ten or more separate experiments.

The lateral force data for the unlubricated silica tip sliding over the HOPG surface in air is similar to earlier studies.¹⁶ In this work we are primarily concerned with the friction coefficient for a single interfacial layer, which corresponds to normal forces greater than 10 nN. The reason for designating 10 nN as force required to reach the single interfacial layer condition are described in the supporting information. The discussion that follows is only for normal loads greater than 10 nN (indicated by the vertical dashed line in Figure 2) when the tip is in contact with a single layer.

The friction coefficient (μ) is obtained from Amontons's Law, $F_L = \mu F_N$, where F_L is the lateral force and F_N is the normal force. Calculated friction coefficients are indicated on the Figure 2. The friction coefficient at 0 V when the normal force is greater than 10

nN is 0.019, similar to the value of 0.20 obtained at -1.0 V and -1.5 V, but the absolute lateral force decreases markedly with potential. The friction coefficient at +1.0 V is 0.012, much lower than the values obtained at negative potentials. This is a consequence of the smoother anion-rich interfacial, consistent with the line trace in Figure 1, where sliding is smooth and stick slip events are minimal. The friction coefficient for +1.5 V is 0.001. This value is much less than 0.01, which defines superlubricity.

Fig. 2. Lateral force versus normal load in air and in [HMIm] FAP as a function of applied potential for a sharp AFM tip ($r \approx 5$ nm) sliding on a HOPG surface over 100 nm at $6 \mu\text{m}\cdot\text{s}^{-1}$. The friction coefficient, μ , is extracted from the gradient of the plot when the normal force is higher than 10 nN.

The friction coefficient at +1.0 V is 0.012, markedly lower than the values obtained at negative potentials. This is a consequence of the smoother anion-rich interfacial layer and consistent with the line trace in Figure 1, where sliding is smooth and stick slip events are minimal. The friction coefficient for +1.5 V is 0.001. This value is much less than 0.01, which defines superlubricity.

Identifying suitable lubricants for carbonaceous surfaces is critical for applications, such as heat assisted magnetic recording (HAMR) devices, which employ amorphous carbon overcoats to protect the magnetic medium against corrosion and wear.²⁰ Conventional high end lubricants are unsuitable for HAMR devices because they are unable to withstand the harsh operating conditions. On account of their thermal stability, ILs are promising candidate materials.

Conclusions

AFM has been used to show that [HMIm] FAP, a room temperature IL, is an extremely effective lubricant for the silica – HOPG interface. Because [HMIm] FAP is composed solely of cations and anions, the interface lubricity can be externally controlled *in situ* by application of a potential bias to the HOPG surface; when the potential is changed, the composition of the interfacial layer responds, which alters the frequency and magnitude of stick slip events, hence the energy dissipated and friction. At +1.5 V, the anion-rich interfacial layer is “super-lubricating” and friction falls to immeasurable values.

Notes and references

^aCentre for Advanced Particle Processing and Transport, The University of Newcastle, Callaghan, NSW 2308, Australia

^bSchool of Chemistry, Division of Surface and Corrosion Science, KTH Royal Institute of Technology, SE-100 44 Stockholm Sweden

*Corresponding author: rob.atkin@newcastle.edu.au

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