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Study of In-Plane and Interlayer Interactions During Aluminum Fluoride Intercalation in Graphite: Implications for the Development of Rechargeable Batteries

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ABSTRACT: The electrolyte intercalation mechanism facilitates the insertion and extraction of charge into the electrode material in rechargeable batteries. Aluminum fluoride (AlF₃) has been used as an electrolyte in rechargeable aluminum batteries with graphite electrodes, demonstrating improved reversibility of battery charging and discharging processes; however, the intercalation mechanism of this neutral molecule in graphite is so far unknown. In this work, we combine scanning tunneling microscopy (STM) in ultrahigh vacuum conditions, calculations based on density functional theory, and largescale molecular dynamics simulations to reveal the mechanism of AlF₃ intercalation in highly oriented pyrolytic graphite (HOPG). We report the formation of AlF₃ molecule clusters between graphite layers and their selfassembly by graphene buckling-mediated interactions and explain the origin and distribution of superficial *blisters* in the material. Our findings have



implications for understanding the relationship between the mobility and clustering of molecules and the expansion of the anode material. This, in turn, paves the way for future enhancements in the performance of energy storage systems.

KEYWORDS: intercalation, graphite, AlF₃, STM, DFT, molecular dynamics, battery

INTRODUCTION

Renewable and sustainable energy storage technologies are nowadays a strategy to mitigate climate change, environmental pollution, and fossil fuel scarcity.^{1,2} Electrochemical energy storage, particularly rechargeable batteries, is considered one of the solutions to supply or back up clean electricity in portable devices. While lithium-based rechargeable batteries have been developed for various applications and successfully commercialized, much research has focused on exploring alternative materials that are abundant in nature and less reactive, which reduces self-ignition risk.^{3,4} In this sense, research on alternatives to lithium (Li) in rechargeable batteries is dominated mainly by systems with sodium (Na),^{5,6} magnesium $(Mg)^{7,8}$ or aluminum (Al).⁹⁻¹¹ The anode material is equally important to charge carrier ions. Graphite shows potential as an anode material for rechargeable metal-ion batteries because of its high abundance and low cost.^{12,13} The systems with superior rate performance and cycling stability are obtained through a unique potassium-solvent cointercalation mechanism in natural graphite.¹³ Recently, graphite intercalation compounds (GICs) involving aluminum ions (Al-GIC) have emerged as a promising type of rechargeable batteries due to their high gravimetric density, lower reactivity, and easy handling.^{14,15} Aluminum ion rechargeable batteries (AIBs) have the redox property of involving three electrons during electrochemical processes resulting in a higher volumetric

energy density than Li batteries, which is attracting increasing attention from researchers.^{9,16–19} While the most investigated compounds in this class are AlCl₃,^{20–24} recently, aluminum fluoride AlF₃ is proposed as a potential candidate for electrolytes in batteries composed of graphite cathodes and aluminum anodes.^{25,26} However, one of the main challenges lies in understanding the mechanisms governing the electrochemical performance of graphene anodes for rechargeable batteries.^{12,13} Infrared spectroscopy and X-ray diffraction¹³ measurements have demonstrated the intercalation and co-intercalation mechanism of large molecular complexes. Yet a complete outline of the interplay of graphene interactions with molecules and between the molecules remains unclear. The reason for this is the inaccessibility of the system for in situ measurements under well-defined conditions.

In this paper, we focus on graphite as an anode material and AlF_3 molecule as an electrolyte applying a 2-fold multiscale approach based on the systematic nondestructive experimental

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Figure 1. (a) Schematic side view of the different HOPG roughness quality used in the RBS experiments to determine the dependence of the vertical penetration depth of AlF_3 on the topology. (b) STM-UHV preparation and characterization of AlF_3 intercalated in the HOPG. (c, d) RBS experimental spectra (represented by black squares) and fit (full line). In their insets: a bullet of the model obtained from each fit indicates the atomic percentage and depth of the intercalations. Schemes a, c, and d adapted from Candia et al.²⁸

investigation of the intercalation process using scanning tunneling microscopy (STM) under ultrahigh vacuum (UHV) conditions and large scale molecular dynamics simulations of multilayer graphite surface, complemented with density functional theory (DFT) calculations. While a complete outline of intricate interactions of various ions and molecular complexes remains elusive, the comprehensive findings concerning AlF₃ could provide valuable insights that can be extended to understand the intercalation process for a broader class of materials. On its own, AlF₃ has been proposed as an electrolyte in Al batteries with graphite cathodes, since cyclic voltammetry (CV) showed that it protects the electrode during the cycling process, as well as, improves the reversibility, durability, and charge transfer of the device.^{25–27} The computational results suggest that using the AlF₄ anion instead of AlCl₄ could increase the specific capacity and operating voltage of an eventual rechargeable battery.²⁷ A notable experimental study of AlF₃ by Wang et al.²⁵ documented a compelling phenomenon: the introduction of a small quantity of AlF₃ into the liquid electrolyte resulted in improved battery reversibility. The potential utilization of AlF₃ molecules as guest species within the graphite matrix not only provides a platform for understanding solvent attributes of AlF₃ but also represents a route for comprehending its incorporation dynamics. Recently, we found that AlF₃ molecules are incorporated through the steps-edges present on the HOPG surface, locally separating the carbon layers from the substrate without forming chemical bonds and altering its local density of states (LDOS).²⁸ Our theoretical study on the

bulk,²⁹ showed that the AlF₃ molecule is energetically unstable on HOPG surfaces and instead intercalates in stable nonplanar configuration due to attractive van der Waals forces between the HOPG layers. Despite the progress in the study of AlF₃, the mechanism of the intercalation of this molecule as a function of the concentration of intercalating molecules should be understood.

The results presented in this study support the concept of mixed staging for the intercalation of AlF_3 in graphite. We explore the topographical and electronic properties of AlF_3 molecules intercalating between HOPG layers. The STM images are acquired at room temperature (RT) for different exposure doses. The experimental results are compared with DFT calculations and molecular dynamics simulations, allowing us to make conclusions about interactions and structures within the material, which influence the mobility of molecules and clustering, the anode material expansion, and the resulting performance of the system for energy storage and in particular rechargeable batteries.

EXPERIMENTAL AND THEORETICAL SETUP

In Figure 1, we describe the methodologies employed to obtain and characterize samples based on our previous investigations.²⁸ The roughness of the substrate plays a determinant role in the thickness restriction of AlF_3 interlayer aggregates, and this phenomenon occurs due to diffusion from the stepped edges into the interlaminar space of the host material. Figure 1a shows a schematic lateral representation of two different quality types of HOPG used in the experiments, specifically HOPG with a low and high density of staggered edges, identified as "HOPG A" and "HOPG B", respectively, Bruker grade I



Figure 2. Topography STM images (30 nm \times 30 nm) of HOPG after the deposition of (a) 1.2 and (b) 3 ML of AlF₃ at 300 K. Both images were acquired with a sample bias voltage of V_S = 500, 375 mV and tunnel currents I_T = 0.001, 0.002 nA, respectively. (c, d) Height threshold obtained by applying the "flooding" procedure to images a and b.

and II. Figure 1b illustrates the deposition, intercalation, and characterization process performed by STM under ultrahigh vacuum (UHV) conditions. On the other hand, Figure 1c and d shows the experimental data obtained by RBS (represented by squares), accompanied by simulated spectra generated from fitting models, represented by lines. In addition, a general descriptive scheme encapsulating the various components used in the data fitting is included. The interleaving process originates predominantly from these staggered edges. As a result, in the context of an ideal defect-free graphite (not depicted here), intercalation would lack feasibility. In a more practical scenario, an 'A' type HOPG sample would result in a thin interlayer, while a 'B' type would lead to a thicker one. For our experiments, we selected substrates ascribed to the "HOPG A" type resulting in a 24 nm penetration depth of AlF₃. In the Supporting Information, you can access a summary of the relevant experimental results obtained through previously published RBS studies. For a more comprehensive perspective refer to Candia et al.²

STM-UHV. Highly ordered pyrolytic graphite (HOPG from Bruker, UK, 12 mm \times 12 mm \times 1 mm) substrates were used for all of the experiments. The clean HOPG surfaces were obtained by tape cleavage in air and immediately loaded into the secondary reaction chamber of the STM-UHV, to be transferred after depositions to the main chamber of the system. AlF₃ molecules (CERAC INC., Milwaukee, Wisconsin, USA, 99.5%) were thermally deposited in the HOPG surface normal direction, from a Knudsen cell charged with the anhydrous salt heated at 900 K, 200 mm apart from the substrate. The deposition was achieved under UHV conditions (during evaporations at a pressure in the high range of 10^{-10} mbar) by a rate between 6×10^{-3} and 2×10^{-2} ML s⁻¹, and keeping the substrate at room temperature (RT). STM imaging was performed by using a homemade Beetle scanning tunneling microscope in a UHV chamber with a base pressure in the low 10^{-10} mbar range. All STM

measurements were acquired at room temperature in the constant current mode using electrochemically etched tungsten (W) tips, with bias voltages and tunneling currents between 200 to 800 mV and 0.001 to 0.02 nA, respectively. These polycrystalline W tips were routinely cleaned by Ar^+ ion bombardment in UHV. Acquisition and image processing was performed using the WS×M free software.³⁰

DFT. *Ab initio* calculations on the framework of DFT were performed using OpenMx3.9 package (Open source package for Material eXplorer),^{31,32} which incorporates norm-conserving pseudo-potentials and pseudoatomic localized orbitals (PAOs). The electronic exchange-correlation effects were treated within the generalized gradient approximation (GGA) as the functional proposed by Perdew, Burke, and Ernzerhof (PBE).³³ We used the DFT-D3 approach for the correction of van der Waals interactions.³⁴ Basis functions were created using a confinement scheme and labeled as Al7.0-s2p2d2, C6.0-s2p2d1, and F6.0-s3p3d2f1 where Al, C, and F denote the chemical element, followed by the cutoff radius (Bohr radius), and the last set of symbols represent the primitive orbitals e.g., p2 indicates the use of two orbitals for the p component.

A cutoff energy of 300 Ry in the numerical integration and solution of the Poisson equation and a *k*-point mesh of $3 \times 4 \times 1$ was used for the self-consistency calculation. To study the changes in the graphite surface under AlF₃ intercalation, we employed three graphite layers, termed as L₁, L₂, and L₃ that adopt a Bernal AB stacking structure type for the HOPG, to model six systems, which we denote as (i) AlF₃|¹₀, (ii) AlF₃|²₀, (iii) AlF₃|²₁, and (vi) AlF₃|³₁, where the superscript indicates the number of molecules intercalated between layers L₁ and L₂ (see Figure S2 in the Supporting Information). The orthorhombic supercells have dimensions of a = 1.704 nm (*x*-axis), b = 1.721 nm (*y*axis), and c = 3.00 nm (*z*-axis), with 336 carbon atoms belonging graphite. The interlayer initial spacing was set as 0.4 nm. Full structural relaxation of atomic positions was performed up to a convergence force below $0.02 \text{ eV}/\text{\AA}$.

The redistribution of charge density induced by the interaction between graphite and AlF₃ molecules was defined as follows: $\Delta D = D_{AlF_3l_1} - D_{AlF_3} - D_{Gr}$, where ΔD is the difference charge density, $D_{AlF_3l_1}$ is the charge density of each one of the aforementioned systems, and D_{AlF_3} and D_{Gr} are the charge densities of the isolated AlF₃ and pristine graphite molecules, respectively. The charge transfer between graphite and AlF₃ molecules was calculated via a Mulliken population analysis.

MD. In our atomistic model, a graphite region of 25×25 nm and seven layers of carbon atoms were filled with AlF₃ molecules. Periodic boundary conditions were established in the plane, leaving the system free on the axis orthogonal to the carbon layers. The bottom-most layer of carbon atoms is rigid and plays the role of the bulk, while all others are allowed to thermally move at 300 K. Thus, bottom-most layer supports and mechanically stabilizes the other layers. The AlF₃ molecules are intercalated in the same number among the top six layers. There are no AlF₃ molecules present between the bottom-most carbon layer and the subsequent mobile one. If there are no AlF₃ molecules situated in other carbon layers, then this is due to the selection of the cut position. The density of AlF₃ molecules per layer varies between 0.015 and 0.03 AlF₃/nm². We opted for these densities to align with the overall apparent area of the blisters observed in the experiments, namely, Figure 2a and b.

The interatomic forces within graphite were derived using the appropriate AIREBO potential.³⁵ Interactions between AIF₃ molecules were modeled using Born–Mayer potential parameters.³⁶ The adhesion forces between the carbon atoms in graphite and AIF₃ molecules are modeled as a pure van der Waals interaction with parameters $\epsilon = 6.68$ meV and $\sigma = 3.166$ Å, chosen in accordance with energies and separations obtained from DFT.

The molecular dynamics (MD) simulations were performed using time steps of 0.5 fs and an NVT thermostat in LAMMPS, a commonly used distributed classical MD code.³⁷ The results are shown after 1 ns, when the energy and structure of the system stopped evolving.

RESULTS AND DISCUSSION

In GICs, it is known that invited species (guests) do not intercalate simultaneously in all of the interlayer spaces of the host material. Instead, they do it according to a unique modulated pattern called staging.^{38,39} The stage number n is defined as the number of pristine layers of the material separating two consecutive intercalated interlayer spaces. Therefore, in stage I, layers of graphite and guest molecules alternate one by one; in stage II, two pristine graphite layers separate two guest molecules layers; in stage III, three pristine graphite layers separate two guest molecules layers, and so on. In general, for any GICs, the arrangement of the guest in the layers is not perfect since, depending on the interaction between the host material and the guest, different configurations can be observed, such as the formation of small domains of guest material between the layers. In GICs, the most studied models to explain the intercalation mechanisms are those of Rúdorff-Hoffman (RH)⁴⁰ and Daumas-Herold (DH).⁴¹ The RH model proposes a sequential filling in which empty and guest-baring layers are obtained alternatively without structural distortions of the graphite sheets. In contrast, the DH model proposes that the guest can be intercalated between all layers of the host by deforming the material. Some authors have proposed the coexistence of different stages at the same time, i.e., staging stage model.⁴ This could explain some anomalies observed in studies of lithium-ion intercalation in graphite from X-ray diffraction and entropy measurements for stages I and II experiments.^{43,44}

So far, it has been demonstrated experimentally and theoretically that the intercalation of AlF_3 in graphene

generates deformations or "blisters" on the surface.²⁸ In this work, we will focus on the intercalation mechanism of AlF_3 in HOPG, and to facilitate the discussion of results, we will divide this section into two parts: (i) Morphology of AlF_3 Blisters in HOPG, where we present the experimental arrangement of the blisters on the graphite surface using STM, and (ii) Revelation of the Arrangement of Blisters in HOPG, where we make use of theoretical DFT calculations and MD simulations to discuss the modeled topography of three and seven layers of graphite with intercalated molecules. We compared the experimental and theoretical results to determine the number of AlF_3 molecules that form the blisters. At the end of this section, we propose a potential mechanism of the AlF_3 molecules intercalation.

Morphology of the AIF₃ Blisters in HOPG. In order to experimentally explore the topography and electronic characteristics of the intercalation of AlF₃ molecules between the HOPG layers, we performed STM images of the system at RT and different exposure doses. The deposition rate of AlF₃ molecules was varied between 6×10^{-3} and 2×10^{-2} ML s⁻¹, while the coverage ranged from 0.8 to 3.5 ML. Our experimental analysis is based on data collected from four different experiments; however, in this section, we only present the corresponding result at those doses comparable with the results obtained with molecular dynamics. In Figure 2a,b, we show the topography STM images of HOPG surfaces after the deposition of 1.2 and 3.0 ML of AlF₃, respectively. The results for the other two doses can be found in the Supporting Information. In both images, we observe bright regions on a dark brown background, corresponding to blisters generated by clusters of AlF₃ molecules intercalated with an inhomogeneous distribution beneath the topmost graphite layer.²⁸ The density of these clusters is observed to be higher for the sample that has been more exposed, indicative of a correlation between the intercalation density and exposure dose. Comparing both images, it is apparent that the size of the blisters varied with the deposited dose. In addition, it is observed that although the blister distribution across the graphite surface seems to be random for both doses, we found clusters of blisters characteristically located along a straight line, which we have indicated by the black dashed-line rectangles in Figure 2a and b. To clarify both the size and the positions of the blisters, using the free software WS \times M,³⁰ a topographic flooding-type procedure is applied to images of Figure 2a and b, which are shown in Figure 2c and d, respectively. This procedure allows us to identify, count, and measure the clusters of AlF₃ molecules, highlighting the areas that are above a threshold defined by the program. In our case, we set this threshold to 0.25 nm enough to minimize the noise inherent in the image acquisition of the images and highlight only the AlF₃ clusters without affecting morphological characteristics. For ease of visualization, a color scheme was chosen to represent the cluster height. Thus, focusing preferentially on clusters within the dashed line rectangles, values between 2.5-3.0 nm and 0.3-0.5 nm are obtained for the diameters and apparent heights, respectively. At the same time, it is clearly observed how the average distance between the nearest blisters in each correlated set (we compared between dashed line rectangles in Figure 2a and b) decreases from 5 to 1.5 nm when the AlF₃ dose is increased. Figure 3 shows the evolution of the density of blisters (number per area, nm^{-2}) formed on the substrate and their average apparent area as a function of dose. As expected, the blister density cells on



Figure 3. Variation of the blister density and their average apparent area as a function of the AlF_3 molecule dose deposited on a HOPG substrate at 300 K.

the surface increase monotonically with the dose. The trend for the average apparent area of a blister is different. There is a significative increase at low doses (from 0.8 to 1.2 ML), followed by a plateau in the size of a single blister.

Given that STM solely focuses on the topography of the outermost atomic layer of the system, we are faced with a substantial challenge in achieving a definitive understanding of the intercalation dynamics. While our recent publications have confirmed that AlF_3 molecules integrate into the substrate via

step-edges and surface defects, inducing local separation between the carbon layers of HOPG without forming chemical bonds, yet influencing the local density of states (LDOS), we are still in a stage of partial understanding regarding the dynamics of this intercalation process. Therefore, in the following sections, we will address this topic in depth. Utilizing density functional theory (DFT) and molecular dynamics (MD) calculations, we present a comprehensive interpretation of the intercalation mechanism that aligns with results obtained from scanning tunneling microscopy (STM) on the surface.

Revealing the Arrangement and Size of the Blisters in HOPG. To understand the inherent dynamics of the mechanism of intercalation and to determine if any of the alternative RH, DH, or mixed-stage models fit the system under study, DFT calculations and MD simulations are performed from modeling three and seven layers of graphite with intercalated AlF₃ molecules, respectively. Figure 4a-c shows the results obtained for the geometric optimization of two intercalated systems by DFT. In Figure 4a and b, we depict side views for the $AlF_3l_2^2$ and $AlF_3l_1^3$ systems, respectively, along with a top view in Figure 4c showing the relaxed geometry of the clusters with two and three molecules involved in each of the aforementioned models. In addition, Figure 4a and b show superimposed charge density differences induced by the interaction between the molecules and graphite, represented by blue and green shaded regions. Figure 4d and e provide the MD results, where the top and side views of the spatial arrangement of the clusters are observed for two densities of molecules per layer 0.015 and 0.03 AlF₃/nm²,



Figure 4. (a-c) are the theoretical results from DFT. (a, b) Geometric optimizations and difference charge density for $AlF_{3}l_{2}^{2}$ and $AlF_{3}l_{1}^{3}$ systems, respectively, where the superscript indicates the number of molecules intercalated between layer L_{1} and L_{2} and the subscript the number of molecules intercalated between layer L_{2} and L_{3} . Green regions correspond to D > 0, i.e. higher electron charge density due to intercalation, and blue regions correspond to D < 0, i.e., lower charge density due to intercalation. (c) Top view of the $AlF_{3}l_{2}^{2}$ and $AlF_{3}l_{1}^{3}$ systems. (d-g) Theoretical results from MD. (d, e) show the top and side views of the spatial arrangement of the clusters for two densities of AlF_{3} molecules per layer of 0.015 $AlF_{3}/$ nm² and 0.03 AlF_{3}/nm^{2} , respectively; in order to facilitate visualization, we have established the color of the clusters, according to the height at which they are on the *z*-axis. (f, g) Results of the topography of the last layer after the formation of the clusters intercalated for the same density per layer.

respectively. To facilitate visualization, we have established a color scale for the clusters, according to the height at which they are on the z-axis, set to zero at the bottom-most graphite layer. On the other hand, Figure 4f and g show images as a color map of the topography of the topmost layer produced by the intercalated clusters shown in Figure 4d and e. In this case, the height difference (Δz) is measured from the level of the topmost unperturbed graphite layer. Since intercalation mechanisms are complex processes, we will discuss our results based on (1) In-plane interactions, defined as those produced between molecules located in the same layer of the host material, and (2) interlayer interactions, established between molecules located in different layers of the host material.

In-Plane Interactions. From DFT calculations, we determined that the intercalation process causes a charge transfer up to 2.63 e⁻ from the graphite to the molecules for threemolecule clusters (see more details in Supporting Information, section 3A). The electronic transfer redistributes the charges by polarizing the graphite sheets, which leads to the formation of local "transverse dipoles" between the molecules and the graphite, where molecules gain electrons while the graphite loses them. The transverse dipoles calculated by DFT, are visualized in the shaded regions of Figure 4a and b, where the green regions correspond to the different charge density ΔD > 0, i.e., higher electron density after the charge transfer due to intercalation, and the blue regions correspond to difference charge density ΔD < 0, i.e., lower charge density upon intercalation.^{9,45} These dipoles, which have components mainly on the z-axis, locally separate the graphite layers and elastically deform the material, playing a relevant role in the interactions between molecules in the same xy-plane, as described below (for more details on the theoretically calculated heights, see Table S1 of the Supporting Information).

According to DFT and MD theoretical results, the AlF₃ molecules approach each other, forming small clusters parallel to the graphite xy-plane. Each intercalated molecule extends the C–C σ bonds of graphene to up to 2%. A way for the system to reduce elastic energy is by pushing individual molecules into clusters. In turn, the elastic deformation of graphite results in an effective attractive force between molecules in the same plane. The pressure generated by the deformation of the layers is transferred into the internal pressure of the blisters.^{46,47} In this sense, the deformation of graphite drives the kinetics of clustering and coalescence of AlF₃ molecules in a given graphite plane. Since the blister obtained theoretically and experimentally have a height and radii of less than 1.0 and 1.5 nm, we estimate the pressure inside the blisters from the linear plate model,⁴⁸ using the expression of eq S2 (see more details in the Supporting Information). According to this model, the pressure, expressed in terms of the adhesion energy, is inversely proportional to the square of the radius of the blister.⁴⁷ Consequently, the pressure is higher in small blisters, and the pressure difference drives the molecules to diffuse from smaller blisters to larger ones. In this work, with the linear plate model and DFT, we estimate a pressure of 6.40, 4.06, and 3.01 GPa for blisters generated by intercalation of groups of one, two, and three AlF₃ molecules, respectively -- these values are on the order of the pressures reported by Wang et al.⁴⁶ and Villareal et al.⁴⁹ for blisters with radii smaller than 1 nm. It is important to note both from experimental (Figure 3) and theoretical results (Figure 4f and g), that no *xy*-plane contains blisters with diameters larger than

3 nm. This appears to indicate the existence of a critical coalescence value. This outcome is mainly due to elastic deformation and the generation of transverse dipoles by the molecules between adjacent layers of the graphite. This critical coalescence number could explain why the average area of the blisters remains almost constant for doses higher than 1.2 ML, as shown in Figure 3.

By analyzing the STM images and our DFT and MD results, we have estimated that blisters with diameters in the range of 1.3 to 2.0 nm are made up of clusters of two to six AlF_3 molecules, respectively. The size of the blisters formed between the L_1 and L_2 layers depends on the concentration of the intercalated molecules. According to the results obtained by MD, when the density of molecules per layer is 0.015 AlF_3 / nm², the blisters on the surface have smaller diameters. In contrast, for a density of 0.03 AlF_3/nm^2 , the diameters increase. This is consistent with the experimental data presented in Figure 3, which indicates that the most significant increase in the average area of the blisters occurs for doses lower than 1.2 ML.

Regarding the height of the blisters and according to the topography modeled by calculation with three graphite layers by DFT and seven layers by MD, the clusters deform the graphite layer such that the blister reaches the apparent height of 0.22 nm (see Figure 4). It should be noted that experimentally the apparent height could increase, since, on the one hand, the innermost clusters could push everything upward and, on the other hand, there could be an overestimation during acquisition due to unknown tip conditions.⁴⁶

Interlayer Interactions. Figure 4d and e depicts the spatial arrangement of clusters along the z-axis. The atoms of the molecules are colored according to their vertical position from blue for the molecules in the lower layer (z = 0 nm) to red for those in the upper layer (z = 2 nm). According to the results, it is not observed for any of the two densities of AlF₃ molecules that the average size of the clusters varies with the depth. This observation is evident in Figure 4d, where the clusters in the lower layers (represented in blue) exhibit sizes similar to those in the upper layers (represented in red). However, the most striking feature is the alignment of the clusters obtained in the MD simulations. The topography images of the MD simulations in Figure 4f and g clearly show the formation of blisters of different diameters in the topmost layer, which are aligned and separated about 4 nm apart from each other in the xy-plane. The self-organization of clusters in a line is observed for both of the modeled densities. The alignment direction of the blisters is random and does not correlate to any crystallographic orientation of the HOPG, as indicated by the dashed boxes in the molecular dynamics figures. Such random alignment is also evident in the experimental STM image, see the dashed line box in Figure 2b. A relevant aspect to highlight from these MD results is the role played by the innermost clusters since how the blisters are aligned on the surface depends on this; see the inset of Figure 4d and e. Below the surface, the formation of clusters between the different layers prevents larger structures from forming within a given layer. As a result of this interlayer self-assembly, blisters in the topmost layer remain approximately 4 nm apart from each other, despite the elastic forces that attempt to coalesce them, see Figure 4f. Since the results of the MD simulations were able to reproduce the experimental characteristics of the blisters in terms of their alignment and size distribution, they

can be employed to gain a deeper understanding of the processes taking place within the clusters below the surface. According to MD, the clusters between neighboring layers do not stack vertically. The reason behind this is the elastic deformations of graphite and the repulsive interaction of local transverse dipoles. The insets in Figure 4d and e, which show a side view of the highlighted regions, reveal the depth distribution of the clusters that form blisters observed in the topmost layer (shown in Figure 4f and g, respectively). Each region framed by the dashed line boxes represents a superstructure formed by intercalated clusters and displaced laterally from each other, between different pairs of layers. A "local staging" is observed in each superstructure, indicating the coexistence of "mixed stages". For instance, for the dilute system of 0.015 AlF_3/nm^2 , the organization of the molecules combines stages III and IV, while for the densest system of $0.03 \text{ AlF}_3/\text{nm}^2$, it combines stages IV and V. This arrangement gives rise to an aligned distribution of the clusters and explains the average distance of 4 nm between blisters at the topmost layer in Figure 4f and Figure 4g, and also in the STM image of Figure 2b corresponding to the experiment.

CONCLUSIONS

In this work, we employed a combination of scanning tunneling microscopy (STM), density functional theory (DFT) calculations, and molecular dynamics (MD) simulations to gain insight into the process of AlF₃ intercalation in highly oriented pyrolytic graphite (HOPG). Experimentally, we investigated the intercalation mechanism of thermally dosed AlF₃ molecules perpendicularly to the HOPG surface at room temperature under ultrahigh vacuum conditions (in the high range of 10⁻¹⁰ mbar). STM images obtained for varying molecule doses revealed that the blisters are not uniformly distributed over the graphite surface. Besides, it was observed that some blisters align locally with random orientations and without following any preferential crystallographic direction; see the line and dashed rectangle in Figure 2b. Since STM only probes the surface of the system, we supplemented our experimental results with theoretical DFT calculations and MD simulations, which allowed us to propose a plausible explanation for the local alignment of the blisters observed on the surface.

We used DFT and MD simulations to study in-plane and interlayer interactions between AlF₃ molecules and graphite. The in-plane interactions involve the arrangement of AlF₃ molecules between two graphite layers. The findings include the formation of AlF₃ molecule clusters, resulting in localized elastic deformation graphite layers. Charge transfer between graphite and AlF₃ molecules induces the formation of transverse dipoles. The molecules tend to form clusters between two graphite layers driven by pressure differences. The pressures stemming from adhesive van der Waals forces between layers of 6.40, 4.06, and 3.01 GPa are estimated from DFT calculations for blisters containing one, two, and three intercalated molecules, respectively. The interlayer ordering of clusters reveals that clusters formed in deeper layers of the material direct the alignment of the surface blisters. These three-dimensional superstructures extend several layers into the depth of the material and connect through the bulk of material surface blisters arranged in a local line. The movement of the observed surface clusters is therefore constrained by neighboring deeper clusters. Our model-based findings provide

insights into the arrangement and behavior of blisters on the material's surface.

An important finding is the existence of superstructures visible in the experiment as surface blisters arranged in a local line and separated by an average of 4 nm. Every cluster affects the layers around it. Due to neighboring clusters in graphite layers under or above, AlF₃ clusters are quenched together and cannot get closer or grow. They cannot also stack on top of each other, since the stacking would result in a sharp increase in elastic energy required to deform graphite layers. Therefore, AlF₃ clusters avoid stacking on top of each other. As a result, the clusters group laterally next to each other, sharing the deformation of graphene to reduce elastic energy. Daumas and Herold postulated a model, in which the graphene layers are flexible and deform around clusters of the intercalated species.⁴¹ In the Rúdolf-Hoffman model, layers are not elastic, and molecules intercalate by separating these layers.⁴⁰ Our results underline the effect of the elasticity (deformability) of the host material (graphite) on the evolution of intercalation. Based on our results, clusters arrange via elastic interactions in graphene. The local deformations of graphene sheets and resulting local strains lead to mixed stages since neighboring clusters are separated by one layer of graphene, while simultaneously superstructures are separated by several nanometers. We can deduct what is an outcome of this process at higher densities: one expects the growth of clusters, while they avoid vertical stacking. The process will continue until distances between the AlF₃ clusters sufficiently decrease and the density of AlF₃ within one layer becomes sufficiently high. At this point, the clusters will coalesce into the full AlF₃ layers, removing the elastic strain on host material (graphite) layers.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.3c03120.

Summary of previous results by RBS of the system under study; experimental STM images of the HOPG before and after evaporation of 0.8 and 3.2 ML of AlF₃; computational details of the six models studied by DFT, reporting the formation energies, charge transfer, and some distances of interest between the molecules; detailed calculation of the pressures of the blisters formed by one, two, and three intercalated molecules (PDF)

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Notes

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paramount importance within rechargeable battery systems, owing to its intrinsic correlation with battery capacity, performance, and safety aspects. In the context of high-performance lithium batteries, an approximate operational voltage of 3.7 V is commonly observed. With regard to diffusion, our previously published theoretical study²⁹ highlighted the presence of low diffusion energy barriers associated with AlF₃ intercalants. This characteristic is poised to accelerate the charging process in a potential battery predicated upon this solvent.

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