Interfacial properties of ionic liquids investigated by atomic force microscopy

A. Podestà, M. Galluzzi, S. Bovio, P. Milani

CIMaINa e Dipartimento di Fisica, Università degli Studi di Milano, via Celoria 16, 20133 Milano, Italy

Corresponding author: A. Podestà
E-mail: alessandro.podesta@mi.infn.it

Key words: atomic force microscopy, ionic liquids, interfacial properties.

Introduction

Beside their industrial applications, where their bulk physico-chemical properties are relevant, room-temperature ionic liquids (ILs) can also be used as electrolytes in several devices aimed at conversion and storage of energy, such as electrochemical supercapacitors, Grätzel solar cells and batteries, as well as lubricants in micro electromechanical devices. In these devices ILs are in form of thin films, or they can be spatially confined in nanoscale pores, therefore a key role is played by their interfacial, rather than bulk, properties, specifically pertaining to the solid-liquid interface. In particular, structural-morphological and electrical properties of the first few nanometers of ILs interacting with surfaces of solid electrodes are expected to have the strongest impact on device performance.

Here we report on the characterization of interfacial properties of [Bmim][NTf2] supported on different solid silica and mica surfaces carried out primarily by advanced atomic force microscopy (AFM) techniques.

Results and Conclusions

Thin films of prototypical ILs have been studied on a variety of surfaces of applied relevance, characterized by different surface chemistry (silica, mica and graphite), and different surface morphology (mica, graphite and crystalline silica are almost atomically smooth; amorphous silica has roughness below 1 nm). [Bmim][ntf2], an imidazolium-based IL, has been used because it is widely employed in applications and it is also very resistant to moisture as well as chemically and thermally stable.

The following scientific tasks have been successfully accomplished:

1. Development of suitable protocols for the deposition of nanometer-thick IL layers on selected surfaces;
2. Morphological, structural and mechanical characterization of supported IL films;
3. Characterization of the dielectric properties of supported IL films;

Figure 1 shows a remarkable example of structural reorganization of [bmim][ntf2] deposited on silica by drop-coating, i.e. by spotting a droplet of very diluted IL/methanol solution onto the surface and waiting for solvent evaporation. Topographic maps suggest that in the presence of a (charged) surface, the IL self-assembles in vertically ordered, layered structures, whose heights can easily exceed 50 nm [1-3]. Using different solvents (methanol, chloroform) and by means of X-ray photoemission spectroscopy analysis, we could rule out the hypothesis that this structural organization is the result of the complexation of IL with the solvent. The statistical analysis of AFM topographies maps provided an accurate characterization of the basic molecular step of layered structures, d~0.6 nm, consistent with the size of the cation/anion pair. Remarkably, we measured the same values of the basic step when using different solvents, on all different surfaces (excluded graphite, where extended solid-like domains where not observed). Direct nanomechanical tests confirmed the high mechanical resistance of these structures to vertical loads [2,3]; moreover, upon application of high lateral stresses, the structures presented delamination similarly to lamellar solids [2,3]. Indentation patterns of AFM tip on solid-like IL domains have been directly observed in nanomechanical tests [4], with rupture forces much higher than those reported for solvation layers at the bulk liquid/solid interface by Atkin *et al.* [5].

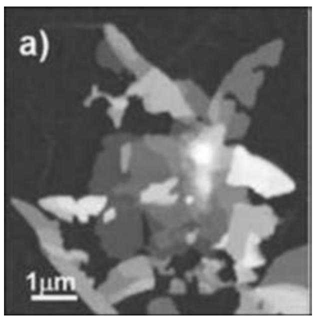

Figure 1. Layered [bmim][ntf2] island on silica.

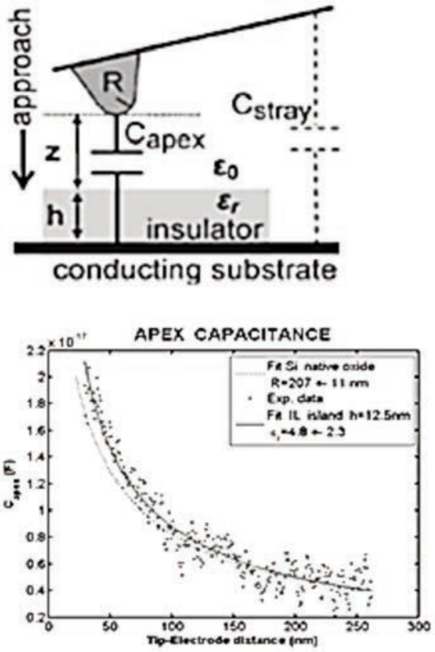

Figure 2. Capacitance vs. Distance spectroscopy on solid-like IL islands.

The observation that supported ILs islands were not disrupted by intense electric fields up to 10^8-10^9 V/m (obtained biasing the AFM with respect to sample during imaging) further confirmed that ions are tightly bound in a solid-like structure. Current-sensing AFM was used to test the dielectric properties of solid-like ILs islands, in particular to verify that, similarly to standard solid crystalline salts, also ILs islands possess dielectric character, with a finite dielectric constant (Figure 2). A static dielectric constant ε_r=3-5 was measured [6], to be compared with higher dielectric constant measured in bulk liquid ILs ε_r=9-13 [7,8].

The interest of our results motivated a sizeable computational effort, primarily represented by the activity of the Belfast and Milano groups, working in close collaboration with our team. Simulation results confirmed the layering of the IL at the interface, with a periodicity that closely matches the experimental one [3]. Moreover, simulations have reproduced semi-quantitatively the indentation patterns observed in AFM experiments [4]. Further simulations and experimental work is needed to fill the residual gap still separating the computational and experimental picture.

Acknowledgments

Thanks are due to M. Sampietro, G. Ferrari and collaborators for providing dedicated front-end electronics for AFM measurements; thanks to Cristina Lenardi, Pietro Ballone, Mario del Pópolo and Nicola Manini for fruitful collaboration along the past years.

References

1. S. Bovio, et al. J Phys Chem B. 2009;113:6600
2. S. Bovio, et al. ACS Symposium Series 2009;1030(Chapt 19):273
3. S. Bovio, et al. J Phys: Condens Matter. 2009;21:424118
4. P. Ballone, et al. Phys Chem Chem Phys. 2012;14:2475
5. R. Atkin, et al. J Phys Chem C. 2007;111:5162
6. M. Galluzzi, et al. in preparation
7. Singh, et al. J Phys Chem B. 2008;112:12968
8. H.Z. Weingartner. Phys Chem. 2006;220:1395