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***In situ* atomic force microscopic studies of the interfacial multilayer
nanostructure of LiTFSI-[Py_{1,4}]TFSI on Au (111): Influence of Li⁺ ion
concentration on the Au(111)/ IL interface**

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Abstract

In this paper we present results on the nanoscale interactions of LiTFSI-[Py_{1,4}]TFSI with Au (111) using cyclic voltammetry and atomic force microscopy (AFM). Raman spectroscopy was used to understand the Li⁺ ion coordination with the TFSI⁻ ion and showed that with increase in LiTFSI concentration in [Py_{1,4}]TFSI, the Li⁺ ion solvation structure significantly changes. Correspondingly, the force-distance profile in AFM revealed that at lower concentrations of LiTFSI (0.1 M) a multilayered structure is obtained. On increasing the concentration of LiTFSI (0.5 M and 1 M), a significant decrease in the number of interfacial layers was observed. With change in the potential, the interfacial layers were found to vary with an increase in the force required to rupture the layers. The present study clearly shows that Li⁺ ions vary the ionic liquid/Au (111) interface and could provide insight into the interfacial processes in ionic liquid based lithium batteries.

Keywords: Ionic Liquids; *In situ* AFM Force Spectroscopy; Interfacial nanostructures; Raman Spectroscopy; Lithium batteries;

Introduction

Ionic liquids (ILs) are considered as potential non-flammable electrolytes for various Li metal and Li ion batteries^{1, 2}. Compared to traditional organic battery electrolytes, the properties of ionic liquids can be tuned by changing the cations and anions, thereby making it possible to design ILs specific for battery technology³. Their low volatility and high decomposition temperature also makes ILs attractive electrolytes for Li batteries.

The structure of the solid-liquid interface governs the electrochemical reactions where both charge transfer and mass transfer phenomena take place. The solid-liquid interface in ILs is considerably different from aqueous systems due to the difference in solvent-solvent and solvent-solid interactions. ILs are comprised of only cations and anions which are generally large and asymmetric in nature. Theoretical studies have shown that the ion-surface interaction is strong in ionic liquids and is mainly due to electrostatic attraction and van der Waals forces⁴⁻⁶. Furthermore, due to relatively uniform and high density of ions without any molecular solvent, models such as Stern and Gouy-Chapman are not valid in ILs. Recently, a number of studies using *in situ* atomic force microscopy (AFM) and scanning tunneling microscopy (STM) have shown that ILs arrange in an orderly layered structure at the solid-IL interface including on charged electrodes⁶⁻¹². High resolution X-ray reflectivity studies have also been performed on various charged and uncharged substrates and confirmed the formation of layered structure with strong interfacial layering at the IL/substrate interface¹³⁻¹⁵. Perkin¹⁶ recently used surface force apparatus (SFA) to analyze IL structure confined between two atomically smooth surfaces. A similar layered structure as seen from X-ray reflectivity analysis and AFM was observed using SFA¹⁶. Furthermore, it has been shown that the interfacial structure is affected by changing the IL cation or anion which affects electrodeposition processes¹⁷⁻¹⁹.

Only quite a few interfacial studies have probed the change in the interface on addition of lithium salts in ILs. From *in situ* STM, lithium underpotential deposition (UPD) was investigated on Au (111) from 0.5 M lithium bis(trifluoromethylsulfonyl)amide (LiTFSI) in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py_{1,4}]TFSI). The UPD process was found to occur ~1 V positive to the bulk deposition of lithium and the growth process followed a layer-by-layer mechanism²⁰. The addition of 0.05 wt% LiCl in 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate ([HMIm]FAP) also changed the interface²¹. From force-separation measurement using AFM, it was found that at open circuit potential (OCP) the addition of LiCl in the IL changes the interface to an attractive force compared to a repulsive force obtained for pure IL. By changing the electrode potential, the force changes back to repulsive indicating the interfacial structure is stronger²¹. *In situ* STM was also used to evaluate the interfacial structure in 0.1 M LiCl-(1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, ([Py_{1,4}]FAP)²². In the potential regime between -0.8 V and -1.4 V vs Pt quasi-ref electrode, a herringbone reconstruction was observed. At more negative potentials, gold dissolution took place. Gold dissolution in the cathodic regime was related to the formation of Li⁺Au⁻ which then dissolved in [Py_{1,4}]FAP²². As LiTFSI-[Py_{1,4}]TFSI/1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM]TFSI) are potential ionic liquid electrolytes for lithium batteries, infrared and Raman spectroscopy has been applied in the last few years concerning the lithium ion solvation²³⁻²⁹. From IR spectroscopy, it was found that Li⁺ interacts with the sulfonyl oxygen atoms of TFSI. On addition of LiTFSI to [Py_{1,4}]TFSI, a small shift to lower wavenumbers was shown in the ν_{aSO_2} stretching²³. From Raman spectroscopy and density functional theory (DFT) calculations, the formation of [Li(TFSI)₂]⁻ was shown when the concentration of Li was between 0.08 and 0.2 M. However, Borodin et al³⁰ showed from molecular dynamics (MD) simulations that besides the formation of [Li(TFSI)_n]⁽ⁿ⁻¹⁾⁻, formation of lithium aggregates also occur. From Raman spectroscopy a progressive decrease in coordination number below 2 was

observed on increasing the concentration of LiTFSI above 0.2 M. On reaching 0.4 M, the coordination number was found to be about 1 and was suggested to be due to the formation of aggregates such as $[\text{Li}_m(\text{TFSI})_n]^{(n-m)-}$ where $n/m < 2$ ^{25, 31}. However, Raman spectroscopy for higher concentrations (> 0.4 M) has not yet been explored.

In this paper we have evaluated the LiTFSI-[Py_{1,4}]TFSI interface on Au (111) using cyclic voltammetry and AFM by changing the Li ion concentration (0.1 M, 0.5 M and 1 M) in the ionic liquid. The change in the force-separation was also observed by changing the potential of the Au (111) electrode. Raman spectroscopy was used to understand the Li ion solvation in the IL. By correlating the Li ion solvation from Raman spectroscopy and the force-distance profile from AFM, both ordered and disordered interfacial structures were identified with change in the concentration of LiTFSI.

Experimental section

[Py_{1,4}]TFSI ionic liquid was purchased in the highest available quality from Io-Li-Tec (Germany) and was used after drying under vacuum at 100 °C to achieve a water content to below 2 ppm. The water content was measured using Karl-Fisher titration. LiTFSI (99.95%) was purchased from Sigma Aldrich. Raman spectra were recorded with a Raman module FRA 106 (Nd: YAG 1064nm) attached to a Bruker IFS 66v interferometer. For Raman analysis, the electrolyte was sealed in a glass capillary inside the glove box and the spectra were obtained at an average of 250 scans with a resolution of 2 cm⁻¹.

For electrochemical measurements, the working electrode in the experiment was Au (111) purchased from Agilent Technologies. Platinum wires were used as a counter and a quasi-reference electrodes which gave good stability in the ionic liquid throughout the experiments. The electrochemical cell was made of Teflon and clamped over a Teflon-covered Viton O-

ring onto the substrate, yielding a geometric surface area of 0.3 cm^2 . Prior to the experiments, the Teflon cell and the O-ring were cleaned in a mixture of 50 : 50 vol% of concentrated H_2SO_4 and H_2O_2 (35%) followed by refluxing in distilled water.

The electrochemical measurements were performed inside of an argon-filled glove box with water and oxygen contents below 2 ppm (OMNI-LAB from Vacuum Atmospheres) by using a VersaStat II (Princeton Applied Research) potentiostat/galvanostat controlled by powerCV and power-step software. The scan rate during cyclic voltammetry was 5 mV sec^{-1} .

Force curves were collected using a Molecular Imaging Pico Plus AFM in contact mode. A silicon SPM-sensor from Nano World was employed for all experiments presented in this study. The spring constant was 6 N/m. All force curves were acquired at room temperature in an argon-filled glove box.

Results and Discussion

The Raman spectra of $\text{LiTFSI}[\text{Py}_{1,4}]\text{TFSI}$ with varying lithium ion concentrations in the range between 290 and 600 cm^{-1} , and 2700 and 3200 cm^{-1} are compared in figure 1a, b. From figure 1a, certain changes in the peak intensities of SO_2 are noted. An increase in intensities is seen at both $\rho(\text{SO}_2)$ and $\tau(\text{SO}_2)$ positions at 313 , 326 , 339 and 352 cm^{-1} , whereas $\omega(\text{SO}_2)$ at 398 cm^{-1} shows a decrease in intensity which indicates that TFSI^- changes its conformation on addition of lithium. It has been previously shown experimentally and theoretically that lithium ions coordinate with the two sulfonyl groups present in the TFSI^- through the O atom²⁶ and the results in figure 1a confirm this observation. Furthermore, it has been established that the TFSI^- ion involves two conformers cisoid (C_1) and transoid (C_2) which are in equilibrium^{26, 32} and the lithium ion coordinates with either one or both conformers as $\text{Li}(\text{C}_1)_2$, $\text{Li}(\text{C}_2)_2$ and $\text{Li}(\text{C}_1\text{C}_2)$.

Figure 1(a) Comparison of Raman spectra of LiTFSI-[Py_{1,4}]TFSI with varying Li ion concentration in the range between 290 and 600 cm⁻¹. The Raman was normalized at 299 cm⁻¹ indicated by a black circle, (b) between 2700 and 3200 cm⁻¹

In the case of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM]TFSI), it was shown that peaks occurring between 315 and 353 cm⁻¹ increase²² which is similar to what is observed in figure 1a for [Py_{1,4}]TFSI. The peak positions of $\rho(\text{SO}_2)$ and $\tau(\text{SO}_2)$ in figure 1a correspond to C₁ conformer³³, thus indicating that for 0.1 M LiTFSI, lithium preferentially forms Li(C₁)₂ type coordination. The $\omega(\text{SO}_2)$ at 398 cm⁻¹ corresponds to C₂ conformer²⁹ and in figure 1a it is evident that an increase in LiTFSI to 0.5 M and 1 M affects both C₁ and C₂ intensities indicating the formation of Li(C₁)₂, Li(C₂)₂ and also Li(C₁C₂) type coordinations. The Raman spectrum of [Py_{1,4}]⁺ is observed in the region of 2700 and 3200 cm⁻¹ as shown in figure 1b. It is evident that until 0.5 M LiTFSI, no change occurs in the vCH₂ ring modes and alkyl chains. However, on addition of 1M LiTFSI, a decrease in intensity is evident (figure 1b). At large LiTFSI concentrations, formation of lithium aggregates occur which replace [Py_{1,4}]⁺ and might have resulted in the build up of [Py_{1,4}]⁺ aggregates which led to a decrease in the intensity in figure 1b. Recently, from nuclear magnetic resonance (NMR), formation of [Py_{1,4}]⁺ cation aggregates have been shown³⁴.

Figure 2a shows the Raman peak in the region between 700 and 800 cm^{-1} as this region gives the most significant signals. Pure $[\text{Py}_{1,4}]\text{TFSI}$ gives a prominent peak at 742 cm^{-1} (black line, Figure 2a) which relates to the interaction between TFSI^- anions and $[\text{Py}_{1,4}]^+$ cation. As the interaction between the ion pair is weak it is referred to as ‘free anions’. On addition of 0.1M LiTFSI (red line, Figure 2a), a slight decrease in the free anions intensity is observed and a line broadening appears between 746 cm^{-1} and 750 cm^{-1} . The shoulder has been established to be the formation of ion pairs between TFSI and Li^+ ²⁰⁻²².

Figure 2 (a) Comparison of Raman spectra of $[\text{Py}_{1,4}]\text{TFSI}$ and LiTFSI- $[\text{Py}_{1,4}]\text{TFSI}$ with varying concentrations of LiTFSI in the region between 700 and 800 cm^{-1} . (b) The experimental spectrum of $[\text{Py}_{1,4}]\text{TFSI}$ and the Voigt fit components.

On further increase of LiTFSI to 0.5 M, a decrease in the peak intensity at 742 cm^{-1} is observed and the shoulder occurs between 748 and 752 cm^{-1} . Addition of 1M LiTFSI shifts the peak from 742 cm^{-1} to 748 cm^{-1} indicating that most of the TFSI is bound to Li^+ ions. To obtain quantitative information, the Raman spectra were fitted with Voigt functions. Figure 2b shows the Voigt fit for $[\text{Py}_{1,4}]\text{TFSI}$. As TFSI contains two conformers^{25, 35, 36}, the neat ionic liquid was fit to two components which are represented as I and II in figure 2b.

The Raman spectrum in figure 3a-d shows the Voigt fit on addition of LiTFSI. In figure 3a, the best fit could be obtained by deconvoluting the spectrum to three peaks. Peaks I and II are from the free TFSI⁻ anions whereas peak III is the Li⁺-TFSI⁻ ion pair. From the area of the fits one can extract the average coordination number of the anion around the Li⁺ ion according to equation 1²⁵.

$$N = \frac{A_{III}/(A_{total})}{x} \quad (1)$$

Where A_{III} is the coordinated Li⁺ with TFSI⁻ and x is the Li ion concentration. From equation 1, N for 0.1M LiTFSI-[Py_{1,4}]TFSI was found to be 2. This relates to the formation of [Li(TFSI)₂]⁻ and is in agreement with previous literature^{25-27, 36}.

Figure 3 (a) Voigt fit of the Raman spectra of 0.1 M LiTFSI-[Py_{1,4}]TFSI (b) 0.5 M LiTFSI-[Py_{1,4}]TFSI deconvoluted to 3 peaks (c) 0.5 M LiTFSI-[Py_{1,4}]TFSI deconvoluted to 4 peaks (d) 1 M LiTFSI-[Py_{1,4}]TFSI

On addition of 0.5 M LiTFSI, one can fit the Raman spectrum with three or four peaks (Figures 3b and 3c). In both the cases the χ^2 was greater than 0.999. The coordination number calculated from equation 1 for figure 3b was found to be 0.96 whereas for figure 3c (the area of the components III and IV were added) was found to be 1.1. The four component split may be useful as the components can be related to the two TFSI conformers. Recently, Pitawala et al³⁶ showed a four component fit for 0.3 M LiTFSI in [Py_{1,4}]TFSI and related it to the existence of Li(C₁)₂ and Li(C₂)₂ configuration. The same group previously showed using density functional theory (DFT) that Li⁺ ions exists as Li (C₁)₂, Li (C₂)₂ and Li (C₁, C₂) configurations³¹. From DFT it was shown that there is a 3 cm⁻¹ shift between Li (C₁)₂ and Li (C₂)₂. From figure 3c, the shift of about 3 cm⁻¹ (3.18 cm⁻¹) was found between the peak fits of components III and IV and might be the formation of two different Li configurations with the TFSI conformers and is consistent with the Raman spectra analysis between 200 and 600 cm⁻¹ in figure 1a and therefore the four peak fit in figure 3c is better than the three fit peak in figure 3b. However as the coordination number is close to one, the formation of aggregates such as [Li_m(TFSI)_n]^{(n-m)-} where n/m < 2²⁵ is also possible. For 1 M LiTFSI-[Py_{1,4}]TFSI, the Raman spectrum was fit with four components and the coordination number calculated was found to be 0.53. The difference in peak shift between components III and IV was found to be 2.31 cm⁻¹ which relates to the formation of Li (C₁C₂) according to DFT calculations. However, the low coordination number most likely relates with the formation of aggregates.

To assess the lithium coordination structure and its influence on the interaction with Au (111), CV and AFM was performed on the electrolytes. The cyclic voltammetry (CV) of LiTFSI-[Py_{1,4}]TFSI with different Li concentrations are compared in figure 4a. At 0.1 M LiTFSI concentration the CV shows only an increase in current from -2.9 V which corresponds to the lithium bulk deposition and partial decomposition of the [Py_{1,4}]TFSI ionic liquid and is consistent with previous observations^{7, 37}. On reversing the scan at -3.5 V, a nucleation loop

is observed which is characteristic of metal deposition. Interestingly a reduction peak is noted at -2.9 V during the anodic scan (C^*) and could be the reduction of lithium on an ionic liquid passivation layer over the electrodeposit. Such phenomenon has been reported in the case of electrodeposition of Si and Si_xGe_{1-x} ^{38, 39}.

Figure 4 (a) CV of LiTFSI-[Py_{1,4}]TFSI with different Li⁺ ion concentration. (b) Expanded area of the cathodic region between 0 and 2 V vs Pt.

On continuation in the anodic scan above 0 V, small increases in current are seen at 0.1 V and 1 V which can be related with oxidation of the deposited product on the Au (111). On increasing the Li concentration to 0.5 M, two reduction peaks C₁ and C_{Li} are seen in the cathodic regime (red curve, Figure 4a). The peak C₁ might be the reduction of TFSI⁻ anion, whereas the C_{Li} corresponds to the reduction of Li and partial decomposition of [Py_{1,4}]⁺. On reversing the scan at -3.5 V, again a nucleation loop is observed at -3.2 V. Two small oxidation peaks, A₁ and A₂ are seen at -2.2 V and -1.74 V, respectively. These peaks could be the oxidation of bulk Li and Li-Au alloy, respectively. On further increasing the Li ion

concentration to 1 M (blue curve, Figure 4a), a large decrease in current is observed from -2.8 V in the cathodic regime which is the bulk deposition of Li combined with the decomposition of the ionic liquid. When the scan is reversed at -3.5 V, a nucleation loop is observed followed by two oxidation peaks A₁ and A₂. The peak A₁ corresponds to Li stripping whereas A₂ could be the oxidation of Li-Au alloy.

As the interfacial processes of LiTFSI-[Py_{1,4}]TFSI has been previously identified between OCP and -1.5 V ²⁰, in the present paper we have studied the interfacial structures in this region. Figure 4b shows the expanded area of CV's only in this region. At 0.1 M LiTFSI concentration, only a slight increase in current is seen from -1.2 V. When the concentration of Li is increased to 0.5 M, an underpotential deposition (UPD) is noted at -0.8 V and is consistent with previous observation²⁰. At 1M LiTFSI concentration, the UPD peak initiates around -0.8 V (C₁, Figure 4b) and forms another peak at -1.2 V (C₂, Figure 4b) which might be the formation of Li-Au alloy.

AFM force-distance experiments were performed at OCP, -0.5 V and -1.0 V vs Pt. Figure 5a-c shows force-separation curves at different potentials for [Py_{1,4}]TFSI. In figure 5a, at OCP, the pure ionic liquid shows 5 discrete steps. From the electrode surface the first layer is at 0.64 nm followed by 1.47 nm, 2.45 nm, 3.35 nm and 4.24 nm. These steps correspond to the rupturing of successive near surface IL layers as the AFM cantilever approaches the Au (111) surface. It is also observed that the force required to rupture different layers decreases with separation indicating weaker ordering of the layered structure far away from the electrode surface until it decays to the bulk morphology at wide separations. Neutron reflectometry showed that there is a presence of excess cations on the Au substrate.⁴⁰ However, from angle resolved X-ray photoelectron spectroscopy (ARXPS), the adsorption of both cations and anions were shown on Au (111) possibly in a 'checkerboard' type arrangement ⁴¹.

Figure 5: Typical force versus apparent separation profile for a silica cantilever approaching an Au (111) surface in [Py_{1,4}]TFSI (a) at OCP (b) at -0.5 V (c) at -1.0 V. (d) Schematic representation of cis conformer of [Py_{1,4}]TFSI at the Au (111)/IL interface (e) Schematic representation of trans conformer of [Py_{1,4}]TFSI

From high energy X-ray diffraction (HEXRD) it has been shown that in [Py_{1,4}]TFSI, the methyl group in [Py_{1,4}]⁺ prefers the oxygen atoms in TFSI⁻.⁴² Therefore from the force separation plot in figure 5a, it can be suggested that the innermost layer comprises of mixed ion pairs or some ordered structure wherein the ring structure of [Py_{1,4}]⁺ lies flat on the Au (111) surface and the TFSI⁻ is interacting with the cation as shown in figure 5d. The size of TFSI⁻ is 1.0×0.5×0.5 nm³ and [Py_{1,4}]⁺ is 1×0.5×0.6 nm³.⁴³ As the size of TFSI⁻ is 0.5 nm along its height and combined with the thickness of the methyl group in [Py_{1,4}]⁺, a value of 0.64 nm is achieved. It was shown using STM and DFT calculations in ultra-high vacuum that on Ag (111), the [Py_{1,4}]⁺ lies flat on the surface and the anion adsorbs in the cis-configuration with the oxygen bound to Ag (111).⁴⁴ STM studies also showed that adsorption structure of [Py_{1,4}]TFSI is similar on both Au (111) and Ag (111). However, due to reconstruction of Au

(111), it was difficult to obtain a clear structure.⁴⁴ Based on these results and the results from force-separation curve in figure 5a, it is proposed that the most likely arrangement of the IL adlayer is as shown in figure 5d. The second, third, fourth and fifth layers have a separation of 0.9 ± 0.1 nm which indicates the presence of ion pairs. Likely, the cis and trans conformers in TFSI⁻ anion co-exists and for trans conformer, the ion pair formation might lead to slightly elongated structure as seen in figure 5e, thereby increasing the separation distance.

On changing the electrode potential to -0.5 V (Figure 5b), the pure ionic liquid again shows 5 discrete steps. Assuming zero separation which means that when the cantilever is unable to rupture any further adsorbed layer¹⁹, the innermost layer shows a decreased step size of 0.54 nm with an increased rupture force of 10 nN compared to 5.5 nN at OCP. This is followed by steps at 1.44 nm, 2.3 nm, 3.15 nm and 3.97 nm. The potential of zero change (pzc) for [Py_{1,4}]⁺TFSI on Au (111) is about -0.4 V vs Ag/Ag⁺⁴⁰ which corresponds to about -1.1 V vs Pt quasi-ref electrode. Lauw et al⁴⁰ showed that at both positive and negative potentials of pzc, there is excess of cations present on the gold surface. This indicates that at -0.5 V, there could be a change in configuration of the anion species. This would then affect the interaction between the TFSI⁻ and methyl group in [Py_{1,4}]⁺ and therefore decrease the separation distance in the innermost layer as observed in figure 5b. However, other factors such as changes in ion orientation, composition of the surface layer, compression of adlayer groups under the AFM cantilever are also possible which might have altered the innermost adlayer structure. The increase in the force for rupturing the innermost layer could also be related to better ordering and packing of the ion pairs. The second, third, fourth and fifth separation layers show no significant change within the error limit of ± 0.1 nm which indicates that electric field applied mainly affects the innermost layers.

On changing the electrode potential to -1.0 V (figure 5c), the innermost layer width decreases to 0.48 nm with a force of 10 nN. It was recently shown from video-STM that formation of

rectangular adlayers appear at -1.0 V which corresponded to the planar adsorption of $[\text{Py}_{1,4}]^+$.⁴⁵ This indicates that at -1.0 V, there might be again a change in the configuration of TFSI ions which affects the angle of interaction between the methyl group in $[\text{Py}_{1,4}]^+$ and TFSI, thereby reducing the innermost separation distance in figure 5c. The second to fifth layers are separated by a distance of about 0.8 nm and are consistent with the presence of unaffected ion pairs. Similar observations were also made in ionic liquids with the tris(pentafluoroethyl)trifluorophosphate (FAP)^{11, 19}.

The addition of 0.1M LiTFSI significantly changes the Au (111)/ IL interface as seen in figures 6a-c. A comparison of the force separation curve of $[\text{Py}_{1,4}]$ TFSI and 0.1M LiTFSI- $[\text{Py}_{1,4}]$ TFSI at various potentials is shown in figures S1a-c. At OCP (figure 6a), the innermost layer width is between 0.16 and 0.2 nm and a gradient in the force is noted.

Figure 6: Typical force versus apparent separation profile for a silica cantilever approaching an Au (111) surface in 0.1M LiTFSI- $[\text{Py}_{1,4}]$ TFSI (a) at OCP (b) at -0.5 V (c) at -1.0 V (d) Schematic representation of Li^+ ion interacting with TFSI.

From Raman in figures 1 and 3 it has been established that Li coordinates with the cis conformer of TFSI forming $[\text{Li}(\text{TFSI})_2]^-$ and preferentially binds to the O atoms. Molecular dynamics (MD) simulation has shown that the molecular distance between Li and O atoms are between 0.187 and 0.21 nm for a bidentate configuration⁴⁶ which is a close match with what is observed experimentally for the innermost layer in figure 6a. This suggests that the innermost structure comprises of Li^+ ion adsorbed on Au (111) with the oxygen in TFSI anion interacting with the Li^+ ion possibly in a configuration as shown in figure 6d. As the molecular distance lies in a range of distances, it might have resulted in a gradient of force for the innermost layer in figure 6a. Furthermore, the force applied to rupture the layer is about 15 nN which is much higher than that observed for the pure ionic liquid (Figure S1a). Therefore it can be said that on addition of LiTFSI, the $[\text{Py}_{1,4}]^+$ cation is replaced by Li^+ ion in the adlayer and forms a strong bond with TFSI⁻ anion. The separation distance between the first and the second layer is 0.6 nm indicating the presence of ion pairs of $[\text{Py}_{1,4}]\text{TFSI}$. It appears that the second layer also is affected in the presence of Li^+ ion which results in a stronger interaction between $[\text{Py}_{1,4}]^+$ and TFSI⁻. The separation distance of the third, fourth and fifth layers are about 0.75 ± 0.05 nm and is consistent with the presence of ion pairs of $[\text{Py}_{1,4}]\text{TFSI}$ ⁷. On changing the potential to -0.5 V, the innermost layer shows an increase in force to 17 nN with a slight increase in separation distance of 0.21 nm, figure 6b. As a negative potential is applied, it might result in enriching of Li^+ ions at the interface which then results in an increased force and slight increase in separation distance. The second layer is separated by 0.65 nm from the innermost layer indicating the presence of ion pairs of $[\text{Py}_{1,4}]\text{TFSI}$ wherein the molecular structure is affected in the presence of Li^+ ion similar to that one seen at OCP. The third, fourth and fifth layers are separated by a distance of 0.8 nm which relates well with the presence of ion pairs of $[\text{Py}_{1,4}]\text{TFSI}$. Reducing the potential to -1.0 V, the innermost layer shows an increased separation distance of 0.36 nm, figure 6c. This might be due to enriching of Li^+ ions at the interface as well as a change in the configuration

of Li^+ with TFSI $^-$ from a bidentate to a monodentate configuration. In the monodentate configuration, the Li^+ ion interacts with the single oxygen atom in TFSI $^-$ unlike the interaction with two oxygen atoms for a bidentate configuration and distance between Li^+ ion and oxygen is 0.194 nm⁴⁶. Therefore the monodentate configuration would induce an increased interaction between the TFSI $^-$ and the AFM cantilever and results in an increased separation as seen in figure 6c. Furthermore, it is possible that there is some UPD of Li on Au at -1.0 V as a small current is observed in the CV in figure 4b which might have led to an increased inner layer separation. Further experiments with scanning tunnelling microscopy (STM) are needed to confirm the possibility of the UPD process. The second layer shows a separation of 1 nm from the innermost layer. This indicates the presence of both Li^+ and $[\text{Py}_{1,4}]^+$ cations bound to TFSI $^-$ anion. The separation distance between third, fourth and fifth layers are 0.8 nm and is consistent with the presence of ion pairs in $[\text{Py}_{1,4}]\text{TFSI}$. Thus, at 0.1 M LiTFSI concentration, it is evident that Li^+ ions replace $[\text{Py}_{1,4}]^+$ cations at the innermost interfacial layer and interacts with TFSI $^-$ anions.

On increasing the LiTFSI concentration to 0.5 M, the double layer structure appears quite different compared to 0.1M LiTFSI. Figures 7a-c shows the force-separation plots for 0.5 M LiTFSI- $[\text{Py}_{1,4}]\text{TFSI}$ at different potentials.

Figure 7: Force versus apparent separation profile for a silica cantilever approaching an Au (111) surface in 0.5 M LiTFSI- $[\text{Py}_{1,4}]\text{TFSI}$ (a) at OCP (b) at -0.5 V (c) at -1.0 V.

The overlaid force separation curve at various potentials showing the effect of Li^+ ion concentration on the interfacial structure is compared in figures S2a-c. From figure 7a, it is evident that only four interfacial layers are present in the double layer region compared to five layers as seen in figure 6a. The innermost layer shows a separation of 0.25 nm. From Raman spectroscopy, it was shown that at higher concentration, Li coordinates with both cis and trans conformers of TFSI⁻ ions. MD calculations showed that at higher concentrations, a monodentate configuration exists between Li^+ ion and oxygen atom giving a bond length of 0.194 nm⁴⁴. As in trans conformers of TFSI⁻ the O atoms lie on opposite ends of the SNS bond, the molecular stretching will be more and therefore a higher separation of 0.25 nm is observed in figure 7a. Furthermore, Raman spectroscopy also indicated the formation of aggregates such as $[\text{Li}_m(\text{TFSI})_n]^{(n-m)-}$ where $n/m < 2$ which might also have affected the interface. A lower force of 8 nN is observed compared to 15 nN for 0.1M LiTFSI and might be related to the change in orientation of TFSI⁻ ions. The separation of second layer is about 0.65 nm from the innermost layer indicating the formation of ion pairs which is affected due to the presence of Li^+ ion as seen before for 0.1M LiTFSI. The third and fourth layers are separated by 0.8 nm and is consistent with the formation for ion pairs for $[\text{Py}_{1,4}]^+$ and TFSI⁻. On changing the potential to -0.5 V (Figure 7b), the separation distance between the interfacial layers is almost similar to that at OCP. However, on changing the potential to -1.0 V (Figure 7c), an increased separation to 0.32 nm is observed for the innermost layer. Again this could be due to monodentate configuration of Li^+ bound to TFSI or formation of UPD Li layer on gold. *In situ* STM experiments have previously shown that a lithium monolayer is formed on Au (111) at -0.9 V with 0.5 M LiTFSI concentration. Therefore, the increased separation could be the formation of interfacial layers on underpotential deposited Li. The second, third and fourth layers show a separation distance of 0.8 nm which is the formation of ion pairs of $[\text{Py}_{1,4}]^+$ and TFSI⁻, except that at this potential the ion pairs are not affected by Li^+ ions present at the interface.

The force-separation plots for 1M LiTFSI-[Py_{1,4}]TFSI are shown in figures 8a-c. Unlike at lower concentrations, only three interfacial steps are observed at 0.24 nm, 1.07 nm and 1.97 nm at OCP (Figure 8a, Figure S2a). The innermost layer shows a separation of 0.24 nm and therefore a similar structure as observed in the case of 0.5 M LiTFSI can be expected. The second and third interfacial layers are separated by 0.8 nm. This indicates that the formation of ion pairs of [Py_{1,4}]TFSI at OCP are not affected in the presence of Li⁺ ion which is in contrast to that observed at lower LiTFSI concentrations. From Raman spectroscopy, obvious formation of aggregates is observed in figures 1 and 3. Thus, it can be said from figure 8a that the presence of aggregates might not affect the ion pairs of [Py_{1,4}]TFSI in the second and third interfacial layers.

Figure 8: Force versus apparent separation profile for a silica cantilever approaching an Au (111) surface in 1.0 M LiTFSI-[Py_{1,4}]TFSI (a) at OCP (b) at -0.5 V (c) at -1.0 V.

On changing the potential to -0.5 V, an increase in innermost interfacial layer to 0.33 nm is noted (Figure 8b) compared to that at OCP. At this potential, there could be some UPD of Li as an increase in negative current is seen in figure 4b. This suggests that the innermost layers are formed on UPD Li combined with [Li_m(TFSI)_n]^(n-m) aggregates. The second and third layers show a separation of 1 nm which could be due to the presence of both ion pairs of [Py_{1,4}]TFSI and [Li_m(TFSI)_n]^(n-m) aggregates. On changing the potential to -1.0 V (Figure 8c), only two vague interfacial layers are observed at a separation of 0.2 nm and 0.82 nm with a force of 10

nN and 2 nN, respectively. At this potential, it is clear that there is UPD of Li which affects the interfacial structure as the force curves are not prominent and a more disordered interfacial structure might have formed.

Conclusions

The interfacial nanostructure of LiTFSI-[Py_{1,4}]TFSI has been investigated with *in situ* AFM with varying concentrations of LiTFSI. Raman spectroscopic analysis showed that at 0.1 M concentration, lithium preferentially coordinates with the cis conformer of TFSI ions and forms [Li(TFSI)₂]⁻. On increasing the concentration to 0.5 M and 1 M, the formation of aggregates was observed. From the CV of LiTFSI-[Py_{1,4}]TFSI on Au (111), a UPD was identified when the LiTFSI concentration was 0.5 M and 1 M. Pure [Py_{1,4}]TFSI and 0.1 M LiTFSI-[Py_{1,4}]TFSI showed five layered interfacial nanostructure. It was observed that on addition of Li⁺ ion, the interface significantly changes and the [Py_{1,4}]⁺ ions are replaced by Li⁺ ions at the interface, thereby reducing the separation distance of the innermost interfacial layer. On changing the potential, an increase in the separation distance of the innermost layer was observed which could be related with the change in configuration between Li⁺ and TFSI⁻ ions. On increasing the concentration of Li⁺ ions, an increase in separation distance of the innermost interfacial layers was observed with a decrease in number of interfacial layers which might be due to UPD of Li on Au (111) and formation of aggregates, respectively. Thus, from the force-separation curves and Raman spectroscopy it is evident that high concentrations of LiTFSI (> 0.5 M LiTFSI) in the ionic liquid might not be ideal as the electrolyte for lithium batteries.

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