

GEORG GORBATOVSKI

In situ STM of specific adsorption and
electrical double layer structure
at sp-metal single crystal electrodes



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electrical double layer structure
at sp-metal single crystal electrodes



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1. LIST OF ORIGINAL PUBLICATIONS

- I. O. Oll, M. Väärtnõu, **G. Gorbatovski**, J. Zhao, C. Siimenson, L. Siinor, K. Lust, T. Romann, P. Pikma, E. Lust, Adsorption of anions on bismuth and cadmium single crystal plane electrodes from various solvents and ionic liquid mixtures, *Electrochimica Acta* 319 (2019) 895–908.
- II. **G. Gorbatovski**, O. Oll, J. Zhao, E. Lust, Anion-dependent adsorption of imidazolium ionic liquids at bismuth single crystal electrodes: an *in situ* STM study, manuscript in review.
- III. **G. Gorbatovski**, O. Oll, J. Zhao, E. Lust, *In situ* video-STM study of adlayer structure and surface dynamics at the Bi(*hkl*)|PMImI ionic liquid interface, *Surfaces and Interfaces* 77 (2025) 108027.
- IV. **G. Gorbatovski**, O. Oll, H. Kasuk, P. Pikma, E. Lust, *In situ* scanning tunneling microscopy study of bipyridine adsorption at semi-metallic Sb(111) plane, *Electrochemistry Communications* 105 (2019) 106500.

Author's contribution:

- Paper I:** Performed the *in situ* electrochemical scanning tunnelling microscopy measurements, performed the analysis of the obtained data and participated in the manuscript preparation.
- Paper II:** Performed the *in situ* electrochemical scanning tunnelling microscopy measurements, performed the analysis of the obtained data and was the main person responsible for manuscript preparation.
- Paper III:** Performed the *in situ* electrochemical scanning tunnelling microscopy and cyclic voltammetry measurements, performed the analysis of the obtained data and was the main person responsible for data interpretation and manuscript preparation.
- Paper IV:** Performed the *in situ* electrochemical scanning tunnelling microscopy and cyclic voltammetry measurements, performed the analysis of the obtained data and was the main person responsible for data interpretation and manuscript preparation.

2. ABBREVIATIONS AND SYMBOLS

2,2'-BP	2,2'-bipyridine
4,4'-BP	4,4'-bipyridine
AC	alternating current
AFM	atomic force microscopy
BMPyBF ₄	1-butyl-4-methylpyridinium tetrafluoroborate
C	differential capacitance
C_{dl}	electrical double layer capacitance
C_{min}	capacitance minimum
C_{pseudo}	pseudo-capacitance
C_S	series differential capacitance
c	concentration
C(0001)	basal plane of highly orientated pyrolytic graphite
C, E	capacitance vs. electrode potential curve
CV	cyclic voltammetry
D	diffusion coefficient
DC	direct current
E	electrode potential
E_F	Fermi level energy
E_{min}	potential at capacitance minimum
$E_{\sigma=0}$	potential of zero total charge
$E(t)$	potential at time t
EC	equivalent circuit
EDL	electrical double layer
EIS	electrochemical impedance spectroscopy
EMImBF ₄	1-ethyl-3-methylimidazolium tetrafluoroborate
EMImBr	1-ethyl-3-methylimidazolium bromide
EMImCl	1-ethyl-3-methylimidazolium chloride
EMImI	1-ethyl-3-methylimidazolium iodide
EMImMeSO ₃	1-ethyl-3-methylimidazolium methanesulfonate
EMImOTf	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
EMImTFSI	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
F	Faraday constant
f	frequency in Hz
Fc	ferrocene
Fc/Fc ⁺	ferrocene/ferrocenium redox couple
hkl	Miller indices
HOPG	highly oriented pyrolytic graphite
I	electrode current
I_A	current amplitude
i	imaginary unit ($\sqrt{-1}$)
$I(t)$	current at time t

IL	ionic liquid
j	electrode current density
m	mass of a particle
MD	molecular dynamics
MeSO_3^-	methanesulfonate anion
n	number of electrons
n_{mol}	number of moles of electrons
OTf^-	trifluoromethanesulfonate (triflate) anion
PMImI	1-propyl-3-methylimidazolium iodide
pzc	potential of zero charge
Q	electric charge
R_{ad}	adsorption resistance
R_{ct}	charge transfer resistance
R_{D}	diffusion resistance
rms	root mean square roughness
RTIL	room temperature ionic liquid
S	surface area of the electrode
SC	supercapacitor
STM	scanning tunneling microscopy
t	time
TFSI^-	bis(trifluoromethanesulfonyl)imide anion
UHV	ultra high vacuum
Z	impedance
Z'	real part of impedance
Z''	imaginary part of impedance
Z_{W}	Warburg-like finite-length diffusion impedance
$\delta c_{\text{red}}/\delta x$	reduced species concentration gradient
μ	molecular dipole moment
v	potential scan rate
π	Pi number
Φ	phase angle shift
χ^2	chi-square function
ω	angular frequency

3. INTRODUCTION

Electrochemical energy storage and conversion devices are the basis of a sustainable energy economy of the future. Batteries and supercapacitors power portable electronics and electric transport, fuel and electrolysis cells interconvert chemical and electrical energy, and dielectric capacitors condition power in countless other systems. The active part of every one of these devices is the interface between two dissimilar phases, at which charge is separated, energy is stored and electrochemical reactions take place. Designing more efficient devices therefore requires detailed, molecular-level knowledge of this interface, the electrical double layer (EDL) [1]. Ions and molecules accumulate at the electrode surface as it is polarised; when a species binds chemically to the surface rather than remaining diffusely distributed nearby, it is specifically adsorbed and becomes an integral part of the compact inner layer, reshaping the interfacial charge distribution and the energetics and reactivity of the surface [2].

The structure and stability of this compact layer depend strongly on the crystallographic plane of the electrode, which sets the balance between adsorbate–substrate, adsorbate–adsorbate, adsorbate–ion and adsorbate–solvent interactions [3]. *sp*-Metal single crystals, such as bismuth, itself often described as pseudo-metallic, and the semi-metallic antimony, are informative model electrodes for this purpose: they offer stable, reproducible surfaces over wide potential windows, and their electronic character and reticular density can be varied systematically to separate the role of the electrode from that of the electrolyte [I]. Most interfacial studies nonetheless concentrate on Pt, Au and C [5,6], leaving these high-hydrogen-overvoltage *sp*-metals comparatively unexplored, even though electronic and crystallographic effects on adsorption are most transparent at exactly these surfaces.

This thesis considers two electrolyte environments that make these effects especially clear. Room-temperature ionic liquids are composed entirely of ions and combine negligible volatility, high thermal stability and tunable, application-specific properties [7,8]; because they contain no solvent, they are also an ideal medium for probing anion specific adsorption without competing solvation. Their interfacial behaviour is strongly anion-dependent, so a systematic comparison across the surface-activity spectrum, from the weakly coordinating BF_4^- and OTf^- through the intermediate MeSO_3^- to the halides Cl^- , Br^- and I^- , is needed to separate the intrinsic adsorption strength of the anion from the influence of the cation and the electrode [II]. In aqueous media, in turn, the self-assembly of organic molecules into ordered two-dimensional layers underpins applications from corrosion-protective coatings to molecular electronics [10]; bipyridine is an informative probe because it can bind through several mechanisms, but whether an ordered adlayer forms depends on a delicate balance of interaction energies together with crystallography, pH and applied potential [11]. This behaviour is comparatively well mapped at metallic electrodes but is largely uncharacterised at semi-metals such as Sb(111) [12,13].

These questions cannot be resolved by area-averaging electrochemistry alone. Cyclic voltammetry and electrochemical impedance spectroscopy capture interfacial kinetics and capacitance, but they are spatially blind to where and how the compact layer reorganises. The primary focus of this thesis is therefore to resolve these processes directly, in real space, by *in situ* scanning tunnelling microscopy (STM), which images surfaces and adsorbed adlayers at atomic and molecular resolution under full potential control. Cyclic voltammetry and electrochemical impedance spectroscopy are drawn on throughout, but only to the extent needed to place the STM observations within their correct electrochemically stable potential window and to support the identification of a given structural change; they are not developed here as independent lines of enquiry.

The main aims of the thesis are to:

- a) resolve by *in situ* STM how the electrode, the crystallography and electronic character of Bi(*hkl*) and Sb(111), and the electrolyte class, solvent-free ionic liquid versus aqueous solution, together govern the composition and reorganisation of the compact layer [I]
- b) map by *in situ* STM the specific adsorption and adlayer structure of imidazolium-based ionic liquids across a full anion series (BF₄⁻, OTf⁻, TFSI⁻, MeSO₃⁻, Cl⁻, Br⁻ and I⁻) on the Bi(111), Bi(001) and Bi(01 $\bar{1}$) planes [II]
- c) resolve by *in situ* STM the potential-dependent phase transitions and iodide-induced surface reconstruction of the Bi(111), Bi(001) and Bi(01 $\bar{1}$) planes at the Bi(*hkl*)|PMImI interface [III]
- d) image by *in situ* STM the adsorption and two-dimensional adlayer formation of 4,4'- and 2,2'-bipyridine at the semi-metallic Sb(111) interface, and establish the conditions for a stable, reversible organic monolayer [IV]

In situ scanning tunnelling microscopy is accordingly the primary method of this thesis; cyclic voltammetry and electrochemical impedance spectroscopy are included as supporting context for the STM observations. Together, this local, real-space imaging and the supporting electrochemical framing advance the understanding of specific adsorption and electrical double layer formation at sp-metal single-crystal electrodes relevant to future energy-storage devices.

4. LITERATURE OVERVIEW

4.1. Ionic liquids

Ionic liquids trace back to Walden's 1914 report of molten ethylammonium nitrate [16], but the field only became broadly practical after Wilkes and Zaworotko introduced air- and moisture-stable imidazolium tetrafluoroborate and hexafluorophosphate salts in 1992 [17]. By the conventional definition an ionic liquid is a salt melting below 100 °C, and a room-temperature ionic liquid (RTIL) is one that is liquid at ambient temperature; the low melting points arise from bulky, charge-delocalised, conformationally flexible ions whose poor packing and weak, non-directional Coulomb coordination frustrate crystallisation [7,8]. Because the cation and the anion can be varied independently, the number of accessible ILs is enormous, and their physical and chemical properties (viscosity, ionic conductivity, hydrophobicity, and the width of the electrochemical stability window) can be tuned almost continuously by structural design; it is this combinatorial versatility that has earned ILs the label of "designer solvents" [7,8]. As electrolytes they combine low volatility, high thermal stability, non-flammability and a wide potential window, which together make them attractive for a broad range of electrochemical technologies, including electrical double-layer capacitors and batteries [7,18,19], dye-sensitised solar cells [20], the electrodeposition of metals and semiconductors [21,22,23], lubrication and tribology [24,25,26], gas separation and CO₂ capture [27,28], electrocatalysis and corrosion inhibition [8]. Of particular relevance to energy storage, IL mixtures containing specifically adsorbing halide anions have been shown to raise the capacitance of carbon supercapacitors well above that of the neat liquid, because a reversible faradaic (pseudocapacitive) contribution is superimposed on the electrostatic double-layer response [29].

The distinguishing feature of an IL electrolyte is the structure of its electrical double layer (EDL), which departs qualitatively from the classical Gouy–Chapman–Stern picture developed for dilute solutions. Because an IL is composed entirely of ions and contains no neutral solvent, the interface cannot relax by reorienting solvent dipoles or by building a dilute diffuse cloud; instead, charge is screened by a dense, spatially oscillating arrangement of counter- and co-ions, and the capacitance–potential response is dominated by lattice saturation and overscreening rather than by a simple diffuse layer [18,19]. In the mean-field lattice-gas treatment of Kornyshev, the finite size of the ions caps the attainable interfacial charge, producing either a bell-shaped or a camel-shaped differential capacitance curve depending on the compacity of the liquid [18]; simplified lattice-ion models reproduced this prediction and traced how ion-size asymmetry governs the crossover between the two shapes [30,31], while extensions incorporating short-range ion correlations and explicit interfacial layering refined the description of the compact region [32,33]. Overscreening (the overcompensation of the electrode charge by the first ionic layer, followed by an alternating, decaying charge profile beyond it) and its transition to lattice-saturation

“crowding” at high polarisation were formalised by Bazant, Storey and Kornyshev [19].

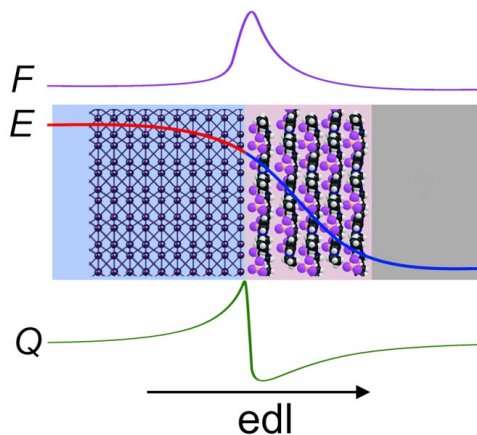


Figure 1. Schematic representation of EDL structure

Direct structural evidence for the predicted layering has come from several complementary probes. Atomic force microscopy first resolved oscillatory force profiles corresponding to discrete, alternating ion layers at insulating surfaces [34] and subsequently at a polarised Au(111) electrode, where the number and rigidity of the layers depend on the applied potential [35]; high-energy X-ray reflectivity mapped the same layering at a charged sapphire interface with sub-molecular resolution [36]; and sum-frequency generation spectroscopy provided a chemically specific view of the orientation of cations and anions in the innermost layer as a function of surface charge [37], consistent with the slow ordering and self-assembly reported within the compact layer of ILs [38]. Molecular dynamics and density functional theory have complemented these experiments (for instance by relating the characteristic capacitance peaks to distinct ion-reorientation regimes and by clarifying temperature and quantum-capacitance effects at the interface [39,40]), but such computational work lies outside the scope of the present study and is noted here only for completeness. A bell-shaped capacitance curve consistent with these structural pictures was also observed directly for an IL at the mercury electrode [41], and this body of work on IL electrolytes for energy-storage devices has been surveyed in several broader reviews [1,42]. Despite all these advances, a fully predictive, quantitative description of ion-surface interactions at metal|IL interfaces is still lacking, owing both to the difficulty of modelling the strong, correlated interactions and to the intrinsic complexity of the systems [43].

4.2. Electrode|electrolyte interface and sp-metal single crystals

Systematic theories of the electrode|electrolyte interface began with Helmholtz's parallel-plate capacitor picture [44], refined by the diffuse-layer treatments of Gouy and Chapman [45,46] and by Stern's combination of a compact inner region with a diffuse outer region [47]. Grahame's precise capacitance measurements at the mercury electrode, and his synthesis of the resulting double-layer theory into the concepts of the inner and outer Helmholtz planes, established the modern quantitative framework and distinguished non-specific from specific adsorption [48,49]; this historical development has been reviewed in detail elsewhere [50]. A recurring theme in the subsequent literature is that the double layer cannot be understood from the electrolyte side alone: the electronic structure of the electrode enters the interfacial capacitance directly, as recognised already in early treatments that made the capacitance depend on the properties of the metal [51], and as elaborated for semiconductor and semi-metal electrodes, where a substantial fraction of the applied potential drops within a space-charge region inside the solid rather than across the electrolyte [52]. This point is central to the present work, because bismuth and antimony are semi-metals whose low charge-carrier concentration (several orders of magnitude below that of typical sd-metals) and small effective electron mass make the electrode contribution to the interfacial capacitance unusually large.

The composition of the compact layer is set by adsorption, described quantitatively since Frumkin's isotherm for specifically adsorbing species and its many later extensions [53,54]. Extracting adsorption parameters from capacitance data requires well-defined surfaces, and single-crystal electrodes are therefore essential for isolating the dependence of adsorption on the crystallographic plane, the potential of zero charge (pzc) and the electronic character of the metal [2,3]. The pzc, in turn, correlates with the electronic work function of the plane and serves as the natural reference potential for adsorption thermodynamics [2]. Systematic single-crystal studies established this picture chiefly for the noble sd-metals: at gold and silver the anion specific adsorption, the potential-induced surface reconstruction and the pzc have been mapped in detail across the low-index planes [55,56], and platinum single crystals remain the benchmark for specific adsorption and electrocatalysis [57]. Bismuth and the semi-metallic antimony extend this comparison to the sp-metal series [55]. Both crystallise in the rhombohedral $A7$ structure and expose stable, reproducible low-index planes over wide potential windows; their adsorption behaviour reflects both the low carrier density and the specific reticular density and bonding of each plane [58], and their surface and electronic structure has been characterised by diffraction and photoemission [59,60]. Quantitative analysis at these electrodes, using the Hurwitz–Parsons–Dutkiewicz surface-excess method, virial isotherms and the electrosorption-valency (partial charge transfer) formalism, has shown that the Gibbs energy of halide adsorption increases both with the reticular density of the $Bi(hkl)$ plane and with the decreasing solvation power of the medium, and that

the anion adsorption activity follows the order $\text{ClO}_4^- < \text{BF}_4^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$; the same framework has been applied across the group's Bi and Cd single crystals from aqueous, non-aqueous and ionic-liquid media [I]. Specific adsorption of halides in particular dominates the capacitive response of Bi(*hkl*) interfaces, both from aqueous solutions and from pure halide ionic liquids [I,61], and the double-layer capacitance at the Bi(111)|IL interface depends systematically on the size and chemical nature of the ions [62].

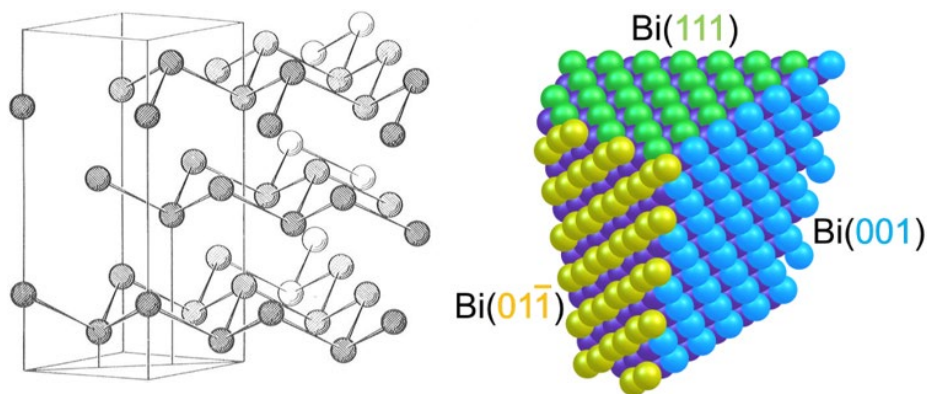


Figure 2. Bismuth crystallographic structure

4.3. Electrochemical characterization techniques

Cyclic voltammetry (CV) provides the first survey of the processes occurring within a potential window and distinguishes adsorption-controlled from diffusion-controlled behaviour through the scan-rate dependence of the peak current, following the classical treatment of Nicholson and Shain [63] and standard texts [64,65]. For an adsorption-limited process the peak current scales linearly with the potential scan rate, whereas for a diffusion-limited process it scales with the square root of the scan rate; the charge circulated under an adsorption peak provides a measure of the surface coverage, and because the potential is swept continuously a capacitive charging current is always superimposed on any faradaic contribution [64]. In single-crystal work CV is used mainly to delimit the region of ideal polarizability and to locate the onset of cation reduction, anion oxidation and metal dissolution, thereby bounding the potential range within which impedance and, subsequently, *in situ* imaging measurements can safely be performed [61].

Electrochemical impedance spectroscopy (EIS) resolves processes of differing time constants by probing the interface with a small sinusoidal perturbation over a range of frequencies, and yields the double-layer capacitance together with the resistive and mass-transfer contributions [66], building on the equivalent-

circuit treatment of a diffusion-coupled faradaic reaction introduced by Randles [67]. In practice the circuit parameters are obtained by non-linear least-squares fitting of an assumed equivalent circuit, whose physical validity is judged both by the reduction in fitting error upon adding each element and by the Kramers–Kronig relations, which confirm that the measured response is linear, causal and stable [68,69]. At solid electrodes the double-layer response is seldom ideally capacitive, and the resulting capacitance dispersion is conventionally represented by a constant phase element; systematic studies have attributed it primarily to atomic-scale surface disorder and to specific adsorption rather than to geometric roughness [70,71,72], and impedance spectroscopy has been applied on this basis to extract anion adsorption rates at single-crystal electrodes [73]. For single-crystal interfaces the frequency-dependent series and parallel capacitances are extrapolated to obtain the equilibrium double-layer capacitance free of faradaic contributions, and the characteristic relaxation time constant provides a compact measure of the overall interfacial kinetics [66,74]. For specifically adsorbing systems the Frumkin–Melik–Gaikazian equivalent circuit, a double-layer capacitance in parallel with an adsorption impedance and a finite-length (Warburg-like) mass-transfer element, describes the slow, diffusion-coupled adsorption step at Bi(*hkl*) interfaces from both aqueous and ionic-liquid media; in the ionic-liquid case the high viscosity and low diffusion coefficient of the medium make the mass-transfer element particularly prominent [1,61]. These methods are indispensable for quantifying the kinetics and capacitance of an interface, yet they share a fundamental limitation: being area-averaging, they report the response of the entire electrode surface and cannot reveal where, or how, the compact layer reorganises. It is this spatial blindness that motivates the use of a local, real-space probe, to which the discussion now turns.

4.4. *In situ* scanning tunnelling microscopy

Scanning tunnelling microscopy (STM), introduced by Binnig and Rohrer [75] and extended to the solid|liquid interface by Sonnenfeld and Hansma [76], images conductive surfaces and adsorbed adlayers in real space at atomic and molecular resolution. The technique exploits the approximately exponential dependence of the tunnelling current on the tip–substrate separation, which confers sub-Ångström vertical sensitivity, while the lateral resolution is set by the sharpness of the metal tip; the measured signal is a convolution of geometry with the local density of electronic states, so that the interpretation of atomic and, especially, molecular contrast requires explicit consideration of the electronic structure of both substrate and adsorbate [77,78,79]. The decisive step for electrochemistry was the introduction of the potentiostatic (four-electrode) configuration, in which the potentials of the tip and the working electrode are controlled independently by a bipotentiostat and the tip is insulated except at its apex, so that faradaic leakage does not overwhelm the tunnelling current and the interface can be followed as the polarisation is changed [80]. Applied to the coinage metals, *in situ*

STM revealed the potential-induced lifting and re-formation of the Au(100) and Au(111) surface reconstructions and the ordering of adsorbed anion adlayers [5,81,82,6]. The sp-metals behave differently: cyclic voltammetry, impedance and STM together show that Bi(*hkl*) and Sb(111) do not undergo fast potential-induced reconstruction within their ideal-polarizability windows, so that the changes observed in the presence of an adsorbate can be attributed to the adlayer rather than to a rearrangement of the metal lattice. This clean, reconstruction-free character is precisely what makes the sp-metals suitable substrates for the interfacial studies pursued in this thesis.

The atomic-resolution imaging first demonstrated for Bi(111) in aqueous media [83] was soon extended to antimony, where both liquid-nitrogen-cleaved and KI + HCl electrochemically polished Sb(111) surfaces proved atomically resolvable and stable, showing no fast reconstruction over the negative potential range from -0.8 to -0.15 V in 0.5 M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ [84]. Together with the earlier characterisation of variously pre-treated antimony crystals [85], this established the baseline that any subsequent adsorption study relies upon: because the bare lattice is stable and reconstruction-free, a potential-dependent structural change appearing once an adsorbate is introduced can be assigned unambiguously to the adlayer rather than to the substrate. Building directly on that foundation, the adsorption of bipyridine at Sb(111) was resolved in detail [IV]. The 4,4' isomer forms a stable, reversible two-dimensional monolayer of parallel molecular rows; the measured coverage and inter-row spacing indicate flat-lying, bi-protonated molecules whose positively charged ends are screened by co-adsorbed, solvated sulphate anions filling the voids between the rows, and the ordering is accompanied by a small, weakly pH-dependent capacitance hump, while stronger negative polarisation drives an irreversible reductive polymerisation that roughens the surface. The 2,2' isomer, by contrast, yields only atomic resolution of the underlying lattice under a much higher level of measurement noise, with no detectable ordered adlayer. That this flat-lying, anion-stabilised packing motif closely echoes the structures resolved by *in situ* STM for 2,2'- and 4,4'-bipyridine on Au(111) [86,87], and for 4,4'-bipyridine on silver where the adlayer additionally mediates a proton-coupled redox cycle [88], means that the extensive metallic bipyridine literature can be carried over to interpret and anticipate the antimony case; at the same time, the sharp contrast between the two isomers demonstrates that, at a low-carrier-density semi-metal, the balance between molecule–surface binding, intermolecular interaction and co-adsorbed-anion stabilisation is finely poised, so that molecular geometry, protonation state and supporting anion together decide whether an ordered layer forms at all. These conclusions frame the organic-adsorption part of this thesis and motivate the systematic comparison of the two isomers pursued here. It should be stressed that this behaviour is governed throughout by pH, which sets both the protonation state of the adsorbate and the stability window of the antimony surface itself; the electrochemical and *in situ* STM data collected for this system confirm that even modest changes in pH alter the outcome substantially, to the point that measurements at higher pH could not be carried out with sufficient surface stability to be

reported. This aqueous, pH-dependent chemistry is accordingly treated here as a self-contained case, and its protonation-driven adsorption mechanism is not extended to interpret the pH-free, aprotic ionic-liquid systems discussed elsewhere in this thesis.

Where such aqueous studies isolate the behaviour of a single organic adsorbate against an otherwise inert supporting electrolyte, the ionic-liquid environment poses the complementary and considerably more intricate question of how the compact layer responds when every species present is potentially surface-active. This setting has been explored most thoroughly at bismuth, beginning with impedance and voltammetry that revealed the strong dependence of the series capacitance and of the mass-transfer-limited double-layer kinetics on the size and structure of both the cation and the anion [89,62]. *In situ* STM then made the corresponding compact-layer structures visible: at the Bi(111)|BMPyBF₄ interface, slow, multilayered adlayers were observed whose very appearance depends sensitively on the STM scanning conditions (tip bias, tunnelling current and scan rate), a result that both established the multilayer nature of the compact region and provided a direct methodological constraint, since it defines the tunnelling conditions under which such a soft interface can be imaged without being perturbed [90]. The decisive role of a specifically adsorbing anion emerged when iodide was introduced: a well-defined two-dimensional superstructure develops at the Bi(111)|EMImBF₄ + EMImI interface within -0.7 to -0.3 V, driven by strong I⁻ specific adsorption and counter-ion co-adsorption, and it desorbs at more negative potentials and gives way to surface roughening once oxidation sets in [91]. Comparison with the surface-inactive Bi(111)|EMImBF₄ system, and the collected thesis work on Bi(111)|RTIL interfaces, confirmed that the ordered layer is a consequence of the halide rather than of the imidazolium framework [92,93]. The interpretive template for this behaviour comes in part from the more extensively studied Au(111)|IL interface, where STM has resolved analogous potential-driven order–disorder transitions of adsorbed anion adlayers [94], where the interfacial capacitance minimum has been correlated with the pzc [95,96], and where high-speed video-STM first captured adlayer dynamics in real time [97].

The picture that emerges from these strands is that anion identity is decisive at bismuth. Dense adsorbed Br⁻ and I⁻ superstructures dominate the Bi(111) response in surface-active RTIL mixtures, with the adsorption activity ordered by the reticular density of the plane [I]; even an organic additive such as 4,4'-bipyridine forms an ordered layer at the Bi(111)|IL interface, though only within a narrow potential range, underscoring how strongly the electrolyte governs the outcome [98]; and residual water further reshapes the nanostructure and adsorption kinetics of the interface, producing anomalous capacitance maxima that are mirrored in the atomic-resolution images and setting the level of dryness required for meaningful measurements [99]. These observations converge on the pure halide Bi(*hkl*)|PMImI system that forms the ionic-liquid part of this thesis, in which high-speed video *in situ* STM captured, in real time, the potential-dependent phase transitions, iodide-induced surface reconstruction and cathodic dissolution of the Bi(111), Bi(001) and Bi(01 $\bar{1}$) planes, and linked the fine-structure

adlayer directly to iodide specific adsorption [III]. Taken together, the accumulated evidence, that iodide drives ordered superstructures bounded by desorption at negative and by dissolution or oxidation at positive polarisation, that the compact layer is multilayered and sensitive to the imaging conditions, that water must be rigorously excluded, and that the plane-dependent electronic and reticular properties govern the adsorption strength, defines both the experimental precautions and the interpretive expectations for the present real-time study, while the absence of any comparable video-rate characterisation of a pure halide ionic liquid at the sp-metals identifies the specific gap that this work sets out to close.

5. EXPERIMENTAL

5.1. Reagents and materials

For the ionic-liquid experiments, high-purity 1-propyl-3-methylimidazolium iodide (PMImI; Merck, 99.9 %, $\text{H}_2\text{O} \leq 300$ ppm) was used as the electrolyte. Reference-electrode calibration additionally employed 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄; Solvionic, 99.5 %) and ferrocene (Fc; Sigma-Aldrich, > 98 %). For the aqueous experiments, all solutions were prepared volumetrically with Milli-Q⁺ water using H₂SO₄ (double distilled, Aldrich), 4,4'-bipyridine (4,4'-BP; Fluka purum, > 99 %) and 2,2'-bipyridine (2,2'-BP; Aldrich, 99+ %); Na₂SO₄ was purified by triple recrystallisation from water and calcined at 700 °C immediately before use to remove organic impurities. Electrode and cell cleaning used concentrated H₂SO₄ (Merck, 95–97 %, EMSURE) and H₂O₂ (Merck). Electrochemical polishing of the working electrodes used a saturated aqueous KI solution (BioUltra, ≥ 99.5 %) acidified with a small, unmeasured addition of concentrated HCl (Sigma-Aldrich, 37 %, 99.999 %); this mildly acidic KI solution, roughly comparable to a 0.5 % HCl content, was used for polishing both the bismuth and the antimony electrodes. Argon (99.999 %) was used to deaerate solutions and to maintain the inert atmosphere throughout cell assembly. All experiments were carried out at 22 ± 1 °C [III,IV].

5.2. Working-electrode fabrication and pretreatment

The bismuth working electrodes were prepared from Bi(*hkl*) single-plane crystals grown by the Czochralski method and cut into cylindrical sections of approximately 3.6 mm cross-sectional diameter. The lateral surface of each cylinder was insulated with polystyrene dissolved in toluene; after the toluene had evaporated, the cylinder was pressed into a heated Teflon holder and left to cool for several hours. The exposed active face was then mechanically polished with progressively finer grades of sandpaper to a mirror-like finish. This mechanical step shortened the subsequent preparation and ensured that an atomically flat, well-defined surface could be recovered by electrochemical polishing immediately before the experiment [III,IV]. Directly before cell assembly, the Bi(*hkl*) electrode was electrochemically polished in the saturated, HCl-acidified KI solution at a current density of $j < 1.5 \text{ A cm}^{-2}$ until a mirror-like, reflective surface was obtained [III].

The antimony working electrode was a basal-plane Sb(111) single crystal. Its surface was electrochemically polished in the same saturated, HCl-acidified KI solution used for the bismuth electrodes, to expose an atomically flat, reconstruction-free face, following the procedure established for the group's Sb(111) single crystals [IV,84]. In both the bismuth and the antimony cases the freshly polished surface was protected until the moment of cell assembly, as described below, to prevent oxidation by airborne oxygen.

5.3. STM tip preparation

The STM tips were fabricated by electrochemical etching of tungsten wire (0.25 mm diameter, 99.9 %; Jülich, Mateck) in aqueous KOH (Sigma-Aldrich, puriss) prepared with Milli-Q⁺ water. Because the tip acts as an independent electrode in the electrochemical STM configuration, where faradaic reactions at its surface would otherwise contribute noise to the tunnelling current, each etched tip was insulated with Apiezon® wax, leaving only the apex exposed. Once coated and cooled, each tip was tested on the freshly cleaved basal plane of highly oriented pyrolytic graphite, C(0001) (SPI), and the tip exhibiting the lowest leakage current and the smallest thermal drift was selected and left to stabilise in the STM scanner overnight before imaging [III,84].

5.4. Reference-electrode calibration

For the ionic-liquid measurements the electrode potential was referred to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. Calibration of the platinum reference-electrode potential was performed by potentiometry in a three-electrode cell prior to the STM experiment. A platinum wire immersed in EMImBF₄ containing 2.5 mM ferrocene served as the working electrode, a second platinum wire as the reference electrode, and a platinum net as the counter electrode. To prevent mechanical mixing of the ferrocene-containing ionic liquid with the reference electrolyte, the PMImI was held in a separate reference compartment isolated by a Luggin capillary. The calibration cell was therefore



and all ionic-liquid potentials reported in this work are given with respect to the Fc/Fc⁺ couple [III,61]. During the STM and electrochemical measurements themselves the potentiostat was operated relative to the platinum reference electrode within the working cell; the potentials quoted throughout this thesis are the corresponding Fc/Fc⁺ values, obtained by applying the calibration offset determined above to the potentials actually applied during each experiment.

5.5. *In situ* STM: ionic-liquid experiments (Bi(hkl) | PMImI)

Before each experiment a small amount of PMImI was dried under ultrahigh vacuum at 100 °C for 72 h until a base pressure of 10⁻⁷ Torr was reached, and the dried liquid was stored in sealed Eppendorf tubes for transfer between glove-box units [III]. A small-volume (0.6 cm³) homemade Teflon cell was used, with a platinum wire reference electrode and a large-area platinum mesh counter electrode (99.9+ %). Prior to assembly, the Pt mesh, cell and reference electrode were cleaned for approximately 30 min in a hot (~100 °C) mixture of concentrated H₂SO₄ and H₂O₂, rinsed repeatedly with Milli-Q⁺ water (18.2 MΩ cm;

total organic carbon ≤ 1 ppb), oven-dried, and transferred to an argon-filled glove box. The cell, counter and reference electrodes, the Luggin capillary and the dried ionic liquid were kept in the argon-filled acrylic glove box for at least 3 h before assembly; the perforated glove-box lid connected directly to the removable STM head (Molecular Imaging PicoSPM), and argon was purged continuously to exclude ambient air [III].

After electrochemical polishing, the bismuth working-electrode surface was deliberately left covered with a drop of the polishing mixture, which acted as a temporary barrier against airborne oxygen during transfer, and the electrode was carried into the assembly glove box. On passing through the air-tight valve, the working-electrode surface was thoroughly rinsed with ionic liquid from an Eppendorf tube to remove any residual polishing solution. The Teflon cell was then mounted on the cell holder and secured with mechanical clamps, and a Luggin capillary, pre-filled with ionic liquid by syringe injection, was fixed to the side of the cell. Immediately before attachment, the working electrode was wrapped with a thin band of plastic polymer to prevent the ionic liquid from leaking out of the cell; once the electrode was in place, the cell was filled with ionic liquid from the remaining Eppendorf tube. The reference electrode was then pressed into the Luggin capillary, bridging the ionic liquid in the cell with that in the capillary and establishing electrolytic contact between the working and reference electrodes. The fully assembled cell was inspected carefully before use, the most common failure modes being ionic-liquid leakage and mechanical collapse of the cell during attachment to the microscope [III].

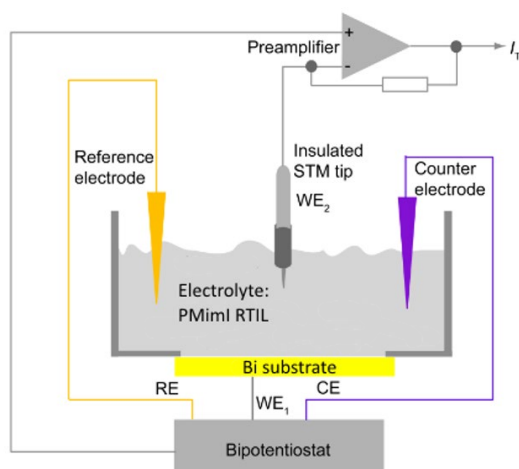


Figure 3. Experimental STM measurement setup

Electrical clamps were then connected to the reference and working electrodes. Immediately on immersion, before any potential was applied, the cell settled at its open-circuit potential (OCP); for the iodide-containing Bi(*hkl*)|PMImI systems

this OCP lay in the range -0.9 to -0.8 V vs. Fc/Fc^+ , just below the onset of iodide oxidation, and was allowed to stabilise for several minutes before proceeding. During this stabilisation period the cell was attached to the main body of the microscope; once the air-tight lid was secured, the assembly was transferred into the Faraday enclosure in which the STM experiment was performed. A substantially more negative potential was then deliberately applied to clean the electrode surface prior to imaging; on applying this potential, an initial current surge was observed, reflecting the decomposition of trace water and the reduction of partially oxidised surface patches remaining after polishing, which decayed over time as the surface was reduced. The cathodic polarisation was then gradually stepped back toward less negative values while keeping the current density measurable, until a potential within the electrochemically stable range identified by cyclic voltammetry was reached; excessively negative potentials were avoided throughout to prevent surface dissolution, the limits again being taken from the cyclic voltammetry data. When idle, the tunnelling current lay in the range 0.02 – 0.06 nA depending on the quality of the tip coating and remained stable throughout the experiment. The initial imaging potential was chosen from within this electrochemically stable range and was subsequently adjusted to the objective of each experiment [III].

5.6. *In situ* STM: aqueous-solution experiments

For the aqueous measurements the supporting electrolyte was 0.5 M Na_2SO_4 containing either 3 or 0.05 mM H_2SO_4 , with 3 mM of the bipyridine additive (either $2,2'$ -BP or $4,4'$ -BP) where present; the solutions were saturated with dry argon before use [IV]. A self-made, hermetically sealed three-electrode cell was employed, with a large platinum counter electrode and an $\text{Ag}|\text{AgCl}$ (saturated KCl) reference electrode connected to the *in situ* STM cell through a Luggin capillary [IV]. The pH range was chosen in accordance with the stability of the antimony electrode.

The freshly electrochemically polished $\text{Sb}(111)$ electrode was submerged into the argon-saturated electrolyte under cathodic polarisation at $E = -0.5$ V vs. $\text{Ag}|\text{AgCl}$ (saturated KCl), so that the surface was protected from oxidation from the moment of immersion [IV]. All STM images were recorded in constant-current mode within a tunnelling-current range of 0.2 – 2.0 nA; the constant-current mode was chosen as being suited to surfaces displaying step-edge topography, since the scanner adjusts the tip height to maintain the set current. Measurements were performed at 22 ± 1 °C [IV].

5.7. Cyclic voltammetry and electrochemical impedance spectroscopy

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to characterise each system, to establish the region of ideal polarizability and to select the electrochemically stable potentials at which STM imaging was performed. For the ionic-liquid systems, CV and EIS were carried out with an Autolab PGSTAT 320 equipped with an FRA II module, inside an MBRAUN LabMaster 130 glove box ($\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 1$ ppm) under argon [III]. For the aqueous systems, an Autolab PGSTAT302N potentiostat was used for both CV and EIS [IV]. For the specifically adsorbing systems studied here, the impedance response was analysed by non-linear least-squares fitting to the Frumkin–Melik–Gaikazian equivalent circuit, in which a double-layer capacitance is placed in parallel with an adsorption impedance and a finite-length (Warburg-like) mass-transfer element, the last being required by the high viscosity and low diffusion coefficient of the ionic liquid [III,61].

The characteristic time constant of each interface was derived from the frequency response of the experimental impedance data; the error bars associated with the time constant correspond to the accuracy of the Gaussian fit of the peak curves. The time-constant versus electrode-potential dependencies were found to follow a trend similar to that of the differential-capacitance curves, indicating a strong correlation between the interfacial charge dynamics and the electrochemical capacitance behaviour [III].

5.8. STM image processing and analysis

The STM images were processed with the Gwyddion software package [100], which was used both for image processing and for surface-roughness analysis, including the root-mean-square (RMS) roughness computed as the quadratic mean of the height deviations of the data points from the mean plane [III,84,100]. For the ionic-liquid systems, interatomic (signal-to-signal) distances within the adlayer were measured with the Gwyddion tools, and the adlayer surface coverage was obtained by dividing the number of resolved features by the single-cell area, with reference atomic densities of the $\text{Bi}(hkl)$ planes taken from the literature [III].

6. RESULTS AND DISCUSSION

6.1. The bare sp-metal | ionic-liquid interface

The interpretation of any adsorbed layer imaged by STM depends on the assumption that the underlying electrode remains structurally inert over the duration of the measurement, and it is this condition that later permits an observed structure to be assigned to the adlayer rather than to the metal. For the sp-metals the assumption is well founded. Whereas the low-index faces of the coinage metals undergo potential-induced reconstruction as the surface charge is swept, cyclic voltammetry and impedance place the Bi(*hkl*) and Sb(111) interfaces within a wide, ideally polarizable window in which no such fast reconstruction of the lattice occurs. The metal therefore provides a fixed reference frame against which the electrolyte organises. *In situ* imaging both confirms this stability and refines it: on electrochemically polished Bi(111) the plateaus remain atomically smooth and triangular, in agreement with the earlier aqueous characterisation of the same plane [83], while the terrace edges are consistently jagged. The distinction is informative, since it indicates that the limited dissolution and redeposition of bismuth that does take place is restricted to the reactive, low-coordination edge sites and leaves the plateau lattice unaffected [99].

Two features of this baseline condition inform the remainder of the chapter. The first concerns the measurement itself. The ionic-liquid layer at bismuth is soft and multilayered, so that the imaged structure is not a passive record but a response to the probe, and an unsuitable tip bias, tunnelling current or scan rate can reorganise the layer that is being examined [90]. The structural conclusions drawn below are accordingly understood to have been obtained under tunnelling conditions mild enough not to perturb the interface. The second concerns the physics that the later sections address. Even before any anion is permitted to adsorb specifically, the series capacitance and the mass-transfer-limited kinetics of double-layer formation already depend markedly on the size and structure of both ions [62,89], which provides an early indication that the anion, once specifically adsorbed, will be the principal factor governing the structure of the compact layer.

6.2. Anion-controlled adlayer order at the Bi(*hkl*) | ionic-liquid interface

The central proposition of this work is that, at a semi-metal, the compact layer is assembled primarily by the anion, and that *in situ* STM resolves this as a graded sequence of interfacial order that follows the specific-adsorption strength of the anion. The claim goes beyond the familiar observation that different anions yield different capacitances; it holds that the real-space structure and the thermodynamically measured adsorption activity are two manifestations of the same underlying interaction. The electrochemical ordering is well established, the

adsorption activity increasing as $\text{BF}_4^- < \text{TFSI}^- < \text{OTf}^- < \text{MeSO}_3^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ [I], and the advantage of combining averaging electrochemistry with local imaging is that each step in this sequence can be shown to correspond to a distinct interfacial architecture rather than merely to a shift in a capacitance value.

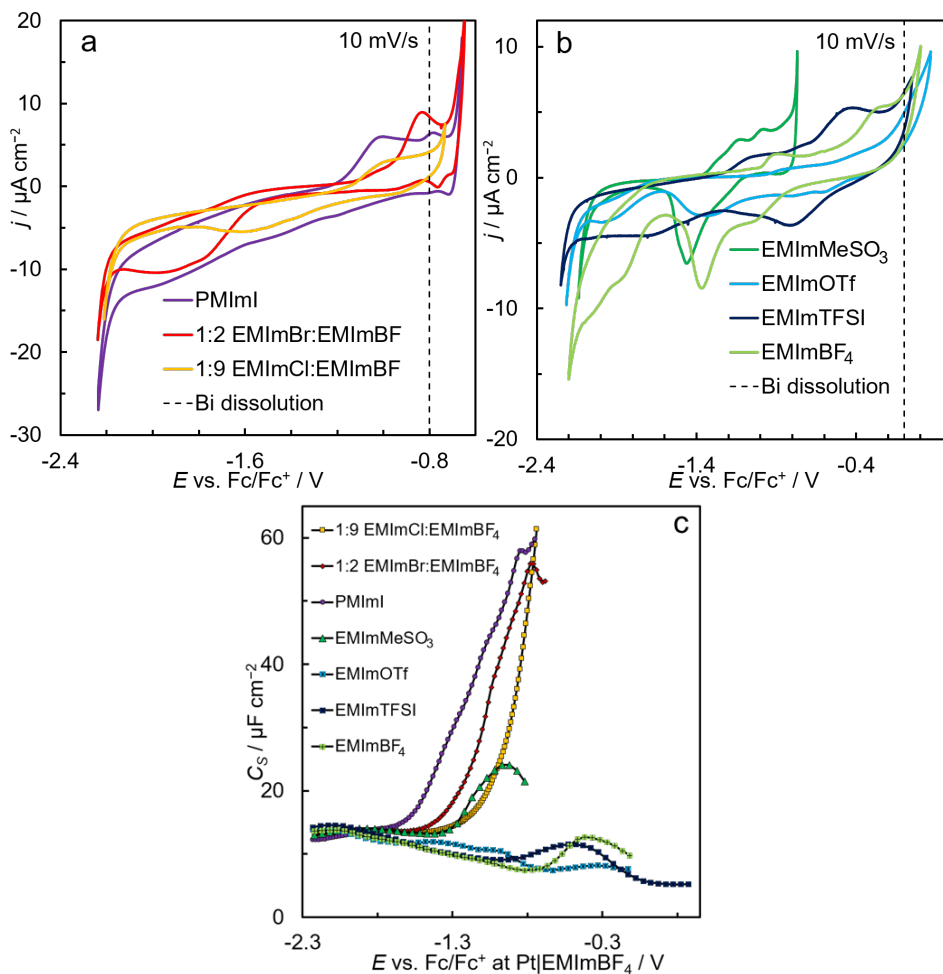


Figure 4. Comparative cyclic voltammograms (a,b) and series capacitance versus potential curves (c) on the common Bi(111) plane across the anion series.

A first, and unexpectedly direct, expression of this equivalence is the range of electrode potential over which each interface can be imaged at all. Because *in situ* STM requires a stable tunnelling junction, the accessible imaging window is itself a local report of the anion|electrode interaction: an ordered, tunnelling-transparent adlayer permits imaging, an insulating adsorbed film blocks the tunnelling current, and strong specific adsorption accompanied by bismuth dissolution re-

moves the stable surface that imaging requires. The boundaries of these windows coincide, within experimental scatter, with the specific-adsorption onsets and the bismuth-dissolution limits determined from the capacitance–potential and voltammetric curves, which confirms that they are set by anion adsorption rather than by instrumental factors and provides an independent, spatially resolved measure of interfacial coupling to complement the area-averaged data [II].

At the weakly coordinating end of the series the anions produce no ordered adlayer that the tip can resolve, and the negatively charged interface is dominated by cation adsorption. For tetrafluoroborate this can be shown directly: across the entire electrochemically stable window the tip resolves an ordered lattice of 0.365 nm spacing, which matches the bare Bi(111) surface measured in aqueous solution [83] and is far smaller than any anion contact distance, so that it is the bismuth lattice itself, and not an adsorbed layer, that is imaged. This uninterrupted, full-window access is the operational meaning of surface inactivity at the local scale. The bis(trifluoromethanesulfonyl)imide anion, which sits beside tetrafluoroborate at the surface-inactive end of the capacitance scale, nonetheless issues an important caution, since at the local scale it does not behave in the same way: the negative half of the window again exposes the bare lattice (0.370 nm), but at positive charge a tunnelling-opaque blocking layer forms. Macroscopic surface inactivity, as defined from the capacitance response, therefore does not by itself guarantee a tunnelling-transparent interface, and the bulky imide evidently assembles into a blocking film at positive surface charge densities [II].

The transition to specific adsorption is therefore the region of interest, and the trifluoromethanesulfonate anion is particularly instructive because it occupies the boundary between a dielectric, film-forming layer and a genuinely specifically adsorbed one. Its adsorption at Bi(111) is reversible and film-like: on positive polarisation a layer forms above $E > -0.9$ V that is impermeable to the tunnelling current, so that imaging is lost, and the original surface is recovered on returning below -0.9 V [99]. The manner in which the layer blocks the current is itself diagnostic, since the response is non-resonant, consistent with the sulfonate group bonding to the surface bismuth atoms while presenting only its fluorine atoms to the tip. That an ordered, if weak, structure nonetheless forms is evident from the honeycomb-like Moiré pattern observed on some plateaus within the stable window, where the adsorbed ions register against the underlying lattice [99]. The pronounced sensitivity of this same OTf[−] layer to residual water, which reshapes the nanostructure and generates anomalous capacitance maxima at positive polarisation [99], is not incidental but defines the level of dryness required before the more strongly adsorbing halides can be interpreted without interference.

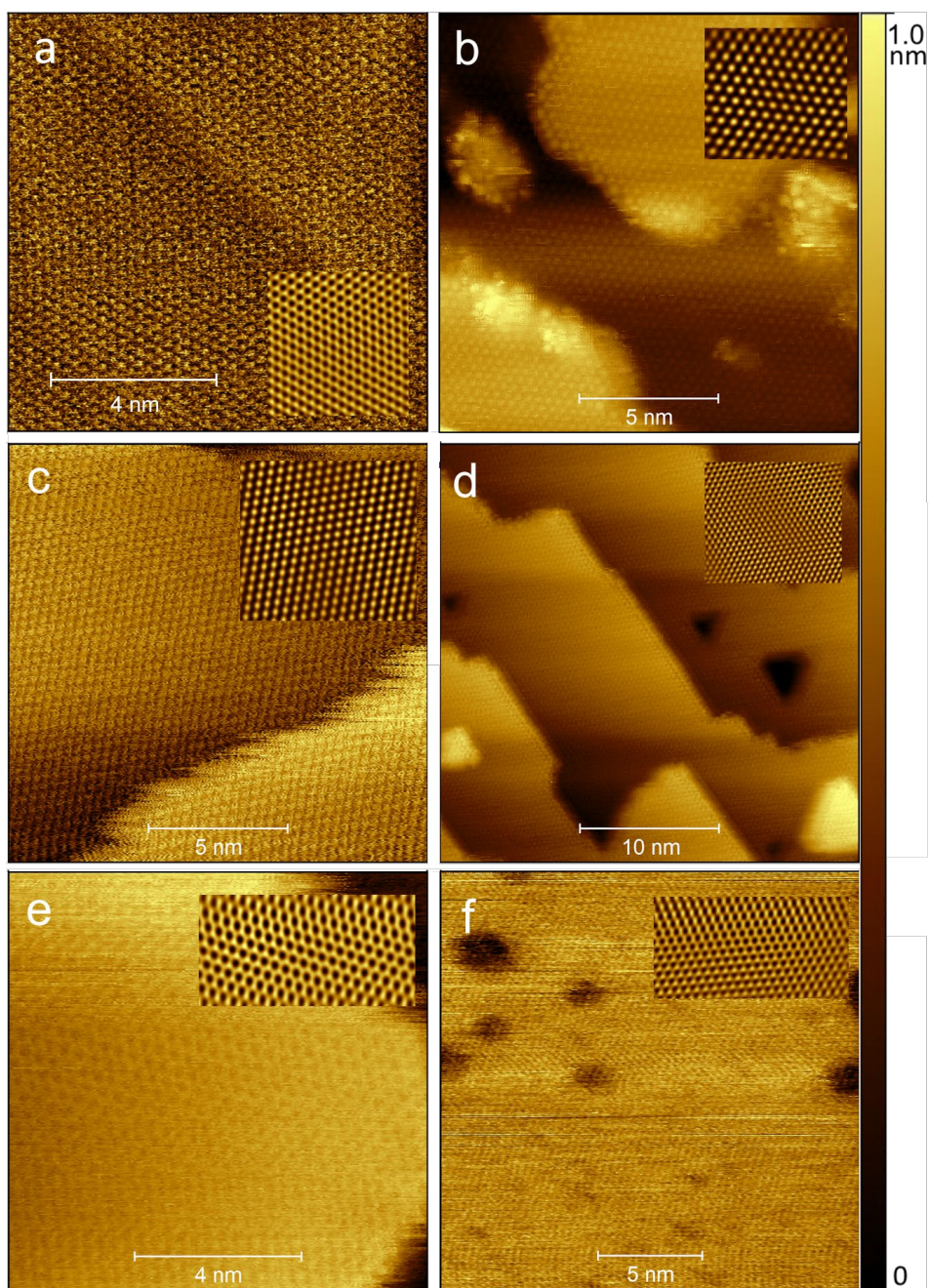


Figure 5. Anion-resolved fine structure on Bi(111): (a) I^- , (b) Br^- , (c) Cl^- , (d) MeSO_3^- , (e) TFSI^- and (f) BF_4^- , each with its fast Fourier transform inset. Panel (a) is adapted from ref. [III].

Higher in the series the faint modulation characteristic of the surface-inactive anions is replaced by a dense, self-supporting overlayer, and the interpretive task shifts from detecting order to establishing that this order belongs to the anion. Chloride remains a borderline case, giving only a weak Moiré structure at Bi(111), whereas bromide and iodide form dense adsorbed layers that dominate the capacitive response and are resolved directly as ordered superstructures [I]. When the chloride and bromide contents are raised to the highest values attainable at room temperature (limited by the solubility of the solid EMImCl and EMImBr salts in liquid EMImBF₄, and thus the closest realisable analogues of a pure halide ionic liquid), ordered fine structure is resolved for both, with spacings of 0.362 nm (Cl⁻) and 0.378 nm (Br⁻) [II]. These values are, however, ambiguous, since they coincide both with the Bi(111) lattice spacing and with the halide contact distances (twice the respective ionic radii), so that a commensurate, contact-packed halide adlayer cannot be distinguished from the bare lattice on spacing alone; that the structure is confined to a markedly narrower window (-1.0 to -1.7 V) than the full-window visibility of tetrafluoroborate, and shows no potential-dependent compression, nevertheless marks it as anion-controlled [II,III]. Two further observations support their assignment to the anions. The first is their robustness, the Br⁻ and I⁻ superstructures persisting over a potential range exceeding one volt with drastic reorganisation confined to the extreme limits [I], a stability more readily reconciled with a specifically bound, partially charge-transferred adlayer than with a labile ionic cloud. The second is a length-scale argument that recurs throughout this thesis: at Bi(01 $\bar{1}$) the imaged periodicity of the OTF⁻ layer, 1.3–1.4 nm, is several times the $\approx$ 0.4 nm bismuth spacing, so that the pattern cannot originate from the metal lattice and must instead reflect the adsorbed anions, the reversible and non-faradaic character of the process indicating that the ordering is electrostatic rather than the result of chemical bond formation [99].

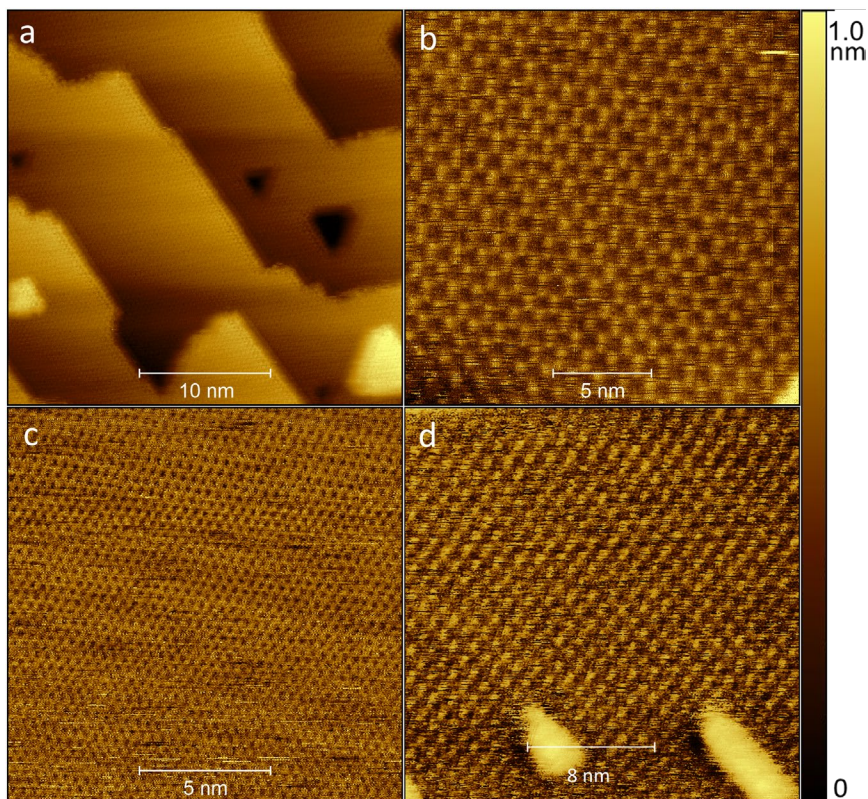


Figure 6. Bi(*hkl*) plane dependence of the fine structure: (a) MeSO₃⁻ at Bi(111), (b) MeSO₃⁻ at Bi(011̄), (c) I⁻ at Bi(011̄) and (d) OTf⁻ at Bi(011̄). Panels (c) and (d) are adapted from ref. [III] and ref. [99], respectively.

The methanesulfonate anion occupies the most diagnostic position in the series, since its capacitance response falls between the perfluorinated triflate and the halides, and its local behaviour matches neither limiting case. At negative charge no distinct adlayer is resolved on Bi(111), only the bismuth lattice, whereas on the denser Bi(011̄) plane an ordered, widely spaced sulfonate adlayer forms, of about 1.3 nm periodicity, that matches the triflate adlayer on the same plane (≈1.35 nm) rather than the close halide spacings [II,99]. The decisive observation, however, appears at positive charge.

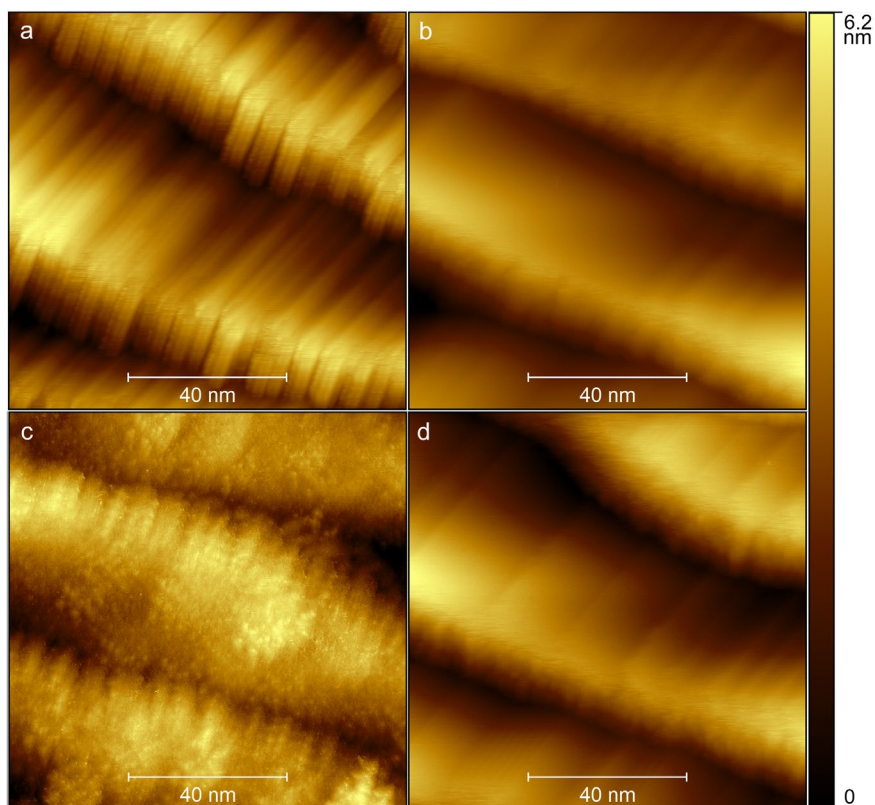


Figure 7. Same-area *in situ* STM sequence for Bi(011̄)|EMImMeSO₃, followed as a potential loop from most negative (−2.1 V, a) to most positive (−0.7 V, c) and back, showing ordered plateaus (−1.2 V, b), a transitional stage, the amorphous state at positive charge, and full recovery of the ordered surface on return to about −1.2 V (d).

6.3. The strongest specific adsorption: potential-dependent dynamics at Bi(*hkl*) | PMImI

If the anion series is understood as a progression of increasing specific-adsorption strength, then 1-propyl-3-methylimidazolium iodide (PMImI) represents its limiting case, and the principal finding of this work is that at this limit the distinction between the adsorbed layer and the electrode surface is no longer clear-cut. The iodide coverage is maximal and its specific adsorption is strong, with the consequence that the adlayer and the metal beneath it evolve together as the potential is scanned. This coupling is inaccessible to averaging electrochemistry and is the reason that high-speed video STM was required [III]. That the three low-index planes respond in three qualitatively different ways demonstrates that the electronic and reticular character of the electrode, treated in the previous section as a modulating influence, becomes at this adsorption strength a controlling one.

Table 1. Structural and electrochemical parameters of anion adlayers on Bi(*hkl*).

System (anion)	Plane	ρ_{atomic} (atoms nm ⁻²)	Coverage (signals nm ⁻²)	d_inter (nm)	E_stab, +(V)	E_stab, -(V)
PMImI (I⁻)	Bi(111)	5.59	6.30	0.428 ± 0.01	-0.8	-2.1
PMImI (I⁻)	Bi(001)	5.28	6.49	0.422 ± 0.01	-1.0	-2.1
PMImI (I⁻)	Bi(01 $\bar{1}$)	6.42	4.18	0.526 ± 0.01	-1.0	-1.5
EMImOTf (OTf⁻)	Bi(01 $\bar{1}$)	6.42	0.634	1.35 ± 0.05	-0.9	-2.1
1:2 EMImBF₄:EMImBr (Br⁻)	Bi(111)	5.59	8.08	0.378 ± 0.01	-1.0	-1.7
1:9 EMImBF₄:EMImCl (Cl⁻)	Bi(111)	5.59	8.81	0.362 ± 0.01	-1.0	-1.7
EMImMeSO₃ (MeSO₃⁻)	Bi(111)	5.59	8.67	0.365 ± 0.01	-0.8	-1.9
EMImMeSO₃ (MeSO₃⁻)	Bi(01 $\bar{1}$)	6.42	0.663	1.32 ± 0.05	-1.0	-1.6
EMImTFSI (TFSI⁻)	Bi(111)	5.59	8.42	0.370 ± 0.01	-0.9	-2.1
EMImBF₄ (BF₄⁻)	Bi(111)	5.59	8.67	0.365 ± 0.01	-0.1	-2.2

The Bi(111) plane (fig. 8) illustrates how strong iodide adsorption can, unexpectedly, stabilise a surface. Its triangular terraces, of step height 4.5 ± 0.2 Å, are retained through tens of polarisation cycles with the plane remaining monocrystalline, and the origin of this resilience is apparent in the potential dependence of the step dynamics [III]. At moderately negative potentials the step-edge fluctuations are strongly suppressed, an effect best interpreted as the mechanical consequence of iodide binding at the terrace edges, since the adsorbed anions stabilise intermediate bismuth species and raise the barrier to the detachment and reattachment of edge atoms. Toward the limits of polarisation this stabilisation is relieved, the edges blurring at the most negative potentials as cathodic dissolution begins and dissolution reappearing at the least negative potentials, yet the surface nevertheless preserves its order because redeposition occurs preferentially at the terrace edges rather than on the plateaus. This last point accounts for an otherwise unexpected observation, namely the absence of amorphous bismuth deposits after prolonged cycling: a surface that redeposits only at its steps does not roughen, so that the Bi(111)|PMImI interface behaves as a dynamically stable, effectively self-healing system rather than one that degrades with cycling.

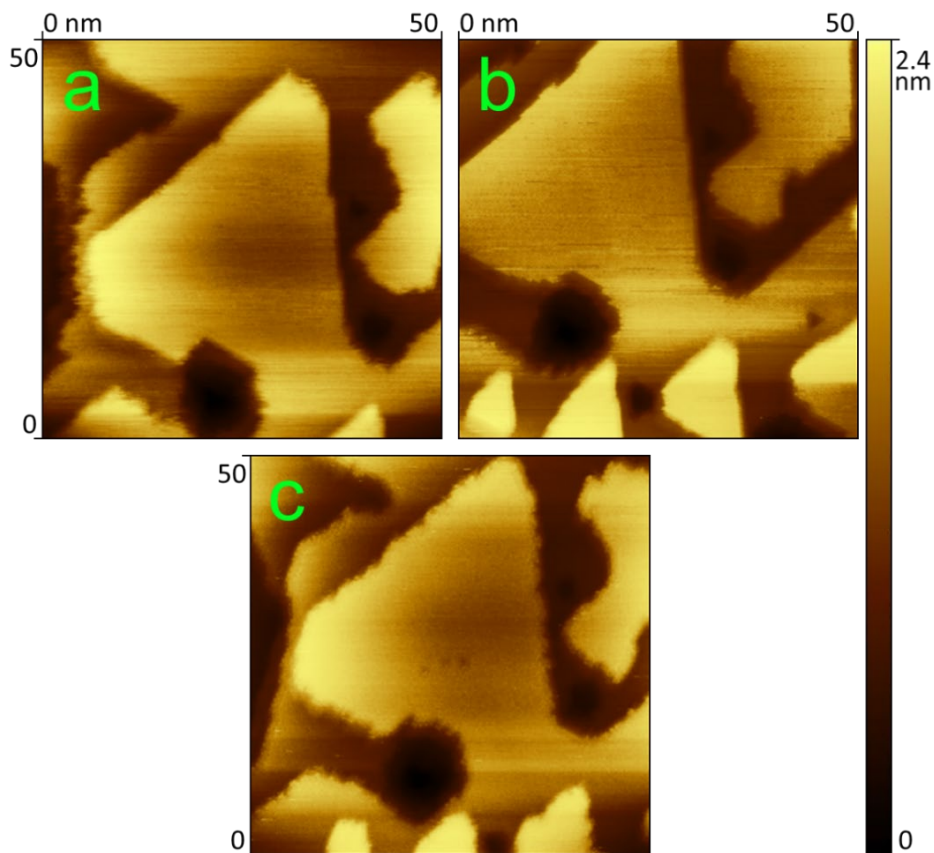


Figure 8. Bi(111)|PMImI interface images taken at $I_f=0.06$ nA; (a) most negative potential at -2.1 V, (b) moderately negative potential at -1.6 V (c) the least negative potential at -0.8 V.

The Bi(001) plane (fig. 9) displays the converse tendency, in which iodide adsorption drives structural change rather than suppressing it, and does so reversibly. As the polarisation is reduced the surface passes through a defined sequence of sawtooth, wave-like and finally rod-like structures [III]. The rods are the most revealing of the three, since they arise not from uniform dissolution but from a spatially directed, fragmentary process that begins at the terrace edges and cuts diagonally into the plateaus; that this carving subsequently arrests, leaving stable rods, points to triiodide formation as the process that limits further dissolution. The significance of the sequence lies in its reversibility, which video imaging shows to be independent of both the direction and the number of polarisation cycles. This reversibility is the decisive argument that the transformation is a genuine, thermodynamically governed surface reconstruction rather than a stochastic dissolution–redeposition equilibrium, a distinction that can be established only by following the same terrace through repeated cycles in real time.

The Bi(01 $\bar{1}$) plane extends the phenomenon furthest, since here the reorganisation is no longer confined to the anion layer but also involves the substrate. The striped plateaus observed at the most negative potentials flatten as the polarisation is reduced, while the terrace edges reorganise into ordered rows through the physical repositioning of bismuth atoms [III]. The operation of two mechanisms together, anion ordering and metal-atom displacement, accounts for the complexity of the transition, but its greater importance is what it reveals about causality. Imaged in the OTf⁻ liquid, the same plane reconstructs in the opposite polarisation direction [99]; since only the anion has been changed, the identity of the adsorbing anion, and not the imidazolium cation common to both systems, must determine the pathway of the transformation. This comparison constitutes one of the strongest single pieces of evidence in the thesis that the anion is the governing variable of the compact layer.

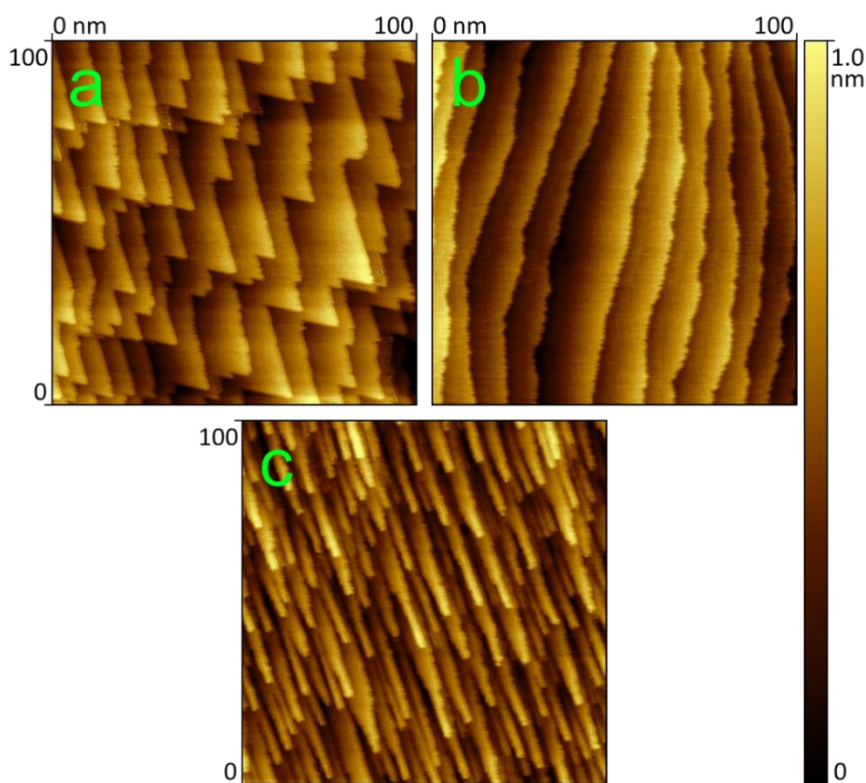


Figure 9. Bi(001)|PMImI under various polarization conditions, images taken at $I_t = 0.06$ nA; (a) saw-tooth like surface at -2.2 V, (b) wave like at -1.2 V, (c) rod like structure at the least negative potential at -0.83 V.

The fine-structure (fig. 10) analysis underlies all three cases, confirming that the imaged periodicity corresponds to the iodide adlayer and, at the same time, turning the STM contrast into a measure of the adsorption. The measured inter-signal distances do not match the bismuth radii but agree with the ionic radius of iodide (0.206 nm), identifying the pattern as a dense iodide overlayer [III]. More subtly, the same features appear as bright protrusions at less negative potentials and as dark depressions at more negative ones, and this inversion carries mechanistic information. Where partial charge transfer from iodide to bismuth is appreciable, that is, where specific adsorption is strong, the tunnelling current flows from the adlayer to the tip and the ions are imaged as protrusions; where the adsorption weakens, the iodide instead obstructs the current from the surface and is imaged as a depression. The contrast is therefore not an artefact but a local readout of the strength of the ion–surface bond. The comparison with aqueous halide adsorption completes the argument begun in Section 6.2. In dilute aqueous solution the iodide adlayer is known to compress under positive polarisation [101], whereas no such electrocompression is observed here, and the explanation follows from the nature of the medium: PMImI is more than two orders of magnitude richer in iodide than a dilute aqueous solution and provides essentially no anion solvation shell, so that a dense adlayer, whose closest iodide approach is already comparable to that reached on Au(111) only at the most positive aqueous potentials, forms at considerably more negative polarisation and cannot be compressed further [III]. The iodide end-member thus expresses the anion-controlled behaviour of the whole series in its most pronounced form, the strongest specific adsorption not only producing the densest layer but coupling it to the metal, so that the compact layer and the electrode reconstruct together, a regime that by its nature can be reached only by local, time-resolved imaging.

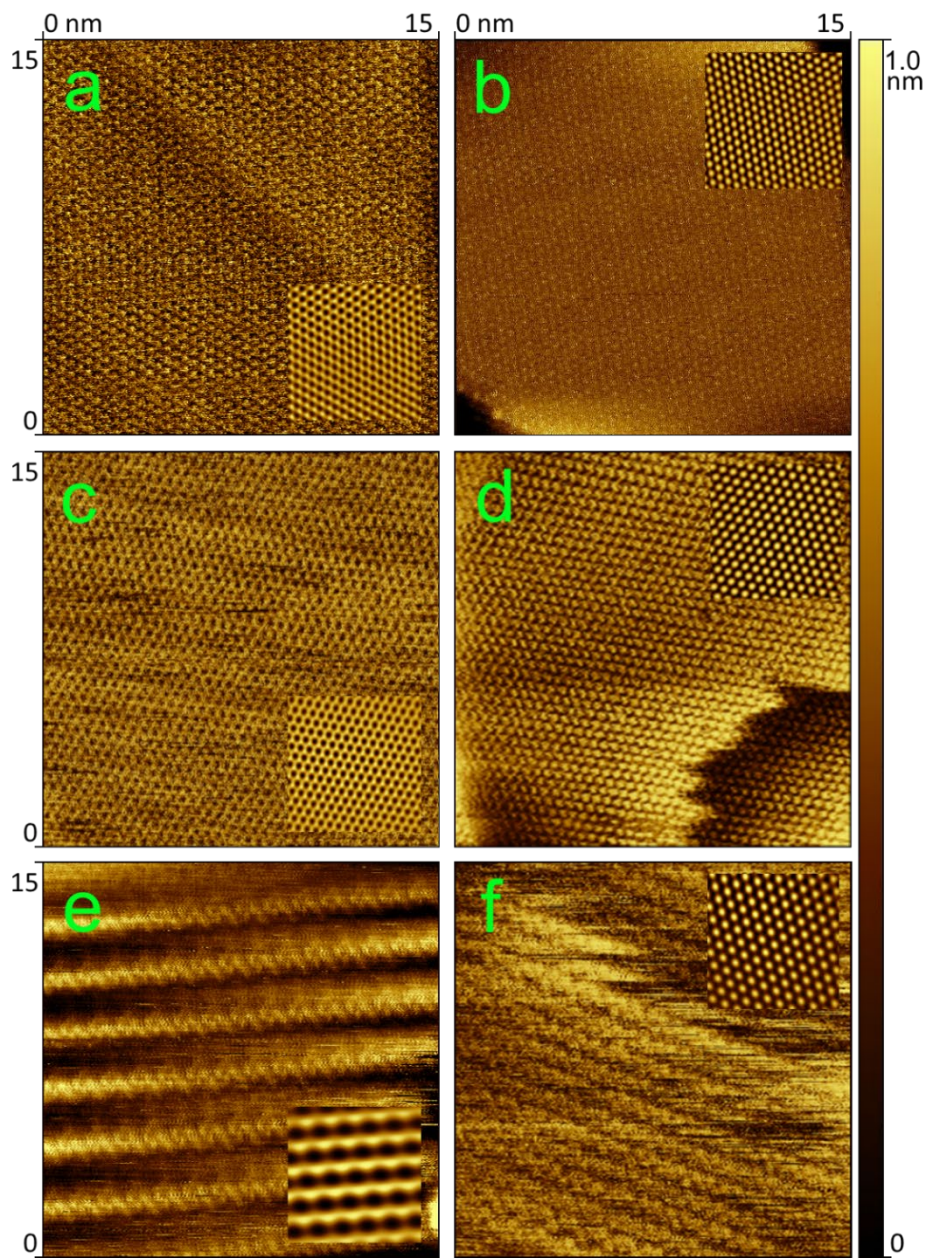


Figure 10. Fine structure images of $\text{Bi}(hkl)|\text{PMImI}$ at different electrode potential, indicated in the figure; (a,d) $\text{Bi}(111)$, (b,e) $\text{Bi}(001)$ and (c,f) $\text{Bi}(01\bar{1})$.

6.4. Organic self-assembly at the semi-metallic Sb(111) interface

The ionic-liquid systems considered so far concern the ordering of the electrolyte's own ions, in which specific adsorption and partial charge transfer are the dominant interactions. The aqueous adsorption of bipyridine at Sb(111) provides a complementary test of the same underlying idea, since here the ordered compact layer is built not by a monatomic anion but by an organic molecule, whose assembly is governed by a different balance of forces: the binding of the molecule to the surface, the lateral interaction between adsorbed molecules, and the stabilising role of co-adsorbed electrolyte ions. That an ordered two-dimensional layer can be formed and imaged on a genuine semi-metal, rather than on the metallic electrodes to which such self-assembly is usually restricted, is itself a significant extension of the phenomenon, and it rests on the same reconstruction-free Sb(111) baseline established for the aqueous surface [84].

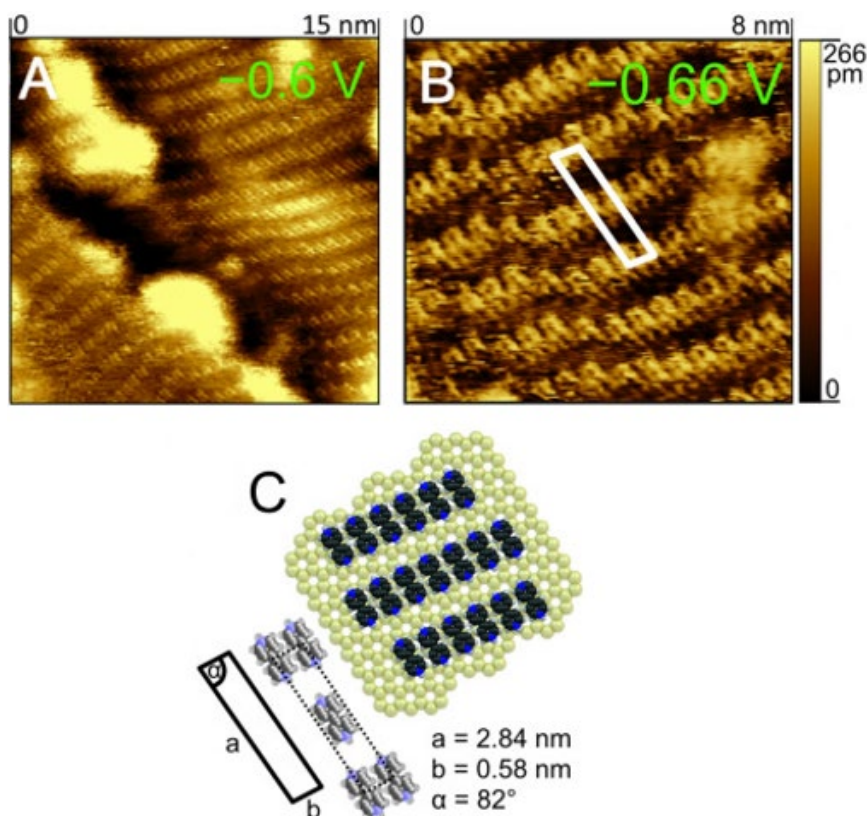


Figure 11. (A,B) High resolution *in situ* STM images of 4,4'-BP self-assembled monolayers at the Sb(111) electrode surface; (C) calculated unit cell dimensions and proposed packing model for 4,4'-BP molecules.

For the 4,4' isomer a stable, reversible two-dimensional monolayer is formed, consisting of parallel molecular rows [IV]. The measured coverage and inter-row spacing indicate that the molecules lie flat and are bi-protonated, their positively charged ends screened by co-adsorbed, solvated sulphate anions that occupy the voids between the rows; the resulting packing, with a surface concentration close to that reported for the flat-lying arrangement on metallic electrodes [74–76], shows that the co-adsorbed anion is not a spectator but an integral part of the ordered structure. The electrochemical signature is consistent with this picture, a small capacitance feature developing on the capacitance–potential curve at the onset of ordering whose position depends only weakly on pH, while the reduced high-frequency capacitance indicates that an adsorbed layer is present even at the more positive potentials [IV]. It is notable that the ordered adlayer is stable across a comparatively wide potential window without undergoing the phase reorientations that are common at metallic electrodes, which suggests that, at the low-carrier-density semi-metal, the balance between molecule–surface binding and lateral interaction favours a single, robust packing rather than a sequence of competing phases.

The contrast with the 2,2' isomer is instructive precisely because the two molecules differ only in the relative position of their nitrogen atoms. For 2,2'-bipyridine no ordered adlayer could be resolved; only the atomic lattice of Sb(111) was imaged, and under a markedly higher level of measurement noise, with some regions obscured by a thick, non-structured organic deposit [IV]. That so small a change in molecular geometry should determine whether an ordered layer forms at all reinforces the more general conclusion of this thesis, namely that interfacial order at a semi-metal is decided by a finely poised balance of interactions, in which the geometry and protonation state of the adsorbate and the availability of a stabilising counter-ion are as important as the strength of the surface bond itself.

A final observation delimits the regime in which this ordered layer exists. At sufficiently negative polarisation the bipyridine is reduced, and the resulting partially reduced species polymerise and deposit as globular structures, preferentially at the terrace edges, so that the surface roughens irreversibly [IV]. The clear separation between the reversible ordering at moderate potentials and the irreversible roughening at negative potentials is important for interpretation, since it distinguishes genuine adlayer formation from a faradaic degradation of the adsorbate. Throughout, the behaviour is governed by pH, which sets both the protonation state of the bipyridine and the stability window of the antimony surface; for this reason the aqueous, protonation-driven chemistry described here is treated as a self-contained case and is not extended to the aprotic ionic-liquid systems, where no such protonation equilibrium exists.

6.5. General discussion: specific adsorption as the organising principle of the compact layer

Taken together, the four systems examined in this thesis support a single, consistent account of the compact layer at sp-metal single crystals, in which its structure is set by specific adsorption and can be read directly by *in situ* STM. Two variables recur throughout. The first is the surface activity of the adsorbing species. Across the ionic-liquid anion series this activity determines, in a graded manner, whether the interface shows no resolvable order, a weak dielectric or Moiré-type layer, a dense electrostatic superstructure, or, at the strongest adsorption, a coupled reconstruction of adlayer and metal. The second is the electronic and reticular character of the electrode plane, which at weak adsorption merely modulates the adlayer but, in the strongly adsorbing iodide liquid, becomes decisive, giving three qualitatively different responses for the three bismuth planes. The medium provides a third, modulating factor: the presence or absence of a solvation shell distinguishes the compressible aqueous halide adlayer from the incompressible one formed in the pure ionic liquid, and the sensitivity of the OTf⁻ layer to trace water shows that even small amounts of a co-adsorbing solvent can reshape the interface.

A further finding cuts across the whole series and is, in itself, methodological: the potential window over which each interface can be imaged is a local diagnostic of the anion|electrode interaction that resolves distinctions the averaged capacitance cannot. Tetrafluoroborate and the bis(trifluoromethanesulfonyl)imide are indistinguishable on the capacitance scale, yet only the former remains tunnelling-transparent across the entire window while the latter forms a blocking film at positive charge; and methanesulfonate, whose capacitance response does no more than place it between the triflate and the halides, is revealed to undergo a fully reversible order-to-disorder reconstruction that neither the halides nor the perfluorinated triflate display. It is in this sense that the identity of the anion, rather than its capacitance-derived surface activity alone, governs the structure, imageability and reconstruction pathway of the compact layer [II].

The aqueous bipyridine system, although driven by a different set of interactions, fits the same framework rather than standing apart from it. In both the ionic and the organic cases an ordered compact layer forms only when the balance between the adsorbate–surface bond, the lateral interactions within the layer, and the stabilisation provided by a co-adsorbed counter-ion is favourable; what differs is the identity of the dominant term, partial charge transfer for the specifically adsorbed halides, and π -interaction with anion screening for the protonated organic molecule. The recurring importance of the co-adsorbed anion, whether as the species that stabilises intermediate bismuth compounds at the terrace edges of Bi(*hkl*)|PMImI or as the sulphate that screens the bipyridine rows at Sb(111), suggests that the composition of the compact layer is more usefully thought of in terms of the whole ensemble of co-adsorbed species than in terms of any single ion.

Two broader points follow. Methodologically, the results demonstrate that local, and where necessary time-resolved, imaging is not merely a complement to classical electrochemistry but is indispensable for the questions posed here. Cyclic voltammetry and impedance identify the potentials at which the interface changes, but they cannot distinguish an adlayer reorganisation from a substrate reconstruction, nor a reversible transformation from an irreversible one; only the direct observation of the surface, in the iodide case through many polarisation cycles in real time, can make these distinctions. The second point concerns scope: the halide adlayers characterised in greatest structural detail elsewhere are those on the noble metals, where diffraction and *in situ* STM have resolved iodine and bromide layers on Au(111), Ag(111) and Pt(111) [102,103,104,105]; the present results indicate that the same organising principle extends to the sp-metals, but with the electronic and reticular character of the substrate exerting a considerably stronger influence on the structural outcome.

7. SUMMARY

This thesis has examined the structure of the electrical double layer and the specific adsorption of ions and molecules at sp-metal single-crystal electrodes, using *in situ* scanning tunnelling microscopy as the primary, real-space probe and cyclic voltammetry and electrochemical impedance spectroscopy as the supporting electrochemical framework. Two complementary electrolyte environments were studied, solvent-free room-temperature ionic liquids and aqueous solutions, on the bismuth Bi(111), Bi(001) and Bi(01 $\bar{1}$) planes and on the semi-metallic Sb(111) plane. Because these sp-metals do not undergo fast potential-induced reconstruction within their ideally polarizable windows, they provided a stable reference surface against which any adsorbate-induced structural change could be assigned unambiguously to the adlayer rather than to the metal.

The central result is that, at a semi-metal, the compact layer is assembled primarily by the anion, and that *in situ* STM resolves this as a graded sequence of interfacial order that follows the specific-adsorption strength of the anion. Across the imidazolium ionic liquids the accessible imaging window itself proved to be a sensitive local diagnostic of the anion–electrode interaction, its limits coinciding with the electrochemically determined adsorption onsets and dissolution limits. The surface-inactive tetrafluoroborate exposed the bare Bi(111) lattice across the entire stable window, whereas the equally capacitance-inactive bis(trifluoromethanesulfonyl)imide formed a tunnelling-opaque blocking film at positive charge, demonstrating that macroscopic surface inactivity does not guarantee a tunnelling-transparent interface. The chloride and bromide mixtures, taken to their highest attainable concentrations, produced ordered fine structure whose spacing was consistent with both the substrate lattice and the halide contact distance, while methanesulfonate occupied a genuinely intermediate position, forming a widely spaced sulfonate adlayer on Bi(01 $\bar{1}$) that underwent a fully reversible order-to-disorder surface reconstruction at positive charge, imageable where the isostructural triflate is not because of the CH₃-versus-CF₃ substitution of the head group.

In its pure iodide liquid the anion series reaches its limiting case, where the specific adsorption is strong enough that the adlayer and the metal reconstruct together. High-speed video STM revealed three qualitatively distinct plane responses: the Bi(111) plane remained monocrystalline and effectively self-healing through an edge-localised dissolution–redeposition equilibrium; the Bi(001) plane passed reversibly through sawtooth, wave and rod structures, the last limited by triiodide formation; and the Bi(01 $\bar{1}$) plane reorganised through combined anion ordering and bismuth-atom displacement, the direction of the reconstruction reversing when iodide was replaced by triflate, which is direct evidence that the anion, and not the common cation, governs the transformation pathway. Fine-structure analysis identified the imaged periodicity as a dense iodide overlayer and turned the potential-dependent inversion of the STM

contrast into a local measure of partial charge transfer, while the absence of electrocompression confirmed the role of the solvent-free medium.

In aqueous solution the same organising principle held for an organic adsorbate. At Sb(111) the 4,4'-bipyridine isomer formed a stable, reversible two-dimensional monolayer of flat-lying, bi-protonated molecules stabilised by co-adsorbed sulphate, whereas the 2,2' isomer produced no ordered layer, showing that interfacial order at a low-carrier-density semi-metal is decided by a finely poised balance of molecule-surface, intermolecular and co-adsorbed-ion interactions.

Taken together, these studies establish that the identity of the anion, rather than its capacitance-derived surface activity alone, controls the structure, the imageability and the reconstruction pathway of the compact layer, modulated by the electronic and reticular character of the electrode plane and by the presence or absence of a solvation shell. The recurring importance of the co-adsorbed species suggests that the compact layer is best understood as a whole ensemble rather than as any single ion. Methodologically, the work demonstrates that local, and where necessary time-resolved, imaging is indispensable for distinguishing adlayer reorganisation from substrate reconstruction and reversible from irreversible change. Finally, the same specific adsorption of halide anions that structures and reconstructs the single-crystal compact layer underlies the pseudocapacitive charge storage exploited in halide-containing ionic-liquid supercapacitors, so that these single-crystal results provide a molecular-scale basis for interpreting the energy-storage characteristics of ionic-liquid-based electrode interfaces.

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9. SUMMARY IN ESTONIAN

Elektrilise kaksikkihi ehitus ja spetsiifiline adsorptsioon sp-metallide monokristallelektroodidel: *in situ* STM uuring

Käesolevas doktoritöös uuriti elektrilise kaksikkihi ehitust ning ionide ja molekulide spetsiifilist adsorptsiooni sp-metallide monokristalsetel elektroodidel, kasutades põhimeetodina *in situ* skaneerivat tunnelmikroskoopiat (STM) ning seda toetavate meetoditena tsüklilist voltammeetriat ja elektrokeemilist impedants-spektroskoopiat. Vaatluse alla võeti kaks teineteist täiendavat elektrolüüdikeskkonda: toatemperatuurised ioonsed vedelikud ja vesilahused, vismuti tahkudel Bi(111), Bi(001) ja Bi(01 $\bar{1}$) ning poolmetallilisel Sb(111) tahul. Kuna need sp-metallid ei rekonstrueeru oma ideaalse polariseeritavuse piirkonnas kiiresti, moodustavad nad stabiilse võrdluspinnale, mille suhtes saab iga adsorbaadist tingitud struktuurimuutuse üheselt omistada adsorptsioonikihile, mitte metallile endale.

Töö keskne tulemus on, et poolmetallil kujundab kompaktse kihi eelkõige anioon ning et *in situ* STM võimaldab seda näha astmelise korrastatuse reana, mis järgib aniooni spetsiifilise adsorptsiooni tugevust. Imidasooliumipõhiste ioonsete vedelike korral osutus kujutamiseks rakendatav potentsiaalivahemik ise tundlikuks lokaalse anioon-elektrood vastastikmõju näitajaks: selle piirid langesid kokku elektrokeemiliselt määratud adsorptsiooni aluspotentsiaalide ja vismuti lahustumispiiridega. Pindinaktiivne tetrafluoroboraat anioon võimaldas kogu stabiilses potentsiaalivahemikus näha metallset Bi(111) võret, samas kui mahtuvuslikult inaktiivne bis(trifluorometaansulfonüül)imiid moodustas positiivsetel pinnalaengutel tunnelvoolu suhtes blokeeriva kihi. See näitab, et makroskoopiline pindinaktiivsus ei taga tunnelvoolu suhtes läbitavat piirpinda. Kloriidi ja bromiidi segud andsid korrastatud peenstruktuuri, mille vahekaugus ühtis nii aluspinnale võre kui ka halogeniidi kontaktkaugusega. Metaansulfonaat hõivas vahepealse positsiooni: Bi(01 $\bar{1}$) tahul moodustas ta laia vahega sulfonaatkihi, mis positiivsel pinnalaengul läbis täielikult pöörduva, korrastatuse kadumise ja taastumisega kulgeva pinna rekonstruktsiooni ning oli kujutatav seal, kus struktuurilt sarnane triflaad mitte: põhjuseks sulforühma CH₃- versus CF₃-asendus.

Puhtas jodiidses ioonses vedelikus jõuab anioonide rida oma piirjuhtumini, kus spetsiifiline adsorptsioon on nii tugev, et adsorptsioonikiht ja metall rekonstrueeruvad koos. Kiire (video-) STM abil ilmnesevad kolme tahu selgelt erinevad käitumised: Bi(111) tahk säilitas monokristalse ehituse ja käitus sisuliselt isetaastavana astmeservades paikneva lahustumis-taassadenemistasakaalu kaudu; Bi(001) tahk läbis pöördvalt saehamba-, laine- ja vardakujulised struktuurid, millest viimast piiras trijodiidi teke; Bi(01 $\bar{1}$) tahk korrastus ümber nii anioonikihi järjestumise kui ka vismutiaatomite ümberpaiknemise kaudu, kusjuures rekonstruktsiooni suund pöördus, kui jodiid asendati triflaadiga. See on otsene tõend, et ülemineku teed määrab anioon, mitte ühine katioon. Peenstruktuuri analüüs näitas, et kujutatud perioodilisus vastab tihedale jodiidkihile, ning STM

kontrasti potentsiaalset sõltuv pöördumine (heledad külmud versus tumedad süvendid) andis kohaliku mõõdu osalisest laenguülekandest. Elektrokompresiooni puudumine kinnitas lahustivaba keskkonna määravat rolli.

Vesilahuses kehtis sama korraldav põhimõte ka orgaanilise adsorbaadi puhul. Sb(111) tahul moodustas 4,4'-bipüridiin stabiilse, pöörduva kahemõõtmelise monokihi pinnaga paralleelselt asetunud diprotoneeritud molekulidest, mida stabiliseerisid kaasadsorbeerunud sulfaatioonid, samas kui 2,2'-isomeeri puhul isekorrastuvat kihti ei täheldatud. See näitab, et korrastatus poolmetalli piirpinnal määratakse molekuli-pinna, molekulidevaheliste ja kaasadsorbeerunud ionide vastastikmõjude peene tasakaaluga.

Kokkuvõttes näitavad need uuringud, et kompaktse kihi struktuuri, kujutatavuse ja rekonstruktsiooni teed määrab aniooni olemus, mitte üksnes selle mahtuvusest tuletatud pindaktiivsus; seda mõjutavad omakorda elektroodi tahu elektroonsed omadused ja aatomtihedus ning solvaatkihi olemasolu või puudumine. Kaasadsorbeerunud osakeste korduv olulisus viitab sellele, et kompaktset kihti on otstarbekam käsitleda kogu osakeste kogumina, mitte üksiku iooni kaudu. Metoodiliselt näitab töö, et kohalik ning vajadusel ajaliselt lahutatud kujutamine on vajalik, et eristada adsorptsioonikihi ümberkorraldust aluspinna rekonstruktsioonist ning pöörduvat muutust pöördumatust. Lõpuks seob sama halogeniidaanioonide spetsiifiline adsorptsioon, mis kujundab ja rekonstrueerib monokristalse kompaktse kihi, uuritud nähtused rakendusliku kontekstiga: just see adsorptsioon on halogeniide sisaldavate ionvedelik-elektrolüütidega superkondensaatorite pseudomahtuvusliku laengusalvestuse aluseks. Seega annavad monokristallidel saadud tulemused molekulaarse tasandi aluse ioonsetel vedelikel põhinevate elektrod-piirpindade energiasalvestuslike omaduste tõlgendamiseks.

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11. PUBLICATIONS

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