

Article

Interaction of Aluminum and Platinum Surfaces with the Ionic Liquids 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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Abstract: The processes at the interface between ionic liquids (ILs) and metals are a key factor for understanding especially in electrochemical deposition, nanoscale tribology applications and batteries. In the present work, the interfaces of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Py_{1,4}]TFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm]TFSI) and platinum and aluminum were investigated by depositing thin IL films and studying them with X-ray photoelectron spectroscopy (XPS) in ultrahigh vacuum. It is found that there is no evidence of a decomposition reaction of either IL on platinum; however, the imidazolium cation of [EMIm]TFSI shows a strong interaction with the surface in the monolayer regime. In contrast, [Py_{1,4}]TFSI and [EMIm]TFSI show massive decomposition on the aluminum surface without applying any electrochemical potential. The spectra for the [TFSI][−] anion components show cleavage of C-F or N-S bonds in both cases. Both cleavage of a single fluorine atom and complete cleavage were observed, leading to further decomposition reactions of the anion. Consequently, new components such as AlOOH, Al(OH)₃, Al₂S₃, Al₂(SO₄)₃ and AlF₃ appear at the interface. In addition, there is also evidence of decomposition of the cation by the splitting off hydrogen atoms or parts of the alkyl chain in both ILs.

Keywords: X-ray photoelectron spectroscopy (XPS); thin films; decomposition; ionic liquids; aluminum (Al); platinum (Pt); [Py_{1,4}]TFSI; [EMIm]TFSI



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1. Introduction

Ionic liquids are of fundamental interest for a wide field of scientific investigations. Due to their wide electrochemical window [1], they are promising for use as electrolytes in electrochemical applications [2]. Here, the understanding of the processes, such as possible decomposition reactions at the interface between an ionic liquid (IL) and a metal, is crucial for electrochemical deposition [3], nanoscale tribology applications [4–6] and batteries. Furthermore, IL can be used for cellulose dissolution [7], drug delivery [8] or as reaction solvent [9]. In particular, the investigation of thin and ultra-thin IL films deposited in UHV, which is possible due to their low vapor pressure [10] and high thermal stability [11], is a frequently used method to study interface processes [12]. In these studies, thin IL films are deposited on respective substrates by physical vapor deposition (PVD) under UHV conditions, while substrate and film are continuously investigated by photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM) [13] or atomic force microscopy (AFM). This process frequently offers useful insights into the nature of the interface and properties such as the wetting behavior, molecular arrangement, electronic structure or IL/substrate interactions [12].

On reference surfaces such as gold, [MMIm]TFSI [14], [EMIm]TFSI [15] or [OMIm]TFSI [14,16] show nearly no decomposition reactions, but on other more reactive substrates a strong interaction can be observed. For example, the interaction of Ni(111) with [MMIm]TFSI and [OMIm]TFSI [12], Cu(100) with [OMIm]TFSI [16] and magnesium with [Py_{1,4}]TFSI [17], tantalum with [Py_{1,4}]TFSI and [EMIm]TFSI [18] show that some of them exhibit clear IL decomposition reactions without any potential applied. Recently, Adhikari et al. [19] demonstrated for 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imides ([MMIm]TFSI) on Cu(111) using AFM, STM and XPS that partial decomposition of IL occurs at around 300 K, and these products form disordered islands and the intact IL continue to form ordered islands. Tribological studies also show decomposition of the numerous ILs, although the shear stress must be taken into account [4–6].

Lithium has also been investigated on various surfaces, such as HOPG with [Py_{1,4}]TFSI [20] or copper with [Py_{1,4}]FSI, [Py_{1,4}]TFSI and [OMIm]TFSI [21]. Here, intense decomposition reactions of the ILs can also be observed, while the ILs act as fluorine, oxygen, sulfur and nitrogen sources.

All these studies show mainly decomposition reactions of the anion, often in TFSI, as the splitting off of fluorine, oxygen or small groups. Possible decomposition reactions of the cation have also been described.

Analogous studies for platinum and aluminum are almost completely absent from the literature, although platinum has an exposed position, especially from an electrochemical point of view. The counter and reference electrodes of numerous electrochemical investigations with ILs using a three-electrode arrangement are often made of platinum, which has proven its worth due to its uncomplicated handling. However, the quality of the reference electrode is significantly affected by the stability and thus by the IL/platinum interface, which will be investigated in the following work.

The production of a clean aluminum-oxide-free surface is quite difficult, which is why this was carried out with in situ metal evaporation in this work. The influence of the aluminum interface is reflected in the studies of Bebensee et al. [3], who obtained different aluminum deposits from [Py_{1,4}]TFSI and [EMIm]TFSI, on one side nano- and on the other side microcrystalline structured. In previous studies, they concluded that the cation in case of [Py_{1,4}]TFSI on aluminum is strongly adsorbed on the surface, which prevents the aluminum nuclei from growing further [22]. The role of the anion in this context has not yet been clarified. Bebensee et al. [3] discuss the influence of irreversible cathodic breakdown due to the cleavage of one N-S bond, which was reported by Howlett et al. [23], but find no evidence for this anion decomposition.

2. Materials and Methods

The ILs, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Py_{1,4}]TFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm]TFSI), were purchased in the highest available quality from Io-Li-Tec (Heilbron, Germany) and were used after drying under vacuum at 373 K for about one week to achieve a water content of below 2 ppm. These ILs were chosen because, as the above examples show, they are among the most commonly used and studied liquids.

The platinum substrates (99.95%) were obtained from EMT Edelmetalltechnik GmbH (Bad Saarow, Germany) and cleaned with acetone (quality grade “for liquid chromatography”, ≤0.05% H₂O) and afterwards annealed in a hydrogen flame.

The aluminum substrates were prepared under UHV conditions, to obtain oxygen-free surfaces, with an inhouse-built metal evaporator, in which different metal wires are wound onto a tungsten filament for evaporation. The tungsten wire (99.98%) acquired from Chempur® Feinchemikalien und Forschungsbedarf GmbH (Karlsruhe, Germany) had a diameter of 0.5 mm. Copper sheets (99.9%, thickness 0.4 mm) of RS components GmbH (Frankfurt am Main, Germany) with a diameter of 10.0 mm were used as underlying substrates for the aluminum deposition. Cleaning was carried out first mechanically with sandpaper and then with acetone. The aluminum wire (≥99.999%, diameter 2.0 mm) was

purchased from Chempur[®] Feinchemikalien und Forschungsbedarf GmbH (Karlsruhe, Germany). Cleaning was first performed mechanically with sandpaper and then by washing with acetone. For the preparation of the aluminum surfaces, a 6.0 mm piece of aluminum wire was spirally wound onto the previously annealed tungsten filament. After the transfer to UHV, the wire was immediately vaporized by applying a current. As nothing of the underlying copper can be detected using XPS, the thickness of aluminum must be more than 10 nm.

The initial basis pressure of the preparation chamber, in which the substrates were cleaned and the ILs and the aluminum were evaporated, was 4×10^{-10} mbar. The basis pressure of the analysis chamber, in which the XPS measurements were performed, was 3×10^{-10} mbar.

Thin films of [Py_{1,4}]TFSI and [EMIm]TFSI were generated by using an TCE-BSC (Kentax GmbH, Seelze, Germany) molecular evaporator. The crucibles were cleaned with isopropyl alcohol (“for liquid chromatography”) and acetone (“for liquid chromatography”) for 15 min in an ultrasonic bath. Both ILs were degassed for a few days under UHV conditions and annealed for a few hours at up to 437 K. The evaporating temperatures were chosen after calibration to 465 K ([Py_{1,4}]TFSI) and 435 K ([EMIm]TFSI). The evaporation temperatures were determined and calibrated on the basis of the results of Deyko et al. [24] and Armstrong et al. [25]; the authors studied the desorption behavior of various ILs in ultra-high vacuum temperature programmed desorption. The temperature near the maximum rate of desorption was selected. During the evaporation of the ILs, the metal surfaces remained at room temperature. Evaporation temperatures were kept constant for about 30 min prior to use. As already sufficiently discussed, manufacturing-related impurities such as Li⁺, Na⁺ or Al₂O₃ usually remain in the crucible at a moderate evaporation temperature; thus, a contamination-free vapor can be assumed [26]. Mass spectroscopy [27] and IR measurements [28] also confirm that physical vapor deposition of ILs under UHV conditions does not lead to any decomposition during evaporation.

An estimation of the equivalent layer thickness of both ILs from the intensity attenuation of Pt 4f and Al 2p was performed according to Cumpson and Seah [29]. Therefore, the effective attenuation length was determined.

X-ray photoelectron spectroscopy (XPS) measurements were performed at room temperature with a SPECS Phoibos 150 hemispherical analyzer (SPECS Surface Nano Analysis GmbH, Berlin, Germany) using a SPECS XR50 M monochromatic Al K α source (1486.6 eV). The XP survey and the detail spectra were recorded with a constant analyzer pass energy of 20 eV. For cleaned platinum asymmetric peak shape, LA(1.2, 85, 70) was used.

The fit of the [EMIm]⁺ cation part in the C 1s spectra was carried out according to Reinmöller et al. [30], who used four peaks: C1 (N=C₁-N), C2 (C₂=C₂), C3 (C₃-N) and C4 (C₄-C₄). The carbon atom in C1 has one bond to each of the two nitrogen atoms in the imidazolium ring, in C2 a double bond to another carbon atom, in C3 a bond to a nitrogen atom and C4 is used to indicate the carbon atoms of the alkyl chain. In the case of [Py_{1,4}]TFSI, the fit of the cation was performed by dividing into C_{hetero} and C_{alkyl}, depending on whether the carbon atom is bonded to another nitrogen atom or a carbon atom [21].

The spectra shown here belong to the pure metal surface and to a surface after 100 s and 800 s IL evaporation time. The corresponding IL layer thicknesses can also be found in the figures.

3. Results

3.1. [Py_{1,4}]TFSI on Platinum

The graphical plot of the equivalent layer thickness as a function of evaporation time (Figure S1, see Supplementary Materials), shows a weaker increase in the thickness with evaporation time at 200 s (1.80 nm), which may have been caused by a change in the growth mechanism. Cremer et al. [14] found an layer-by-layer growth for [EMIm]TFSI on Au(111) up to 10 layers. In the liquid case, force–distance curves on Au(111) at OCP

show four layers at 0.64 nm, 1.47 nm, 2.3 nm and 3.2 nm [31]. Syres et al. [32] obtained a temperature-dependent growth of [OMIm]TFSI on Cu(111). They observe at 300 K initially coalesced IL forming droplets, which later form closed layers.

The Pt 4f detail spectra (Figure 1) show no change in the metallic surface (cf. [33]) at 70.7 eV during the stepwise IL coverage. Similarly, the F 1s and S 2p detail spectra only show the increasing intensities of the anion components at 688.3–688.9 eV (more detailed binding energies at Table S1) and 168.3–168.9 eV, depending on the IL coverage. The C 1s detail spectra show, in addition to the component of the anion (CF_3) at around 292 eV and both components of the cation at 284.9–285.4 eV (C_{alkyl}) and 286.0–286.7 eV (C_{hetero}), aliphatic carbons at 284 eV. As IL coverage increases, their proportion initially increases until they are covered by the IL. In the absence of further decomposition products, an accumulation of vacuum-typical contaminants can occur on the surface that is not completely covered at first. The adsorption of CO from the background pressure is also conceivable [12]. In the O 1s detail spectra, only the component of the anion at around 532 eV is visible, although any oxidized carbon species would be superimposed by the peak of the anion. The N 1s detail spectra also only show the component of the anion at 399–399.2 eV and the cation at 402–402.5 eV and do not give any indication of IL-decomposition. At smaller IL coverage, there are stoichiometrically significantly more nitrogen atoms of the anion, and later it corresponds again to the expected stoichiometric ratio of 1:1. The lower binding energy of sulfur and oxygen from the $[\text{TFSI}]^-$ anion at small coverage can be explained by binding of the SO_2 groups to the platinum surface [34]. Schuschke et al. [35] were able to detect a strongly bound monolayer of $[\text{Py}_{1,4}]\text{TFSI}$ on Pt(111) using infrared reflection absorption spectroscopy (IRAS). They showed that the $[\text{TFSI}]^-$ anion in the cis conformation binds to platinum via both SO_2 groups. Overall, the spectra show no evidence of anion or cation decomposition of the IL $[\text{Py}_{1,4}]\text{TFSI}$ on the platinum surface during stepwise IL vapor deposition.

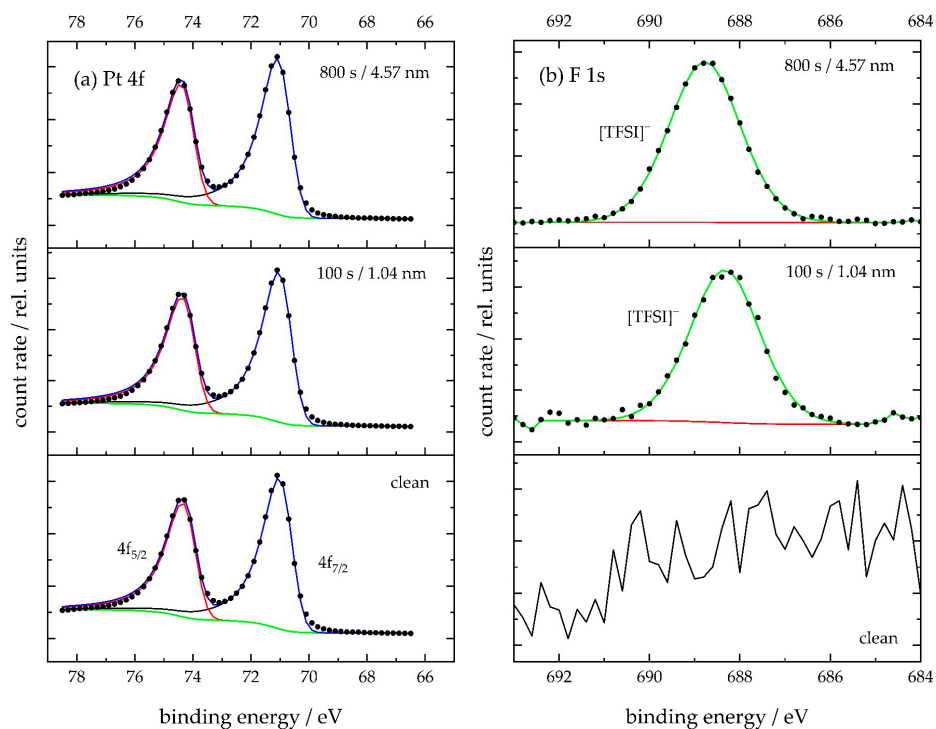


Figure 1. Cont.

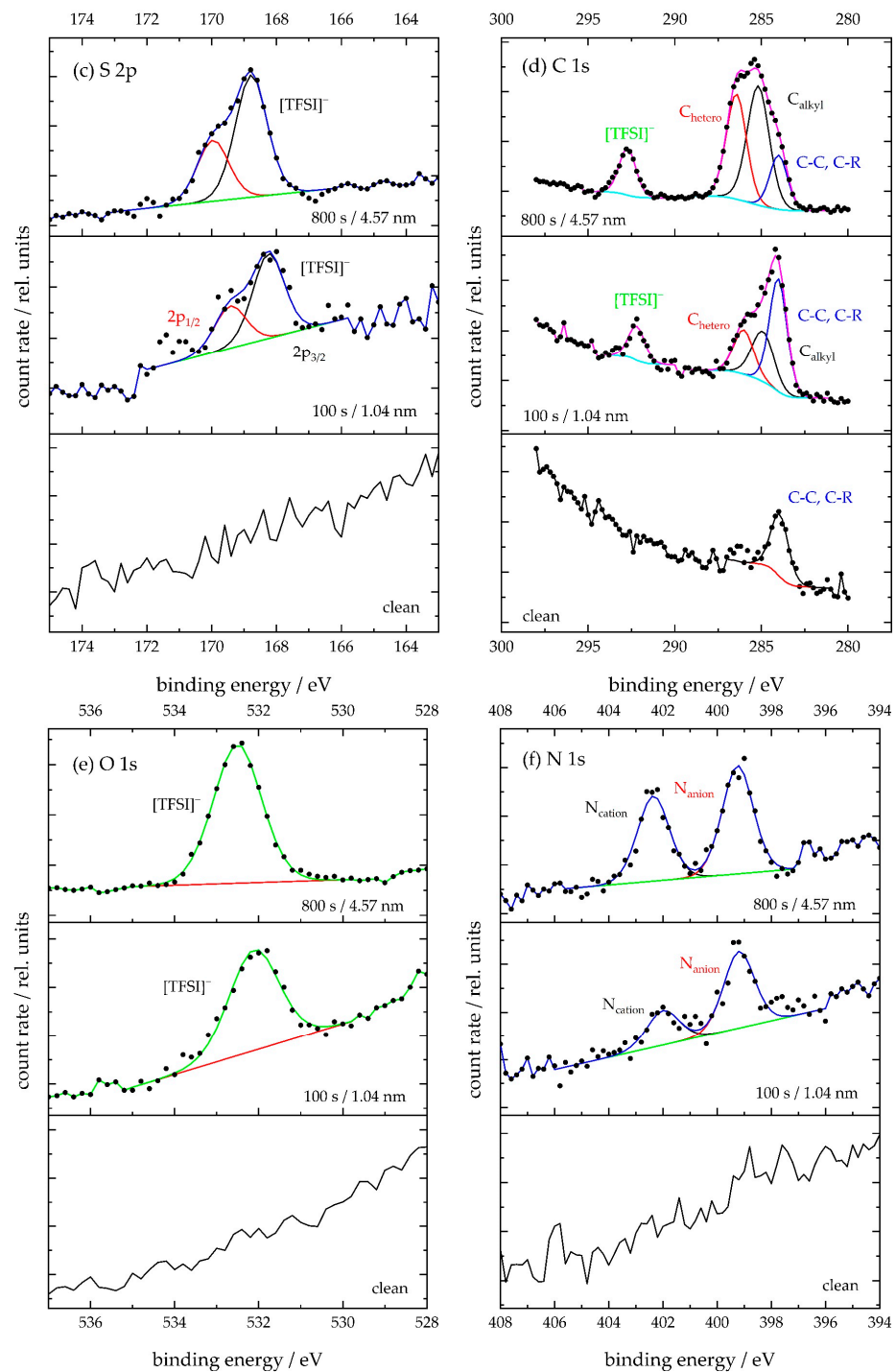


Figure 1. Detail spectra: (a) Pt 4f, (b) F 1s, (c) S 2p, (d) C 1s, (e) O 1s, (f) N 1s of clean platinum surface (**bottom**), with an equivalent film thickness of [Py_{1,4}]TFSI of 1.04 nm (**middle**) and 4.57 nm (**top**).

3.2. [Py_{1,4}]TFSI on Aluminum

The graphical plot of the equivalent layer thickness as a function of evaporation time (Figure S2) shows a weaker increase at 200 s (2.25 nm), which could be caused by a change in the growth mechanism. This decrease occurs later than on platinum (Figure S1).

Figure 2 (bottom) shows the detail spectra of the clean aluminum surface. No further sample preparation is required due to the in situ preparation of the substrate. The detail spectrum Al 2p shows only small amounts of AlO_x (cf. [36]) at 73.8 eV (6.96 at.-%) and Al₂O₃ at 75.1 eV (1.22 at.-%) [37,38]. Metallic aluminum Al 2p_{3/2} is located at 72.8 eV [38–40]. The

C 1s spectra show a small number of aliphatic carbons, presumably due to the transfer or the background pressure. The quantity decreases rapidly with the following IL deposition. The O 1s spectra of the clean aluminum surface exhibit only small traces of oxygen from Al_2O_3 at 532.4 eV [41,42] as well as AlO_x at 531.9 eV, which corresponds to the components in the Al 2p spectra. The F 1s, S 2p and N 1s spectra show no impurities or further components.

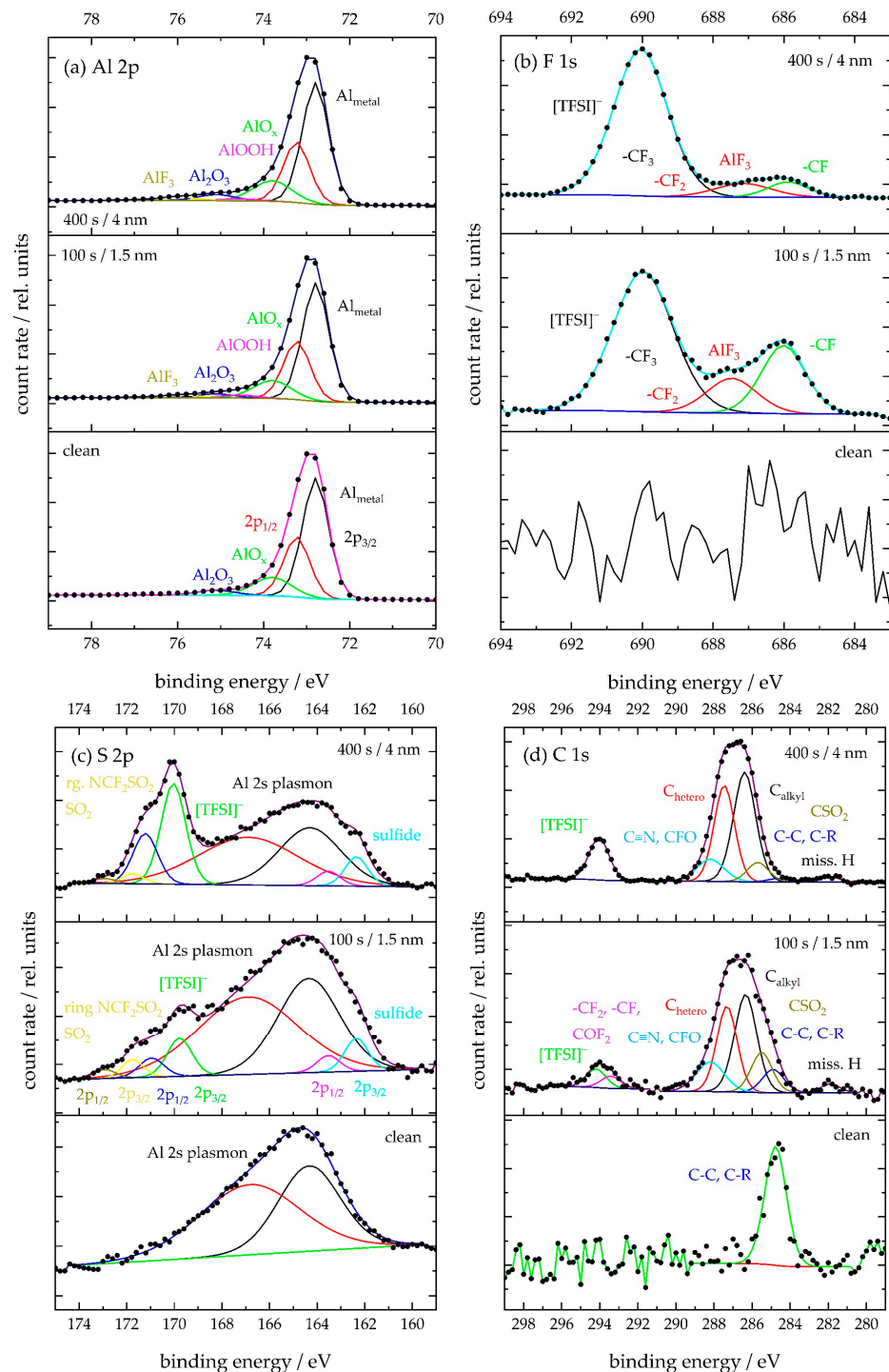


Figure 2. Cont.

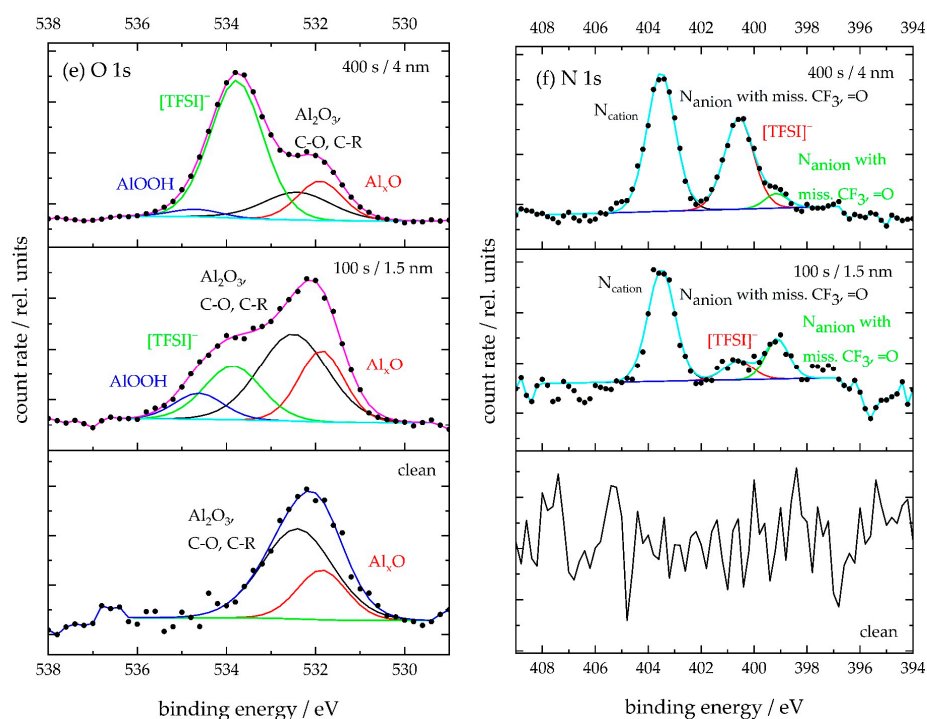


Figure 2. Detail spectra (a) Al 2p, (b) F 1s, (c) S 2p, (d) C 1s, (e) O 1s, (f) N 1s of clean aluminum surface (**bottom**), with an equivalent film thickness of [Py_{1,4}]TFSI of 1.5 nm (**middle**) and 4.0 nm (**top**).

Until the stepwise covering of aluminum surface (Figure 2 middle and top) with [Py_{1,4}]TFSI, three further peaks at 74.6 eV, 75.9–76 eV and 76.6–77 eV can be seen at Al 2p spectra. The first peak at 74.6 eV can probably be assigned to AlOOH [43], Al(OH)₃ (cf. [41]) or Al₂S₃ [44], while the second peak at 75.9–76 eV may be assigned to Al₂(SO₄)₃. The third peak at 76.6–77 eV, depending on the IL coverage, corresponds to AlF₃ [45]. All of them indicate the decomposition of the anion, which must therefore act as a source of fluorine, oxygen and sulfur. The percentage of AlO_x and Al₂O₃ remains almost unchanged; therefore, no further formation of the two components is suspected. The peaks at 532.4 eV and 531.9 eV at O 1s spectra might include the components Al(OH)₃ [45] or Al₂(SO₄)₃ [46] and AlOOH [43]. Buchner et al. [17] also suggest, in reference to their investigations of [Py_{1,4}]TFSI on magnesium, MgO, Mg(OH)₂ and suboxide species at 530.8 eV. They also refer to adsorbed oxygen as a possibility at this peak position. Furthermore, they observed the formation of MgF₂ from the decomposition of the anion. Frerichs et al. [47] reveal the formation of hydroxy groups on aluminum surface from the dissociation of H₂O, which was inserted via a controlled leak valve. The formation of AlOOH and Al(OH)₃ could be caused by residual H₂O, which is desorbed when the IL-evaporator is heated.

Upon the first evaporation of [Py_{1,4}]TFSI, three peaks are formed in the F 1s detail spectrum. The first at 699 eV is associated with the –CF₃ group of the anion [TFSI][–]. The two other peaks at 687.5 eV and 686 eV presumably correlate with –CF₂ and –CF groups from the detachment of fluorine (cf. [48]). The second peak at 687.5 eV is also assigned to AlF₃ as Buchner et al. also reveal for MgO [17]. Initially, a larger proportion of the –CF group is present, while both peaks converge with the increase in IL coverage. Both proportions decrease strongly with the increase in IL coverage, which is why it can be assumed that both species are formed only at the interface and do not enter the bulk phase. The observations from the Al 2p and the F 1s spectra indicate the cleavage of the C–F bond of the anion.

The C 1s detail spectra also show hints of decomposition reactions, primarily of the anion. In addition to the peak of the –CF₃ at 294–294.2 eV, which can be assigned to the anion, another peak at 293.3–293.5 eV is evident. This probably correlates with –CF₂, –CF or –COF₂ groups from the detachment of fluorine, which was already observed in the F

1s spectra. The peaks C_{hetero} and C_{alkyl} of the cation are apparent at 286.3–286.5 eV and 287.3–287.8 eV, depending on the IL coverage. In addition, three further peaks can be seen in the spectra. The peak at 288–288.2 eV probably correlates with the components $C\equiv N$ and CFO [36], which both indicate the detachment of fluorine. The removal of all three fluorine atoms can lead to the formation of a triple bond between the remaining carbon atom and the nitrogen atom of the anion. This releases SO_2 , which can also be seen in S 2p spectra. The remaining $-CF_3$ group of the anion is then shifted to larger binding energies. The binding energy of the $-CF_3$ group consistently decreases with the increase in IL thickness. Similarly, the nitrogen atom in the anion is shifted to larger binding energies and overlaps the peak of the cation. The N 1s detail spectra show here, correlating with this, an initial larger proportion of cations. For the formation of $-CFO$ groups, two fluorine atoms are first detached from the anion. Subsequently, an oxygen atom bonds to the carbon, leaving a $-SO$ group. The S 2p spectra show no hints for $-SO$ groups. Further reactions may be possible. The second peak is located at 285.5–285.7 eV and may correlate with CSO_2 , which is also associated with the complete detachment of all fluorine atoms of the anion and the formation of CO. The peak at 284.6–284.9 eV, which was assigned to aliphatic carbons, could also correlate with the adsorption of CO [12]. SO is also formed as a coproduct. The third peak is located at 281.9–282.1 eV and is probably attributable to the detachment of a hydrogen atom of the cation, showing the decomposition of the cation. The C 1s spectra indicate the cleavage of single C–F bonds as well as all C–F bonds of a single anions. As a result, the S=O and C–S bonds may break, leading to the formation of $C\equiv N$ or O–F and O–C in CFO [48].

The S 2p detail spectra are overlaid by an Al 2s plasmon 3 peak [49]. Starting from the clean surface, the Al 2s plasmon peak was fitted using two peaks with fixed ratio. Their intensity subsequently decreases with the increase in IL coverage, such as the observed intensity decreasing at Al 2p spectra. The peak of the anion is located at 169.8–170 eV. At 171.8 eV, there is another peak, which, as described previously, can possibly be assigned to the formation of $C\equiv N$ from the complete detachment of fluorine from a single carbon. SO_2 is released into the gas phase, and both oxygen atoms bind to the remaining sulfur atom, forming the observed peak. Also conceivable is the formation of a ring NCF_2SO_2 after the detachment of a fluorine atom and an N–C bond is formed [48]. The corresponding $-CF_2$ is also visible at F 1s spectra. Buchner et al. [17] also reveal $-NSO_2$, $-NSO_2F$, $-NSO_2CF_3$ or $-NSO_2F$ fragments. The peak at 162.4 eV correlates with sulfidic species corresponding to the already discussed Al_2S_3 from the Al 2s spectra. Buchner et al. [17] and K. Forster-Tonigold et al. [20] also reveal sulfidic species for $[Py_{1,4}]TFSI$ on magnesium and graphene/lithium surfaces such as MgS , MgS_2 , Li_2S and Li_2S_x . Furthermore, they also describe adsorbed sulfur $S_{2,ad}$ on magnesium [20]. K. Forster-Tonigold et al. [20] also reveal species such as Li_2SO_4 , Li_2SO_3 , Li_2SO_2 and $LiSO$. The formation of SO was previously discussed as well as the possible formation of $Al_2(SO_4)_3$.

The O 1s spectra show the peak of the anion at 533.7–533.9 eV. Another peak is located at 534.7 eV but is only visible at small IL coverage. Therefore, this peak is assigned to decomposition components of the anion.

The N 1s detail spectra show three peaks. The peak of the "intact" cation is obtained at 403.5–403.7 eV. The peak of the "intact" anion is located at 400.5–400.6 eV. As described before, the peak of the anion is probably superimposed on the peak position of the cation after the formation of a $C\equiv N$ bond [48]. At this position, there are also anions from which individual fluorine atoms are detached. As revealed before, the N 1s spectra show here a larger proportion of cations, confirming a superimposed decomposed anion component. The third peak at 399.1 eV may correlate with the anion after detachment of oxygen atoms, which could act as oxygen source for the aluminum. The detachment of hydrogen atoms from the cation is also possible, and corresponding indications can also be found in the C 1s spectra (cf. missing H). K. Forster-Tonigold et al. [20] observe a new peak at about 399 eV after lithium deposition on $[BMP]TFSI$ and assign this to the decomposition of the anion $[TFSI]^-$ without a more precise classification.

Howlett et al. [23] described an irreversible cathodic breakdown due to the cleavage of one N-S bond, which leads to the formation of $\text{NSO}_2\text{CF}_3^-$ and SO_2CF_3^- . Both products can undergo further reactions and form $\text{NSO}_2^- + \text{CF}_3$ and $\text{SO}_2^- + \text{CF}_3^-$ [23]. SO_2 is recognizable as a possible further decomposition product in the S 2p spectra. Forster-Tonigold et al. [20] reveal the formation of LiSO_2CF_3 (S 2p: 166.9 eV, O 1s: 532.6 eV, C 1s: 292.2 eV, F 1s: 688.9 eV) and LiSO_3CF_3 (S 2p: 170.5 eV, O 1s: 534.1 eV, C 1s: 293.9 eV, F 1s: 689.6 eV), which could be formed after the cracking of the N-S bond. The peaks at the corresponding positions can be seen in the spectra, with the exception of the peak at 166.9 eV, which is located at a lower binding energy than the anion. They also obtained $\text{Li}_2\text{N}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{CF}_2)$ at 399.7 eV in the N 1s spectrum, which is also present here.

3.3. [EMIm]TFSI on Platinum

The graphical plot of the equivalent layer thickness versus evaporation time (Figure S3) shows a weaker increase at about 400 s (2.30 nm), later than observed for $[\text{Py}_{1,4}]\text{TFSI}$ (Figure S1).

As in the first section for $[\text{Py}_{1,4}]\text{TFSI}$ (Figure 1 bottom) seen, the clean surface shows only aliphatic carbons and nothing at F 1s, O 1s, N 1s or S 2p spectra. The platinum detail spectra do not indicate any reaction or change with the increase in IL coverage.

The peak of the anion is found in the F 1s detail spectra at 688.3–688.9 eV, depending on the IL film thickness. As in the case of $[\text{Py}_{1,4}]\text{TFSI}$ (Figure 1), there is no evidence for any decomposition reaction.

The carbon peak related to the anion is at 292.2–292.7 eV, and those of the carbon atoms related to the cation are at 286.5–287.6 eV (C1), 285.8–286.9 eV (C2), 285.1–286.4 eV (C3) and 284.4–285.3 eV (C4).

The S 2p spectra show only the peak of the anion at 168.3–168.9 eV, and the anion component at O 1s spectra is located at 532–532.7 eV.

In contrast to $[\text{Py}_{1,4}]\text{TFSI}$ on platinum (Figure 1), three peaks are evident in the N 1s spectra. The peak of the cation is located at 401.9–402.1 eV and the peak of the anion at 399–399.5 eV. The third peak is obtained at 400.3–400.5 eV. Because of the absence of complementary decomposition components, this component is probably caused by charge or adsorption effects of the IL—presumably of the cation. After the first three IL vaporization steps (100 s, 200 s, 400 s), there is no significant intensity at the usual binding energy of the cation. The stoichiometry of cation to anion to the third peak is initially 0:1:1 after the first IL evaporation, 0.25–0.50:1.00–1.50:2 after a few small steps and 2:1:0 in the bulk. Cremer et al. [14] and Beattie et al. [50] describe for $[\text{Py}_{1,4}]\text{TFSI}$ on gold and [HMIM]TFSI on gold two further peaks (at 398.2 eV and 400.5 eV [50]). They assume as cause the interacting anion and interacting cation without any reaction. This description is derived from the studies of Cremer et al. [14], in which they distinguish whether the component is in direct contact with the metal or is part of the physisorbed multilayer [14,50]. In this case, the third peak could be assigned to a cation interacting with the surface (Figure 3 middle and top: $\text{N}_{\text{cation, surf.}}$). Initially, there would be slightly too few cations stoichiometrically, while the sum of the first and additional third peak settles after a few steps at a ratio of about 2:1 compared to the anion, and the results of the N 1s spectra confirm this assumption. Zhang et al. [51] reveal an interaction of platinum nanoparticles in [CMMIM]Cl, which results in a shift of the cation peak in N 1s to a lower binding energy (400.1 eV to 400 eV). They attribute this to a tendency for the electron clouds of platinum to transfer toward the imidazolium cation. Thus, the ring seems to be rather neutral. IRAS measurements of Hohner et al. [34] show a rather flat orientation of the [EMIm]⁺ cation on the platinum surface for an [EMIm]TFSI monolayer on Pt(111). The [EMIm]⁺ loses its orientation in the multilayer. This also indicates a strong interaction of the cation with the platinum. Hohner et al. [34] were also able to use IRAS to make predictions about the adsorption of the [TFSI][−] anion on the platinum surface. This differs slightly from the adsorption of [TFSI][−] in combination with the $[\text{Py}_{1,4}]^+$ cation. In the submonolayer region, the bond again occurs via the SO_2 groups, with one group binding to the platinum via only

one oxygen atom. In the monolayer region, only one SO_2 group binds to the platinum, and the other group lifts off. However, the orientation of the $[\text{EMIm}]^+$ cation does not change. The adsorption behavior could again explain the different binding energy of the anion peak at low coverage and furthermore the differences compared to the $[\text{Py}_{1,4}]\text{TFSI}$.

3.4. $[\text{EMIm}]\text{TFSI}$ on Aluminum

Looking at the graphical plot of film thickness of the evaporated IL versus evaporation time (Figure S4), a change at the growth is visible between 400 s and 800 s (2.4 nm to 3.9 nm). This change is located at a higher film thickness than observed with $[\text{Py}_{1,4}]\text{TFSI}$ (Figure S2).

The clean surface (Figure 4 bottom) shows a composition comparable to that of $[\text{Py}_{1,4}]\text{TFSI}/\text{Al}$ (Figure 2), but small traces of AlF_3 at 76.9 eV and $\text{Al}_2(\text{SO}_4)_3$ at 76 eV can be observed. However, the amount is so small that they can possibly be attributed to deviations in the fit, since the corresponding components are not found in the F 1s or S 2p spectra. Later, the spectra show six components at 72.8 eV, 73.8 eV, 74.6 eV, 75.1 eV, 75.9–76 eV and 76.7–77 eV. They correlate with metallic aluminum, Al_xO , AlOOH or $\text{Al}(\text{OH})_3$ or Al_2S_3 , Al_2O_3 , $\text{Al}_2(\text{SO}_4)_3$ and AlF_3 as already discussed regarding the use of $[\text{Py}_{1,4}]\text{TFSI}$ (Figure 2).

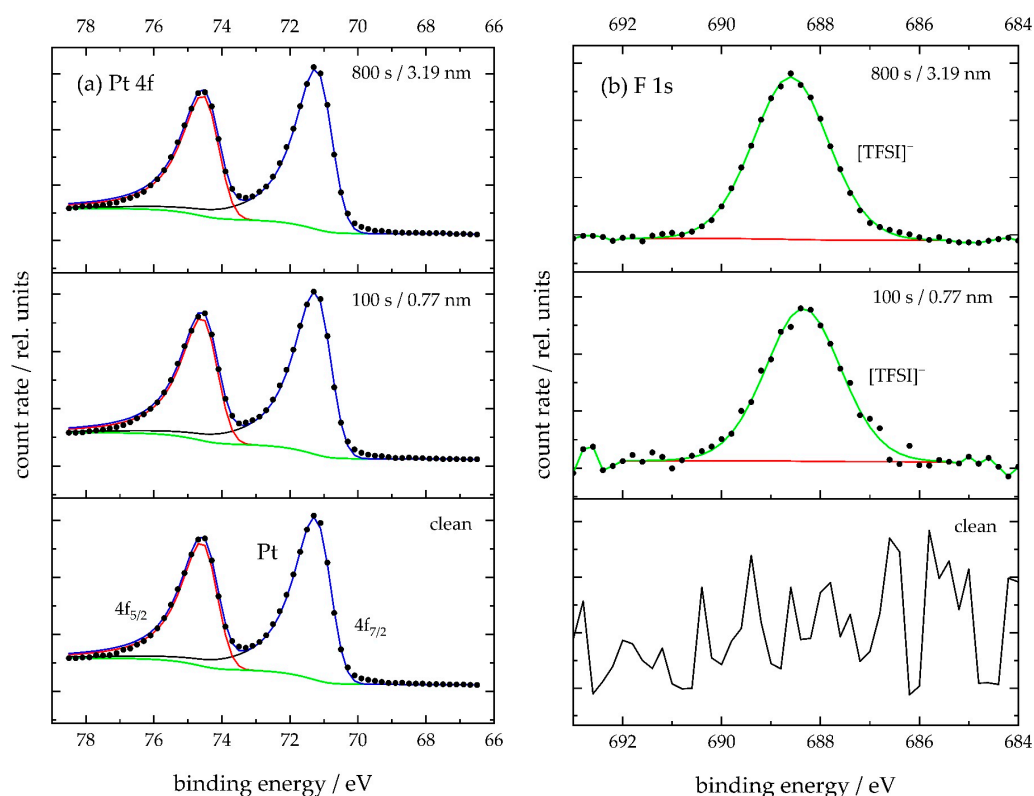


Figure 3. Cont.

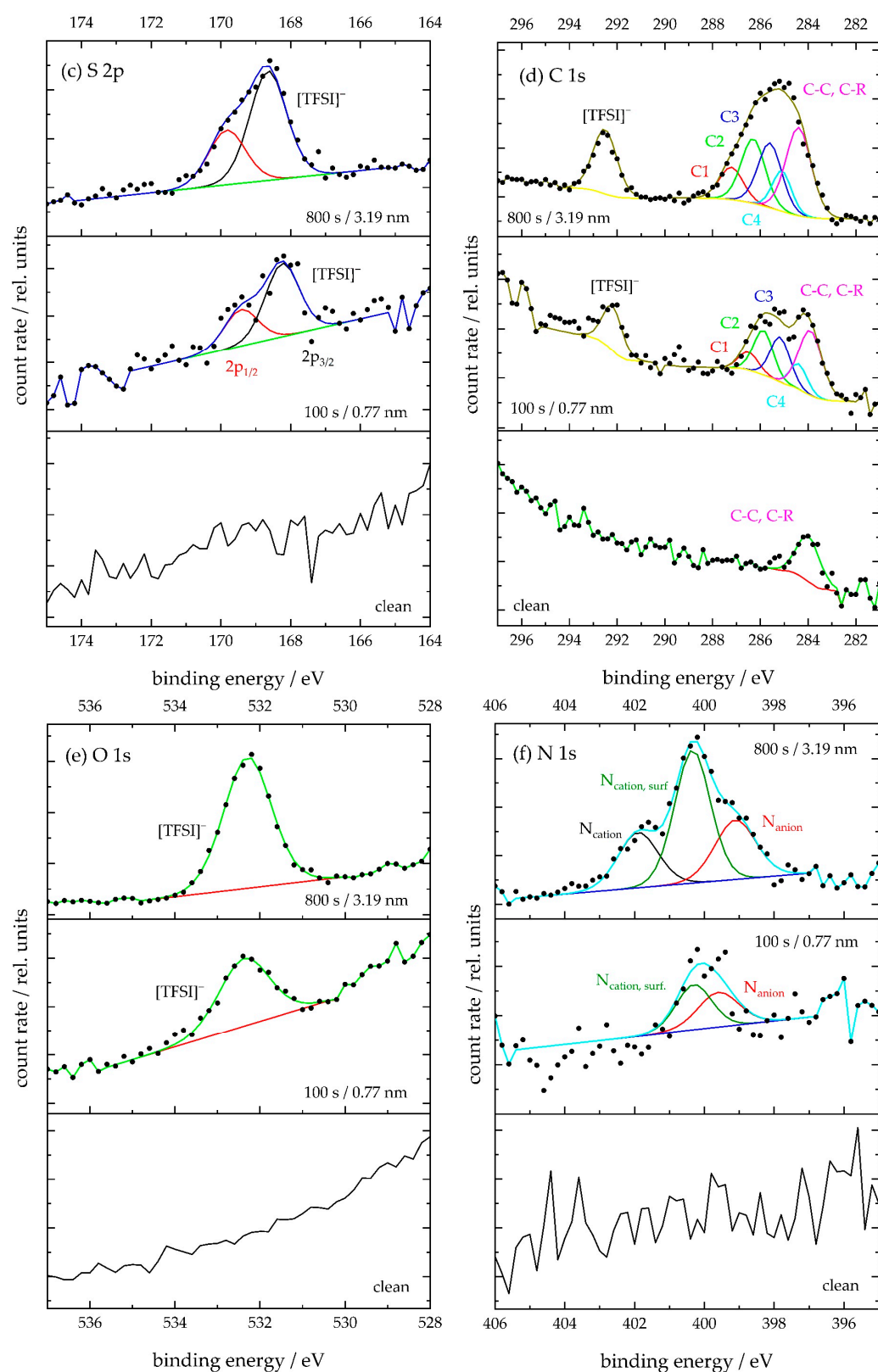


Figure 3. Detail spectra (a) Pt 4f, (b) F 1s, (c) S 2p, (d) C 1s, (e) O 1s, (f) N 1s of clean platinum surface (bottom), with an equivalent film thickness of [Py_{1,4}]TFSI of 0.77 nm (middle) and 3.19 nm (top).

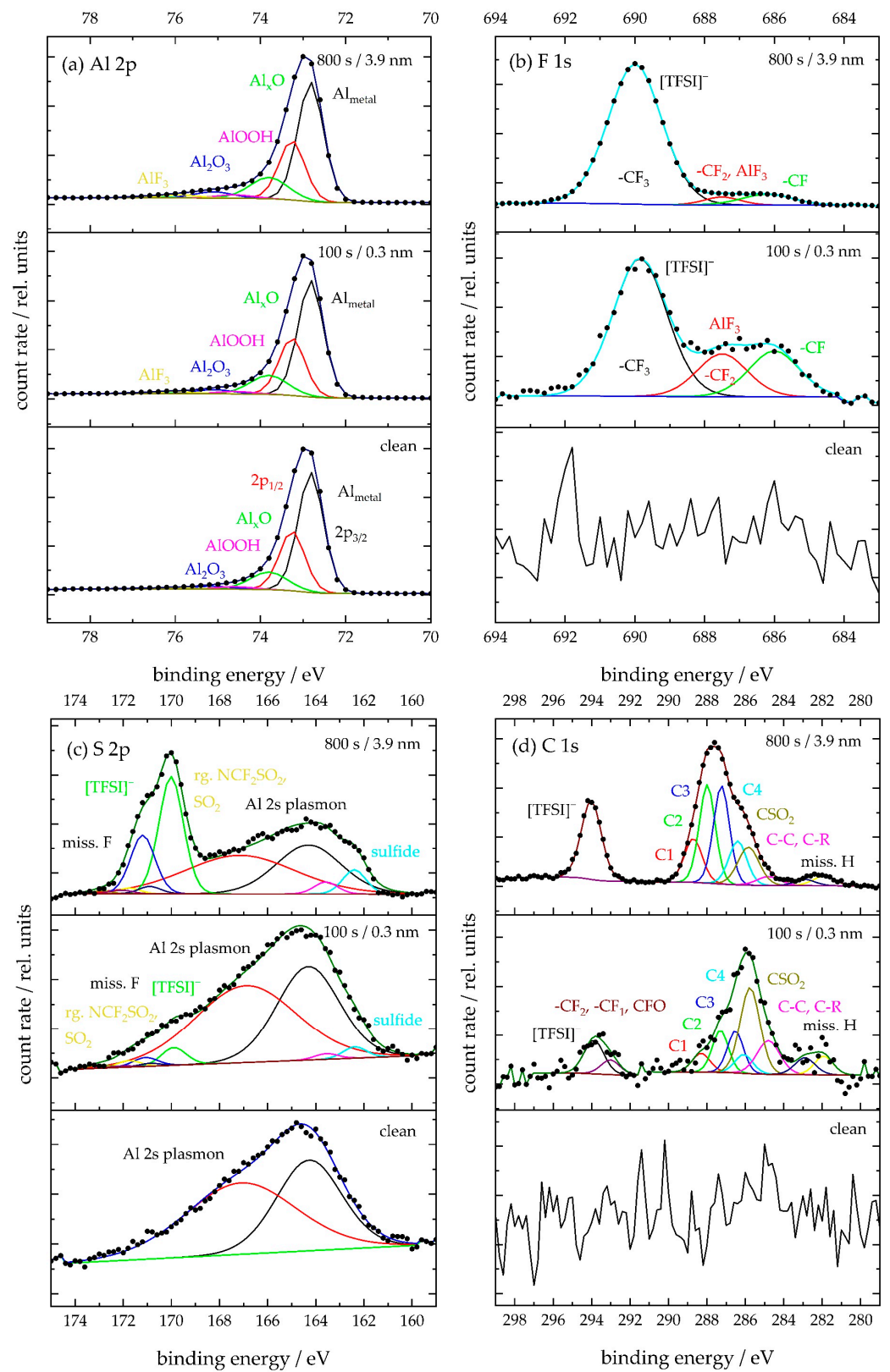


Figure 4. Cont.

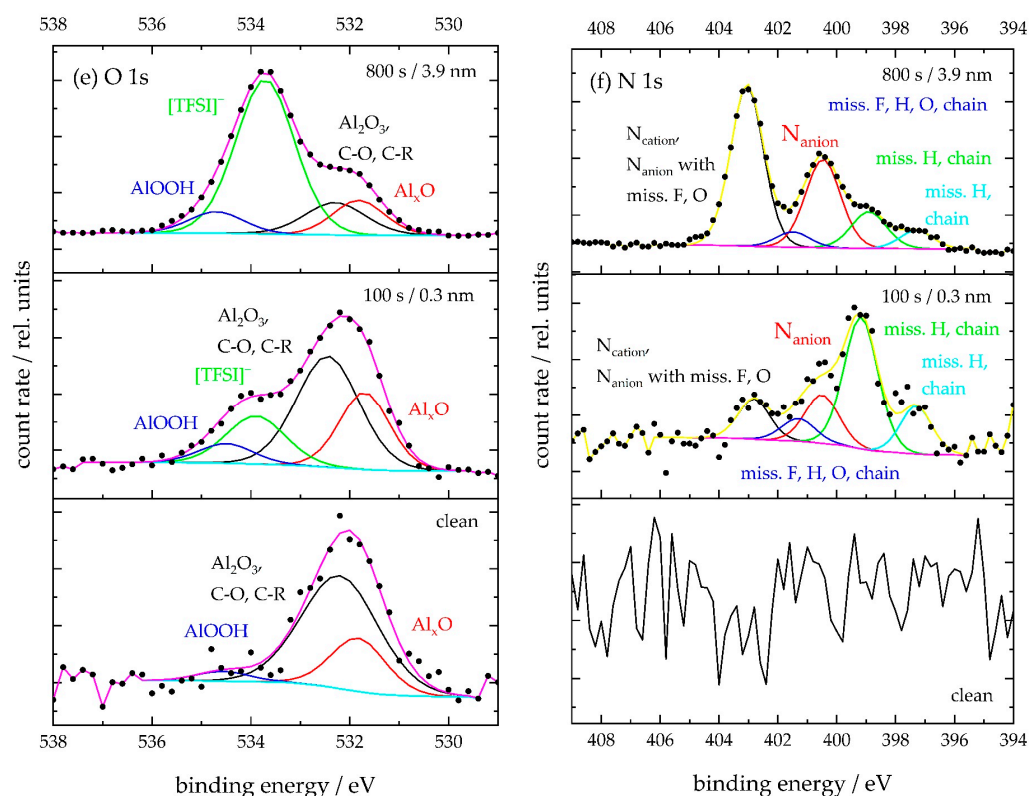


Figure 4. Detail spectra (a) Al 2p, (b) F 1s, (c) S 2p, (d) C 1s, (e) O 1s, (f) N 1s of clean aluminum surface (bottom), with an equivalent film thickness of [EMIm]TFSI of 0.30 nm (middle) and 3.90 nm (top).

Similar to [Py_{1,4}]TFSI/Al (Figure 2), three components can be identified in the F 1s spectra at 689.9–690 eV, 687.3–687.5 eV and 686–686.2 eV, which can probably assigned to -CF₃ of the anion, -CF₂ or TaF₅ and -CF, also from the detachment of fluorine [48]. The ratio of -CF₂ to -CF is more balanced from the beginning than for [Py_{1,4}]TFSI on aluminum, i.e., comparatively more -CF₂ or AlF₃ is formed.

The C 1s spectra show eleven components in total. The anion is obtained at 293.9–294.1 eV, lower than with [Py_{1,4}]TFSI. The components C1–C4 of the cation are located at 288.3–288.7 eV, 287.9–288 eV, 286.5–287.4 eV and 286.1–286.4 eV. Another component related to the anion is located at 292.9–293 eV, which is probably assigned to -CF₂, -CF or CFO due to the detachment of fluorine. A further component related to the anion is at 295.5 eV, which presumably also correlates to the detachment of fluorine and possibly the formation of COF₂. This was not observed during the use of [Py_{1,4}]TFSI. In addition, four further peaks besides the components of the cation are recognizable at 281.9–282 eV, 282.8–282.9 eV, 284.8 eV and 285.8–285.9 eV. The first two, with low binding energies, might correlate with the cation after the detachment of single hydrogen atoms or parts of the alkyl chains (cf. missing H). The third peak corresponds to aliphatic carbons, presumably due to contamination from the vacuum as already observed on platinum. The adsorption of CO is also conceivable. The fourth peak is assumed to be CSO₂ as previously described.

The S 2p spectra show two peaks beside the peak of the anion at 169.9–170 eV. Another peak is at 162.4 eV, which corresponds also to sulfidic species such as Al₂S₃. As revealed previously, the peak at 171.8 eV presumably correlates to C≡N or a ring NCF₂SO₂.

The O 1s spectra show four peaks at 531.7–531.9 eV, 532.3–532.5 eV, 533.7–533.9 eV and 534.5–534.7 eV. They correspond to Al_xO, Al(OH)₃, AlOOH, Al₂(SO₄)₃ and Al₂O₃ or C-O and COR. The fourth peak may be caused by decomposition products of the anion.

Five peaks are obtained at the N 1s spectra at 397.1–397.3 eV, 398.9–399.2 eV, 400.2–400.5 eV, 401.3–401.5 eV and 402.8–403.1 eV. The third peak (400.2–400.5 eV) and fifth peak (402.8–403.1 eV) correspond to the anion and the cation. The cation can also be overlaid

by decomposed anions in which oxygen or fluorine atoms have been detached [48]. The fourth peak (401.3–401.5 eV) probably correlates with decomposed anions after oxygen or fluorine detachment. Also possible here is the detachment of certain hydrogen atoms of the cation as well as the partial or complete detachment of the ethyl or methyl group [48]. K. Forster-Tonigold et al. [20] obtain LiNSO₂ with a comparable peak in the N 1s spectra (N 1s: 400.1 eV, S 2p: 170.3 eV, O 1s: 533.7 eV), which is consistently visible here. The first two peaks correlate with the decomposition reactions of the anion such as fluorine detachment.

4. Conclusions

To gain a detailed insight into the interfaces of Pt/[Py_{1,4}]TFSI and [EMIm]TFSI and of Al/[Py_{1,4}]TFSI and [EMIm]TFSI, thin IL films were deposited on both surfaces and investigated stepwise by XPS. The platinum surface shows no change or the formation of new components in the Pt 4f spectra for both ILs. F 1s, S 2p, O 1s and C 1s show only the components of both ILs and no decomposition reactions of the ILs. In the case of [Py_{1,4}]TFSI, a higher intensity of the anions is detectable first, while in the case of [EMIm]TFSI, another peak forms between the cation and the anion. Since there are no complementary decomposition components at F 1s, S 2p, O 1s and C 1s, the reason could be a stronger interaction of the imidazolium cation with the platinum surface. Furthermore, we also see evidence for a stronger binding of the anion to the platinum surface for both surfaces.

On the pure aluminum surface prepared in situ, both ILs exhibit significant decomposition components in the N 1s, F 1s, S 2p, O 1s and C 1s spectra, mainly due to the cleavage of C-F and N-S bonds. This leads to the formation of AlOOH, Al(OH)₃, Al₂S₃, Al₂(SO₄)₃ and AlF₃ at the interface and other decomposition components. The interaction is mainly with the anion, while the cation shows minor decompositions such as the splitting off individual hydrogen atoms.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings13071182/s1>, Figure S1: Equivalent layer thickness of [Py_{1,4}]TFSI on Pt over total evaporation time; Table S1: Fitting constraints for detail spectra/[Py_{1,4}]TFSI on platinum; Figure S2: Equivalent layer thickness of [Py_{1,4}]TFSI on Al over total evaporation time; Table S2: Fitting constraints for detail spectra/[Py_{1,4}]TFSI on aluminum; Figure S3: Equivalent layer thickness of [EMIm]TFSI on Pt over total evaporation time; Table S3: Fitting constraints for detail spectra/[EMIm]TFSI on platinum; Figure S4: Equivalent layer thickness of [EMIm]TFSI on Al over total evaporation time; Table S4: Fitting constraints for detail spectra/[EMIm]TFSI on aluminum.

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