

AFM Determines Key EDL Properties in Future Ionic Liquid Electrolytes



ASYLUM RESEARCH

Introduction

"...while countless breakthroughs have been announced over the last decade, time and again these advances have failed to translate into commercial batteries with anything like the promised improvements in cost and energy storage."

The above quote was taken from an article on the future of battery technology, published February 2015.¹ While the article mentions batteries specifically, it sums up the problems of all electrochemical storage devices, including electrochemical capacitors, as power limitations and safety concerns hinder their development.² Adding to this problem is the continued miniaturization of device structures, as this needs the development of methods that allow in situ studies of nanoscale dynamics inside an electrochemical cell.

For improving device performance, new materials for both the electrolyte and the electrodes are of interest. For the electrolyte, ionic liquids (pure salts with melting points below 100°C) have received much attention as candidates for electrochemical storage.^{3, 4} This is because ionic liquids offer many desirable properties,

including large electrochemical windows,⁵ high thermal stability,^{6, 7} high conductivities⁸ and low vapor pressure.⁹

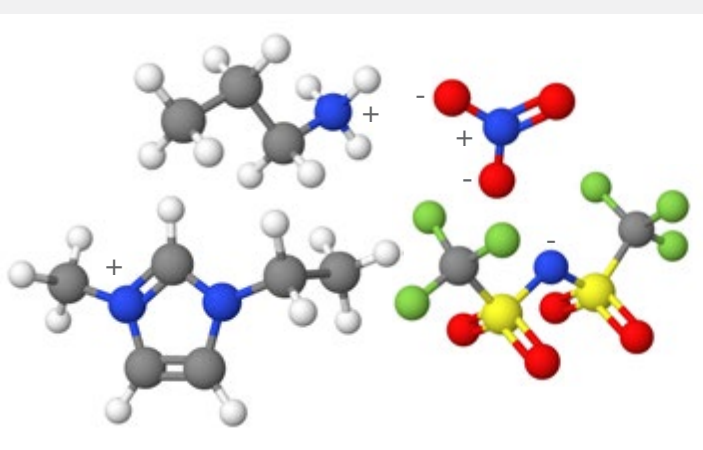
One key area of interest is the interface between ionic liquid electrolytes and the electrode itself. The dynamics occurring at these interfaces determine the performance of devices such as electrochemical capacitors (ECs). Specifically, the electrical double layer (EDL) is of interest, as this consists of strong interactions occurring between the ions close to the electrode surface and the surface itself. These interactions are different from ion interactions in solution, meaning the EDL is a critical factor in determining the performance of any electrochemical storage device. However, while the EDL of conventional electrolytes is well understood, the same cannot be said of ionic liquids.

A unique property of ionic liquids is they form alternating anion and cation layers at solid-liquid interfaces, making them distinctively different from other electrolytes. With increasing distance from the interface, the ion ordering diminishes, resulting in a well-defined EDL structure near the surface. Molecular dynamic (MD) simulations can predict how the ions arrange as a function of electrode material and surface charge, providing a means to help interpret experimental data.

Atomic force microscopy (AFM) can be used to probe the structure of ionic liquids at higher spatial resolutions than other methods, as well as the suitability of these ionic liquids for future energy storage applications. Additionally, AFM offers scientists a more flexible experimental environment than other techniques.

High-Resolution AFM Imaging of the Ionic Liquid EDL

An understanding of the interface between solids and liquids is critical in many scientific fields. This is especially true in charge storage systems, where the interface between the electrolyte and electrode affects device performance. The structure of this interface, known as the electrical double layer, is of particular interest due to the strong interactions taking place between the ions and the charged



Ball and stick molecular models of two commonly used room-temperature ionic liquids. (Top) propylammonium nitrate (abbreviated PAN), and (Bottom) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (abbreviated EMIm TFSI here, also known as [EMIm][Tf2N-]). In all models, carbon atoms are gray, hydrogen atoms are white, nitrogen atoms are blue, sulfur atoms are yellow, oxygen atoms are red, and fluorine atoms are green.

electrode surface. Upon charging and discharging, the ions within the EDL redistribute to compensate for the surface charge. However, unlike the EDL of conventional solvents, the structure of this ionic liquid EDL is not well understood.

Traditionally, scanning tunneling microscopy (STM) has been used to study the lateral structure of ionic liquid layers. However, in liquids, the strong interfacial nanostructure can interfere with the STM signal, making high-resolution imaging difficult. To overcome this limitation, the ionic liquid is often frozen and imaged under ultrahigh vacuum (UHV) conditions. However, this is also problematic because the nanostructure of the interfacial layer in UHV and freezing conditions doesn't represent the true state of the ionic liquid structure under realistic operating conditions.

AFM offers a way to study ionic liquids in situ under realistic conditions. Recently, amplitude modulation AFM (AM-AFM, also commonly called tapping mode AFM) was used to determine the interfacial structure between highly ordered pyrolytic graphite (HOPG) and bulk propylammonium nitrate (PAN), near room temperature.¹⁰ The AFM cantilever was oscillated close to its resonant frequency, with a free amplitude of less than 1 nm. The imaging amplitude set-point ratio was kept greater than 0.7 to minimize the tip-sample force and possible perturbation of the EDL structure. These conditions resulted in the AFM tip probing the interfacial ions adsorbed on the electrode surface with sub-nanometer resolution (Figure 1), without contacting the electrode itself. These conditions could be verified by reducing the set-point ratio, increasing the tip-sample force, until the tip probed beyond the ion layer and made contact with the electrode surface.

This study marked the first time that molecular level structures have been determined within a viscous liquid using AM-AFM. It was also the first investigation of its kind to achieve molecular resolution of the interfacial layer between the electrode (graphite) and the ionic liquid. Significantly, the resolution obtained in this study using AFM was comparable to that achieved for frozen ionic liquid monolayers using STM.¹¹

A second study, also at 25°C, involved high-resolution imaging of the interfacial ion layer between 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIm TFSI) and a HOPG surface.¹² The researchers varied the bias applied to the electrode and added 0.1 wt/wt% Li TFSI or EMIm Cl to the ionic liquid. AFM allowed them to study the effect of these modifications on the ion arrangement at the electrode-electrolyte interface.

Molecular resolution images revealed the presence of sharp rows formed by an anion-cation-cation-anion unit cell on the surface with open-circuit potential, with like ions nearby (Figure 2). Critically, the ion layer nanostructure changed with applied surface

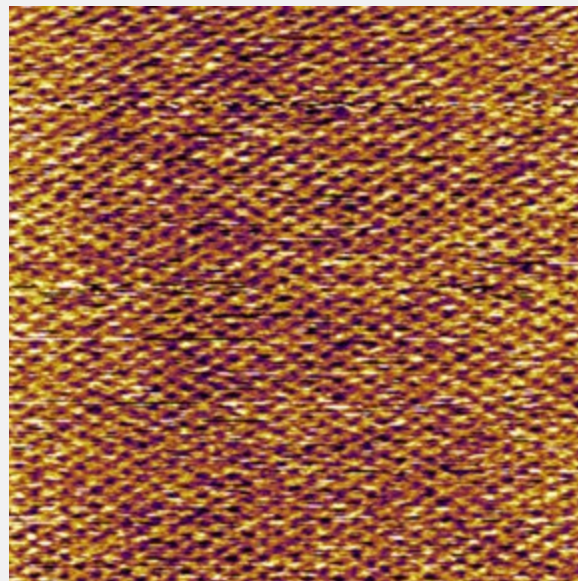


Figure 1: Height image of a PAN-HOPG interface obtained using tapping mode with a scan amplitude of 1 nm. Two-dimensional Fourier analysis confirmed that PAN adsorbs on the HOPG surface with a rhomboidal structure with a lattice spacing of 0.48 ± 0.02 nm, approximately twice that of the underlying HOPG. Adapted with permission from Ref. 10.

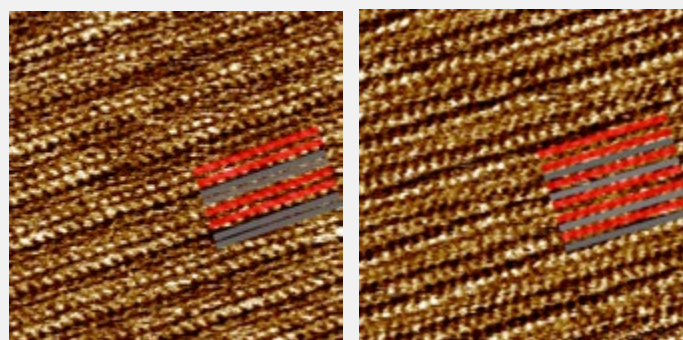


Figure 2: Tapping mode phase images of the IL Stern layer adsorbed to a graphite (HOPG) substrate for both, (Left) the pure IL (EMIm TFSI) and (Right) for an IL solution with added chloride anions (EMIm TFSI + 0.1 wt/wt % EMIm Cl). These images were taken at open circuit potential (OCP) (i.e. with no applied bias), corresponding to 0.26 V vs. Pt for the pure IL and 0.42 V vs. Pt for the solution with added chloride anions. For the pure IL (Top), the phase image reveals alternating pattern of two rows of stiffer regions (lighter areas- example rows highlighted in red) followed by two rows of more compliant regions (darker areas- example rows highlighted in gray). Addition of chloride ions (Bottom) changes this structure, resulting in a pattern of two stiffer rows, one compliant row, one stiff row, then one compliant row. Additional work at applied potentials above and below the OCP (not shown here) ascertained that the stiffer rows must correspond to the IL cations and the more compliant rows correspond to the IL anions. Adapted with permission from Ref. 12.

potential, or when low concentrations of Cl^- or Li^+ ions were present. This study also found experimental evidence to suggest there was an additional layer of cations on top of the ion layer in contact with the graphite electrode surface. This outer layer may screen the effect of the surface potential on the EDL nanostructure.

For the first time, in situ AFM allowed the researchers to distinguish between cations and anions on the electrode surface, as well as determine their exact positions within the ionic liquid layer. As expected, the structure of the ion layer at room temperature was much different from that of frozen monolayers determined by UHV STM.^{11, 13} This work shows that AFM may prove to be a critical technique in defining the EDL of ionic liquids, an important step in their use in future electrochemical systems.

Probing Ion Layering with Force Curves

Electrochemical capacitors (ECs) have advantages over batteries for energy storage, making them an important area of scientific investigation.¹⁴ For example, they have higher power densities (10 kW kg^{-1}) than batteries, and also charge and discharge faster. Unfortunately, their energy density is lower, so much of the work with ECs over recent years has focused on improving their energy density.^{15, 16} One approach is to increase the operating voltage of the EC using ionic liquid electrolytes, thus increasing the stored energy. Using ionic liquids is an advantage when compared to aqueous electrolytes, as applying too high a voltage to an aqueous electrolyte can cause electrolysis and form dangerous hydrogen gas. Ionic liquids can withstand much higher voltages without breaking down. These higher voltages translate into higher energy densities.

The capacitance of ECs is affected by the electrical double layer, which will ultimately be a key factor determining EC performance in future energy storage devices. Further analysis of the EDL will enable the development of models that explain electrochemical behavior and how ionic liquids can be used for electrochemical storage. As an example, scientists might get a better idea of defects in the ion layering. The ion layer is not perfectly uniform, so we need to study this and how these imperfections improve or degrade performance.

The structure of the EDL of an ionic liquid as a function of distance to the electrode surface can be studied using force distance (F-D) curves, which was done on HOPG as a model system for carbon-based EC electrodes.¹⁷ The bias evolution of the ion layering was probed by plotting F-D curves using AFM, shown

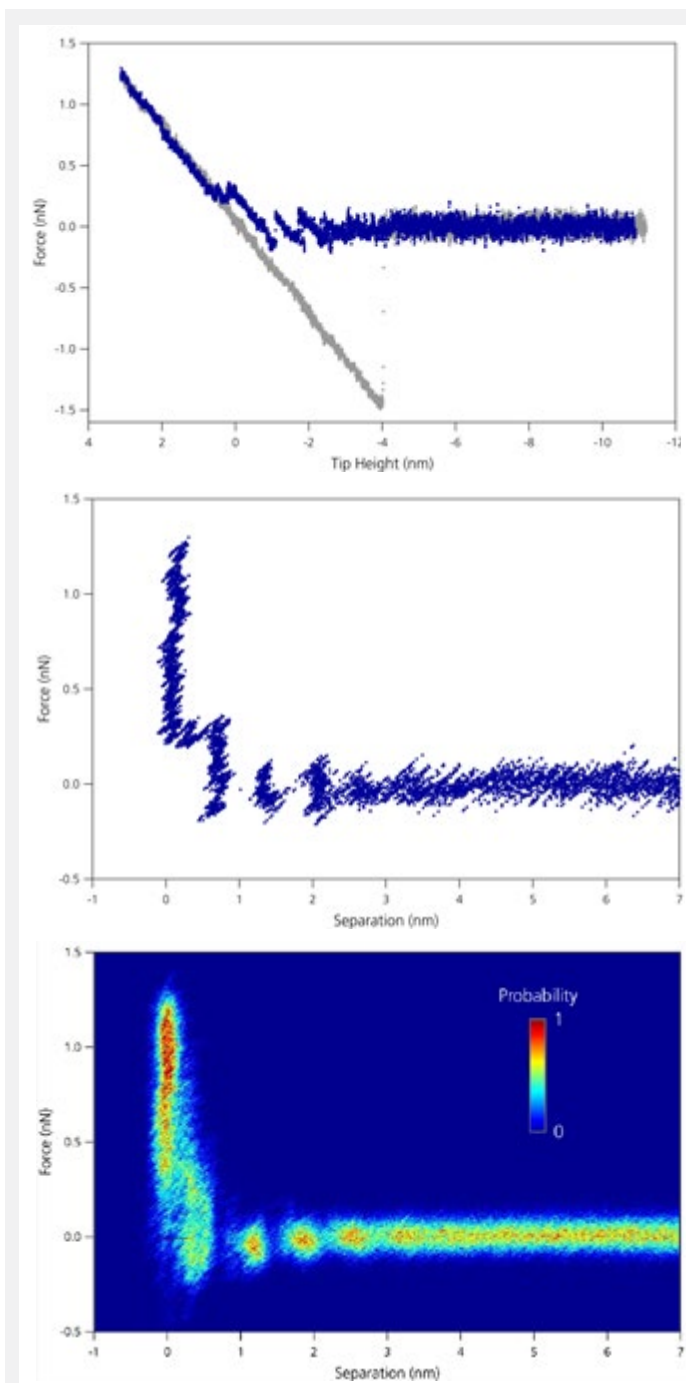


Figure 3: Details of single force–distance curves. (a) Single approach and retract curve showing multiple ion layers. (b) Single force separation plot of curve shown in (a), and 2D histogram of 50 consecutively measured force curves (c). Adapted with permission from Ref. 17.

in Figure 3. The authors gave particular attention to the reproducibility of the F-D curves, something that is often neglected in other AFM studies.

By applying a potential, the authors were able to study the reconstruction of the ion layers using a combination of molecular dynamics (MD) simulations and AFM experiments. The researchers highlight the

excellent agreement between the MD simulations and AFM experiments.

Specifically, the team used AFM to perform force-distance spectroscopies in a droplet of EMIm TFSI ionic liquid on HOPG. In this case, F-D curves were measured at rates between 0.1 and 0.3 Hz, and experiments were performed with uncoated silicon nitride cantilevers with a spring constant of 0.38 N/m. For comparison, curves were aligned along the y-axis to be at zero force far away from the sample.

The F-D curves were used to determine the ion layer positions within the EDL of EMIm TFSI. The first layer was measured to be 0.37 nm from the HOPG surface, with subsequent layers spaced 0.7 nm apart. Two-dimensional histograms were also calculated using 50 F-D curves and showed impressive reproducibility. These statistics were compared with molecular dynamics simulations to obtain a thorough understanding of the ionic liquid EDL on biased and unbiased graphite surfaces. This step is necessary to fully interpret the F-D curves and identify the ion layers.

This combination of MD simulation and experimental AFM force-distance spectroscopy allowed the authors to determine the individual ion layers as anion or cation. Results of the MD simulations suggested the ion layers closest to the electrode surface consisted of anions and cations in two distinct orientations. They also found the arrangement of cations and anions in the layer closest to the surface differed at +1 V and -1 V, when compared with the potential at zero charge. This was attributed to the existence of a Coulombic force between the ion and the electrode. Finally, the ions in subsequent layers (after the first layer) have a characteristic anion-cation pair spacing of about 0.7 nm.

Significantly, the authors suggest this study may allow the future analysis of the ion layering in electrochemically relevant systems for ECs. They suggest that all aspects of the EDL may be investigated using AFM techniques, further improving our understanding of charge storage mechanisms in the field of energy storage.

Using photothermal excitation to improve AFM cantilever response in ionic liquids

As shown by examples here, AFM is a powerful tool for high-resolution imaging of the ionic liquid EDL structure. However, one instrumentation challenge in these experiments is that ionic liquids are highly viscous compared to water, a more common

medium used in AFMs. The high viscosity increases hydrodynamic drag on the cantilever, which means more energy must be directed to the cantilever to drive its oscillation in AC modes (e.g. tapping mode). Most AFMs use a piezoelectric actuator near the cantilever to drive its oscillation (called piezoacoustic excitation). However, the high drive amplitude needed in ionic liquids tends to excite other mechanical resonances in the AFM besides the cantilever. These contaminate the cantilever frequency response with outside resonances, complicating operation and interpretation.

For the best results, it's important the cantilever response is free of these extraneous peaks and that it remains stable with time. A solution is to use photothermal excitation to drive the cantilever directly, instead of the more common piezoacoustic excitation. Photothermal excitation uses a secondary laser focused near the base of the cantilever. The power of this laser is modulated at the resonant frequency of the cantilever, exciting the oscillation by creating a small thermal expansion/contraction. Other mechanical resonances are not affected, so the resulting cantilever response is clean and stable. In fact, photothermal excitation has been shown to improve the signal when imaging in viscous ionic liquids using AM-AFM.^{18, 19}

The use of photothermal excitation in AFM to study the ion layering was demonstrated with the ionic liquid EMIm TFSI on both mica and HOPG surfaces.²⁰ The researchers used AFM to carry out dynamic force-distance and small-amplitude force-distance (SAFD) spectroscopies within the aforementioned systems, with the goal of determining how the substrate (surface) influences the components of resistance to squeeze.

Using F-D spectroscopy, the group was able to measure and compare the layered structure of EMIm TFSI on mica versus HOPG (Figure 4). Significantly, they found stronger and more numerous nanostructure layers on mica, which the group attributed to the stronger surface charge. Significant reproducibility was obtained in the F-D data sets using photothermal excitation, with the authors using 50 data sets for their analysis.

The authors noted two important differences between this study and one of their previous investigations that used piezoacoustic excitation instead of photothermal excitation.²¹ The most fundamental difference is the previous work was unable to resolve

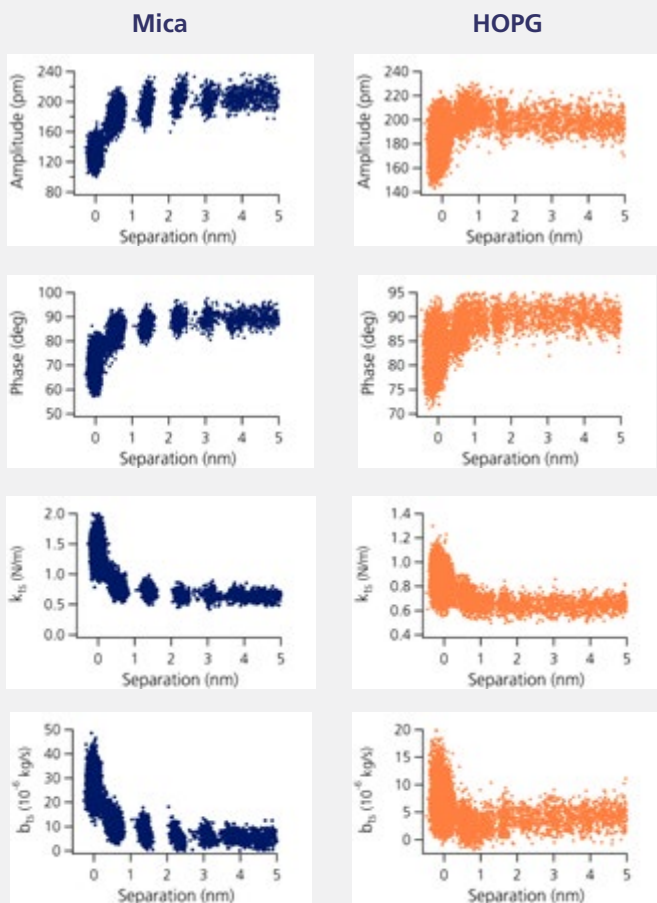


Figure 4: (from top to bottom) Amplitude, phase, k_{15} , and b_{15} for the cantilever response in EMIm TFSI on mica (left) and HOPG (right). The charge-mediated layers on mica are stronger than the templated layers on HOPG. This leads to an increase in resistance to local flow on mica as the preferentially oriented molecules interlock with each other. On HOPG, the opposite effect is observed, whereby the ionic liquid has a slight reduction in flow resistance in the presence of the wall. Adapted with permission from Ref. 20.

the ionic liquid structure at a HOPG interface due to the aforementioned contamination of the cantilever by outside resonances. A more subtle benefit is piezoacoustic excitation must drive the base of the cantilever with a large amplitude to achieve even a small tip amplitude in the viscous ionic liquids. In that case, interpreting the tip motion requires subtracting the cantilever base movement, which itself is difficult to measure accurately. But when photothermal excitation is used, motion of the base is nonexistent and so this makes the analysis simpler and more exact.

Conclusion

Ionic liquids are promising electrolyte materials that may enhance the performance of future electrochemical storage devices. A necessary step toward this becoming a reality is to develop an understanding of the EDL and the dynamics between the electrode and ionic liquid. To that end, AFM offers experimental capabilities not found with other techniques. It also provides the resolution and insights necessary to understand the EDL structure and corresponding interfacial dynamics in ionic liquids.

The Asylum Research Cypher AFM offers unmatched resolution and stability for scientists wishing to perform imaging and spectroscopy in ionic liquids. And when combined with blueDrive photothermal excitation for a more accurate cantilever response, it's the ideal choice for studying the ionic liquid EDL.

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