

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.