DFT study of AlF_3 intercalated in HOPG: a rechargeable battery application

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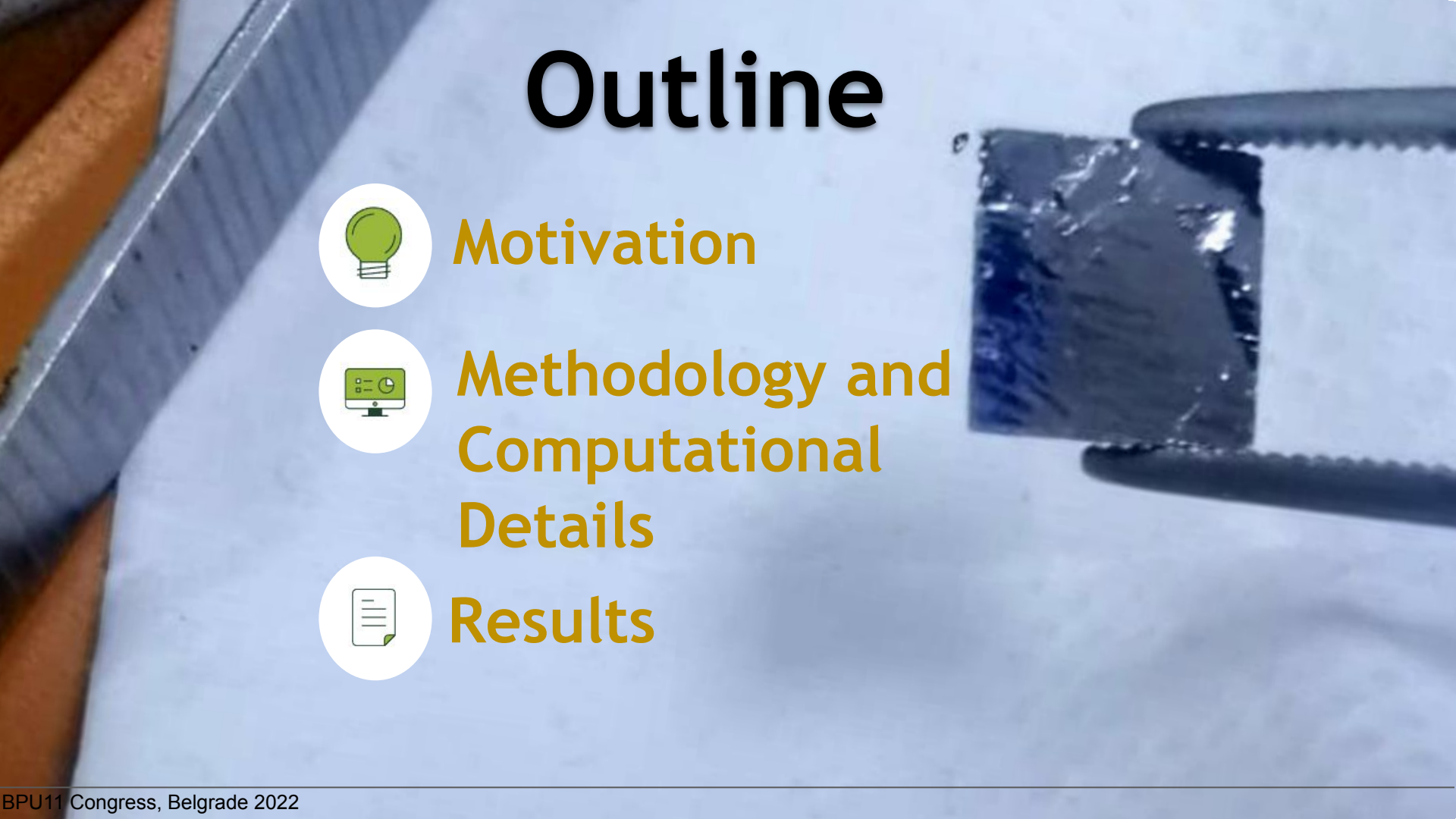
Universidad Nacional del Litoral, Santa Fe, Argentina

Outline



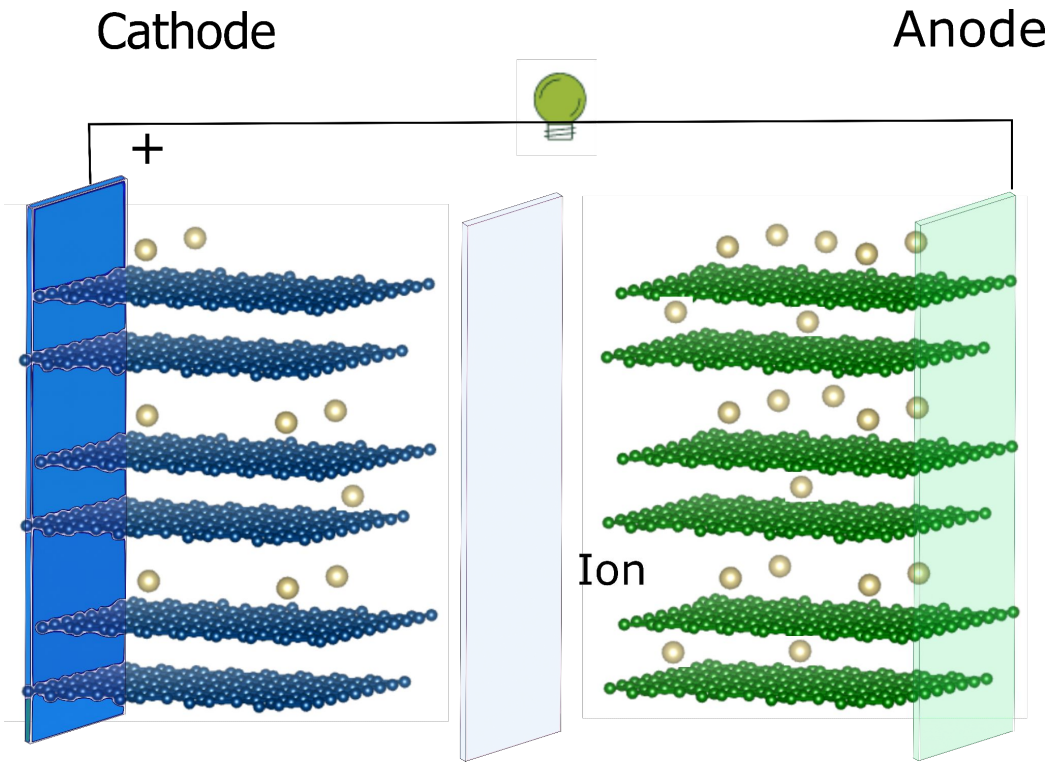
- Motivation
- Methodology and Computational Details
- Results

Motivation

Rechargeable Batteries

- Lower environmental impact
- Portability
- High energy efficiency…

Intercalation/extraction of ions

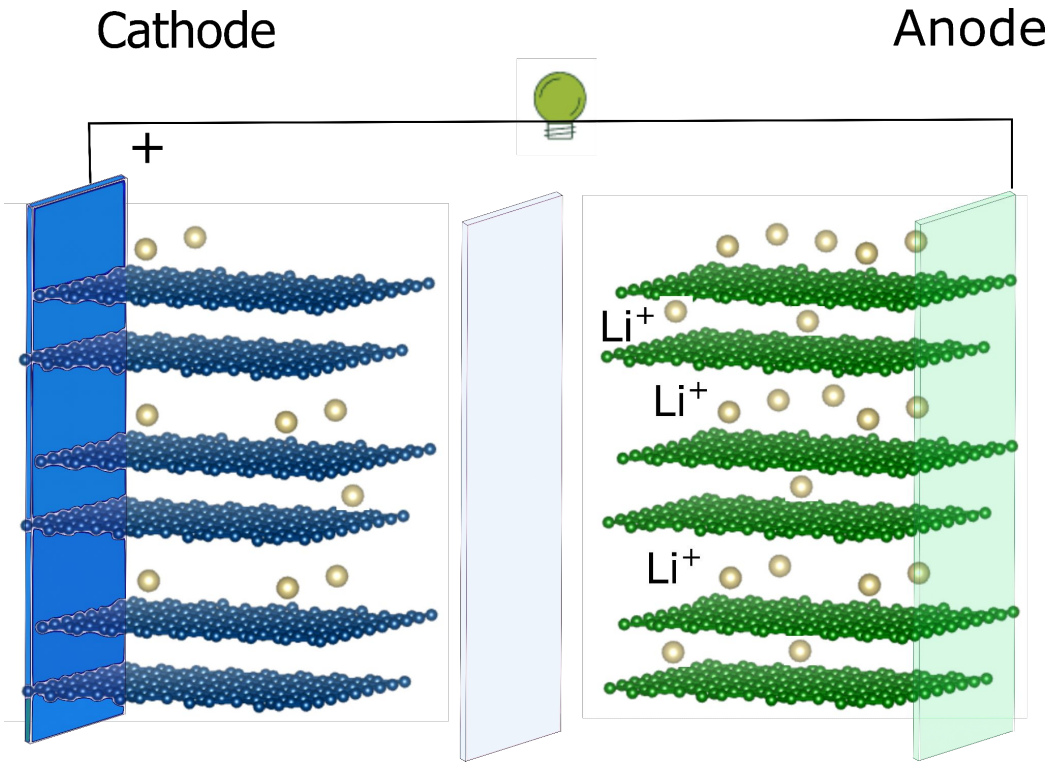


Motivation

Rechargeable Lithium Batteries

-High voltages (3.7 V)
-Charging and discharging cycles (Longer life time)
- High load capacity

-Expensive
-Extremely sensitive to high temperatures
-Risk of bursting

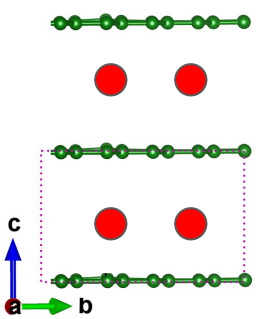


Motivation

Rechargeable Lithium Batteries

Pure ion intercalation

Na^+
Mg^+
K^+
Al^+



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Density Functional Theory Study on Structural and Energetic Characteristics of Graphite Intercalation Compounds

Ken Tasaki*

Chem Soc Rev
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Cite this: DOI: 10.1039/c9cs00162j

Intercalation chemistry of graphite: alkali metal ions and beyond

Yuqi Li, [ab] Yaxiang Lu, [*ab] Philipp Adelhelm, [*c] Maria-Magdalena Titirici [*d] and Yong-Sheng Hu [*abe]

Graphite

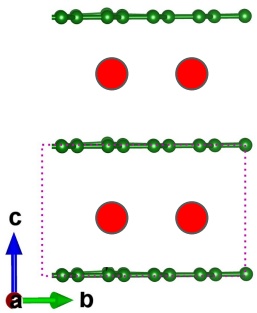
Adsorption, intercalation and diffusion

Motivation

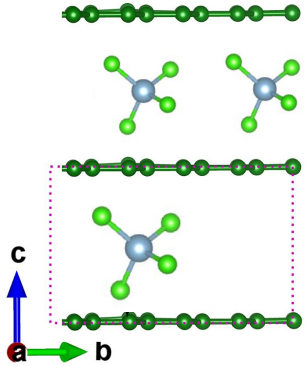
Rechargeable Lithium Batteries

Pure ion intercalation

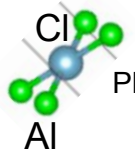
Na^+
Mg^+
K^+
Al^+



Complex anions intercalation⇒ $AlCl_4$




No planar



Planar

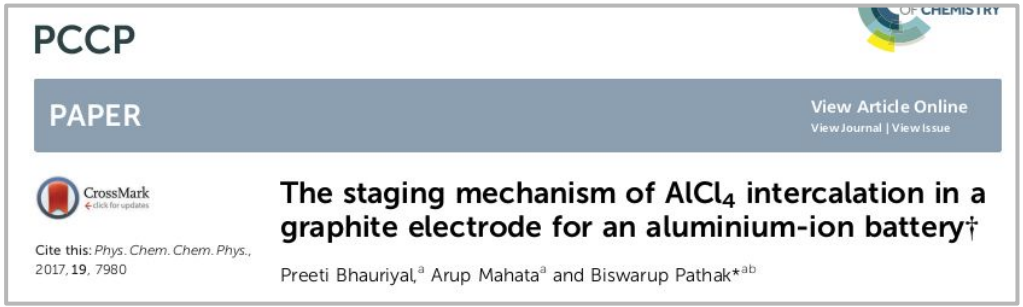
Graphite

Adsorption, intercalation and diffusion

Motivation

Rechargeable **Lithium** Batteries

Complex anions intercalation⇒ $AlCl_4$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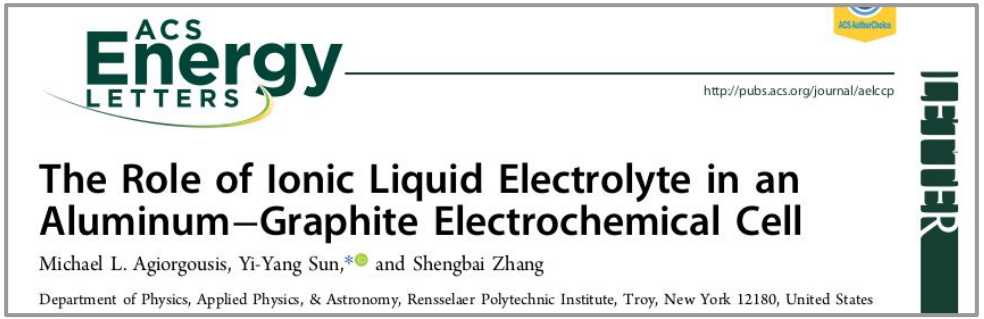
The staging mechanism of $AlCl_4$ intercalation in a graphite electrode for an aluminium-ion battery†

Cite this: *Phys. Chem. Chem. Phys.*, 2017, 19, 7980

Preeti Bhauriyal,[a] Arup Mahata[a] and Biswarup Pathak*[ab]

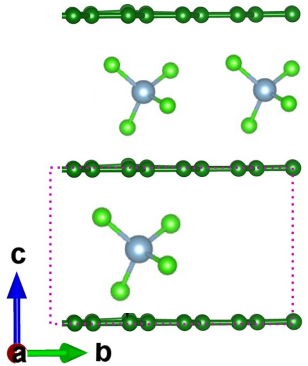

ACS Energy LETTERS

http://pubs.acs.org/journal/aelccp

The Role of Ionic Liquid Electrolyte in an Aluminum–Graphite Electrochemical Cell

Michael L. Agiorgousis, Yi-Yang Sun,* and Shengbai Zhang

Department of Physics, Applied Physics, & Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180, United States

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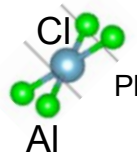


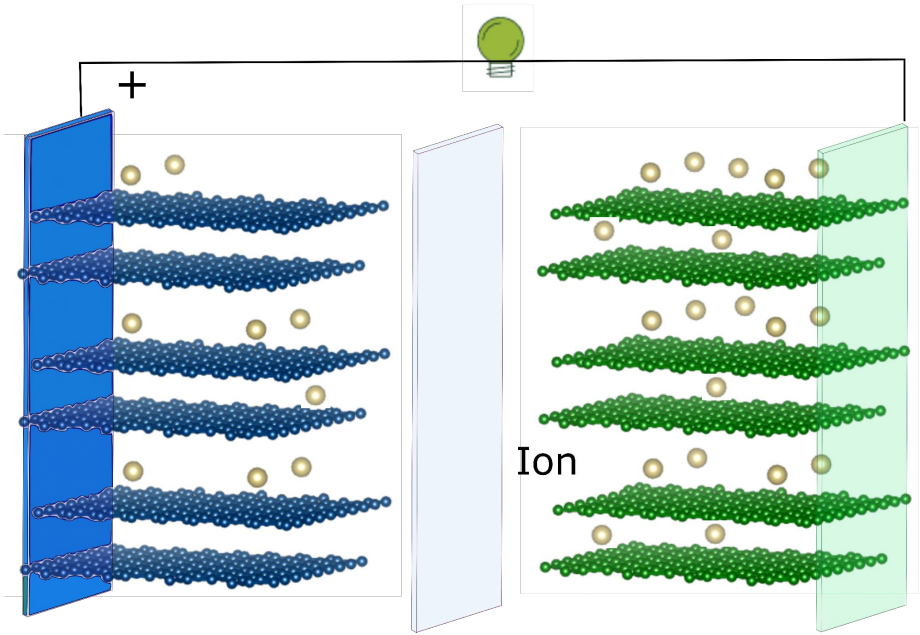
Planar

Motivation

The new emerging challenges point toward the necessity of:

1. Increasing the storage space
2. Exploring other materials layered
3. Understanding and studying the role of solvent components (or electrolytes) in battery performance.

Ions/
Anions/
Complex anions



Solvents

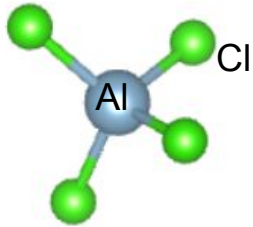
Objective

To study the intercalation and diffusion of Aluminum Fluoride (AlF_3) into graphite.

Solvents Anions

$AlCl^-_4$ Intercalated ⇨ $AlCl_3$ ✚ $AlCl^-_4$

Al-F ⇒ 1.68 Å



Al-Cl ⇒ 2.17 Å

Objective

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	Solvents	Anions
$AlCl^-_4$ Intercalated ⇨	$AlCl_3$	+ $AlCl^-_4$
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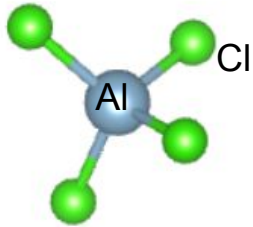

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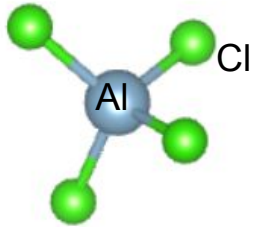


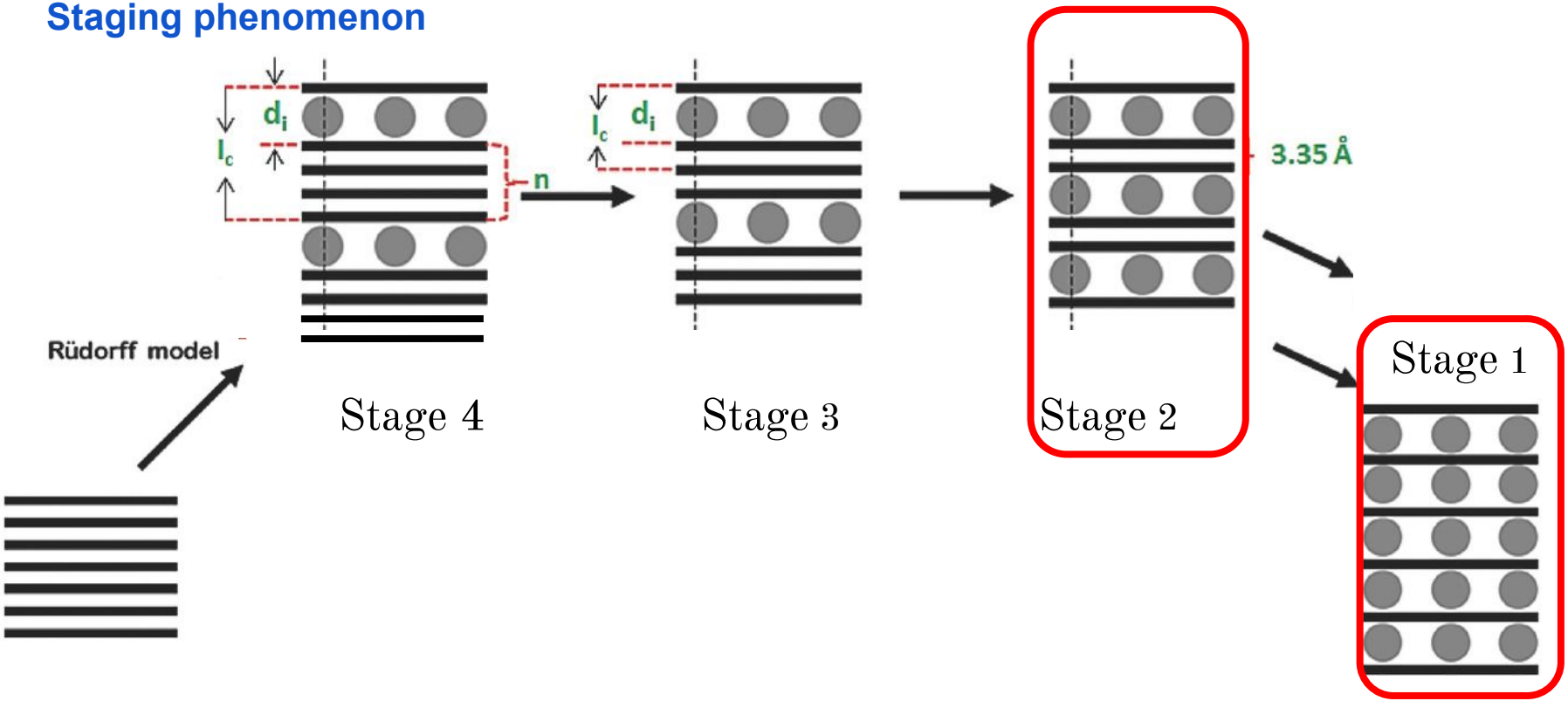
Al-Cl ⇒ 2.17 Å

How understand the mechanism of solvent intercalation?

Binding Energy **Diffusion**

Methodology

Staging phenomenon



Computational Details

Calculations performed in OpenMx software

DFT context with pseudopotential

GGA-PBE exchange and correlation approach

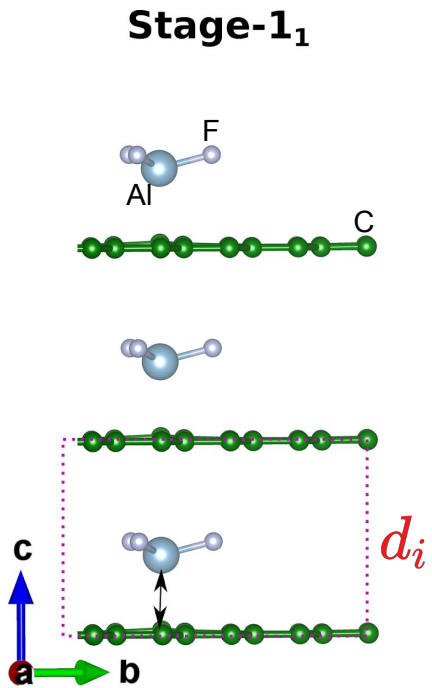
Van der Waals DFT-D3

Nudged Elastic Band NEB

Computational Details

Supercell graphite $4 \times 4 \times 1$

Atoms carbon 36
Each molecule of AlF_3 has 4 atoms



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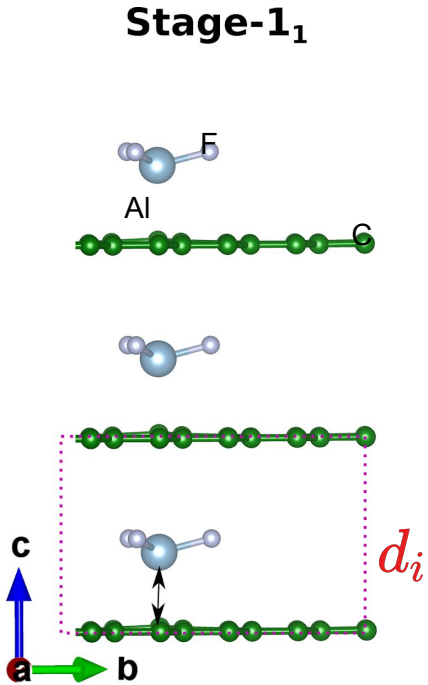
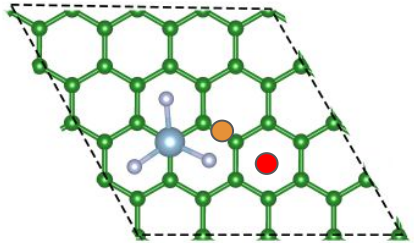
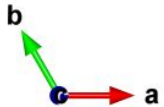
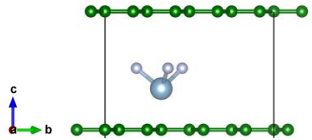
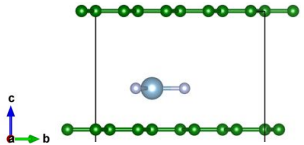








No-Planar



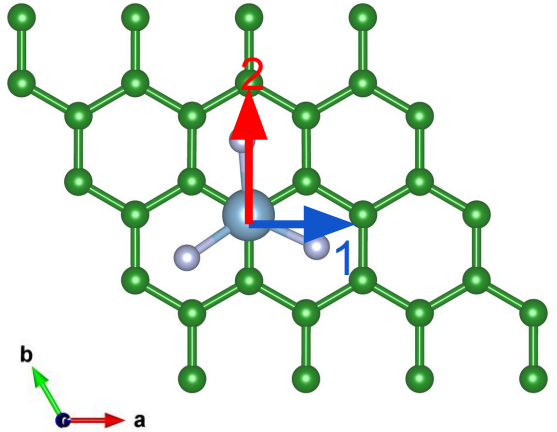
Planar

Results

1. The Most stable Configuration

- Intercalation distances
- Equilibrium configurations
- Charge Transference
- Voltage
- Exploring intercalation with more than one molecule per supercell

2. Diffusion



Results

STAGE 1: The most stable configuration

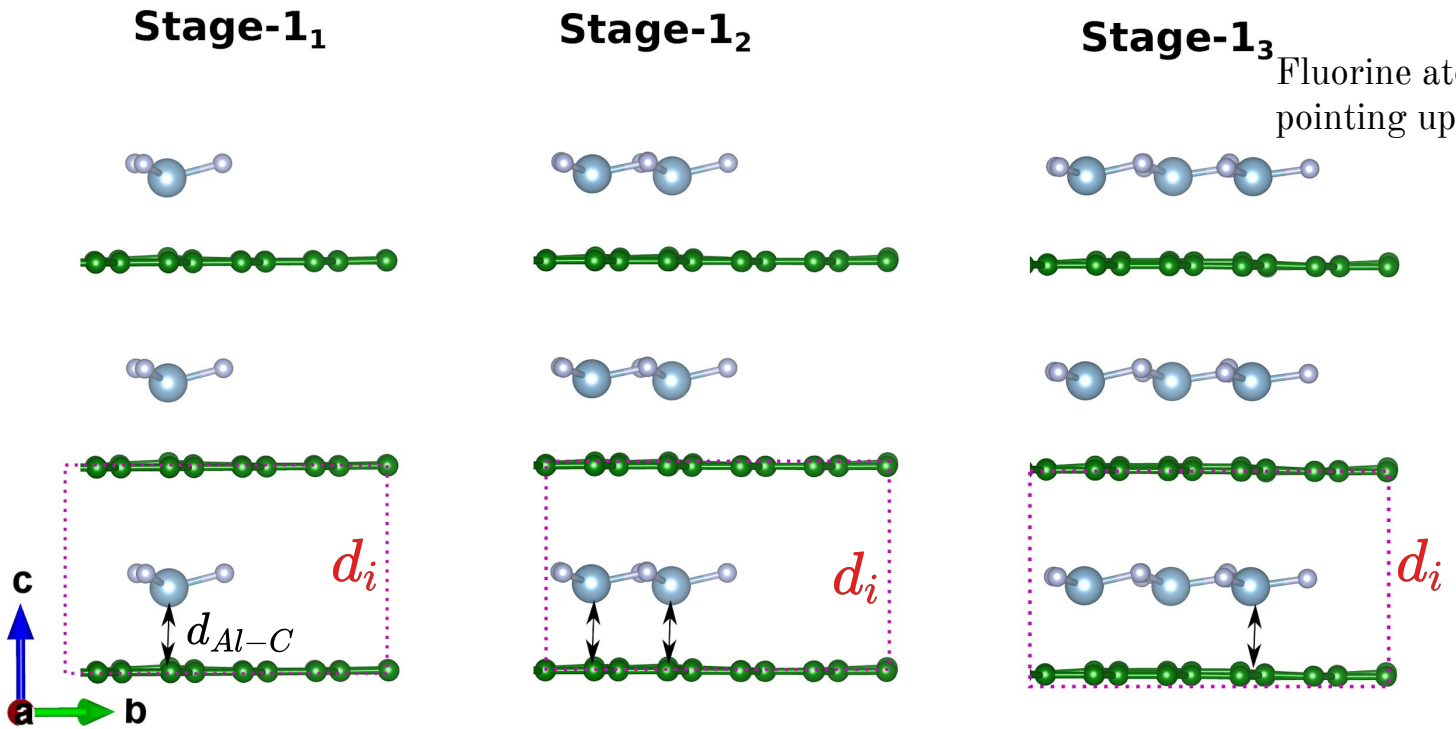
Rodriguez, S.J. et al. Phys.Chem.Chem.Phys 2021,23,19597

$d_i = 6.00\text{Å}$
$d_{Al-C} = 2.28\text{Å}$
$\theta_{F-Al-F} = 116.69^\circ$

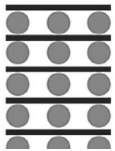
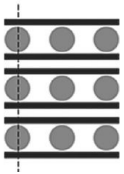
$\vec{a} = 9.80\text{Å}$

$\vec{b} = 9.80\text{Å}$

$\vec{c} = 6.00\text{Å}$

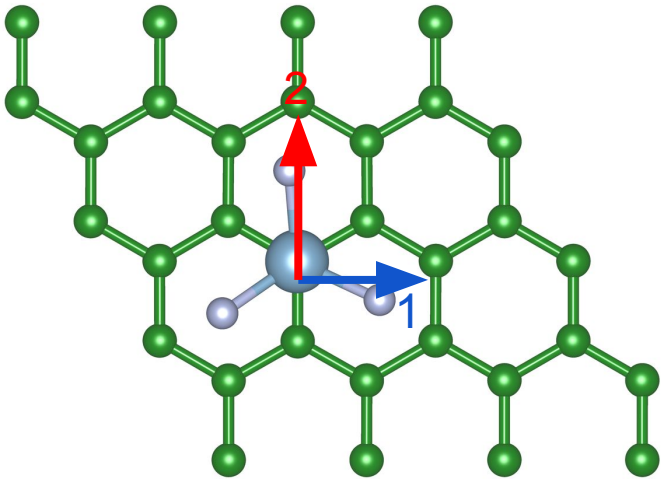


Results

Stage	Nº of intercalated AlF_3 molecules	Intercalated distance d_i (Å)	Formation energy per AlF_3 E_f (eV)	Voltage (V)
1 	1	6.00	-2.50	3.43
	2	6.12	-2.17	3.44
	3	6.13	-1.88	3.46
2 	1	5.33	-2.06	2.35
	2	6.10	-2.09	3.55
	3	6.12	-1.69	3.64

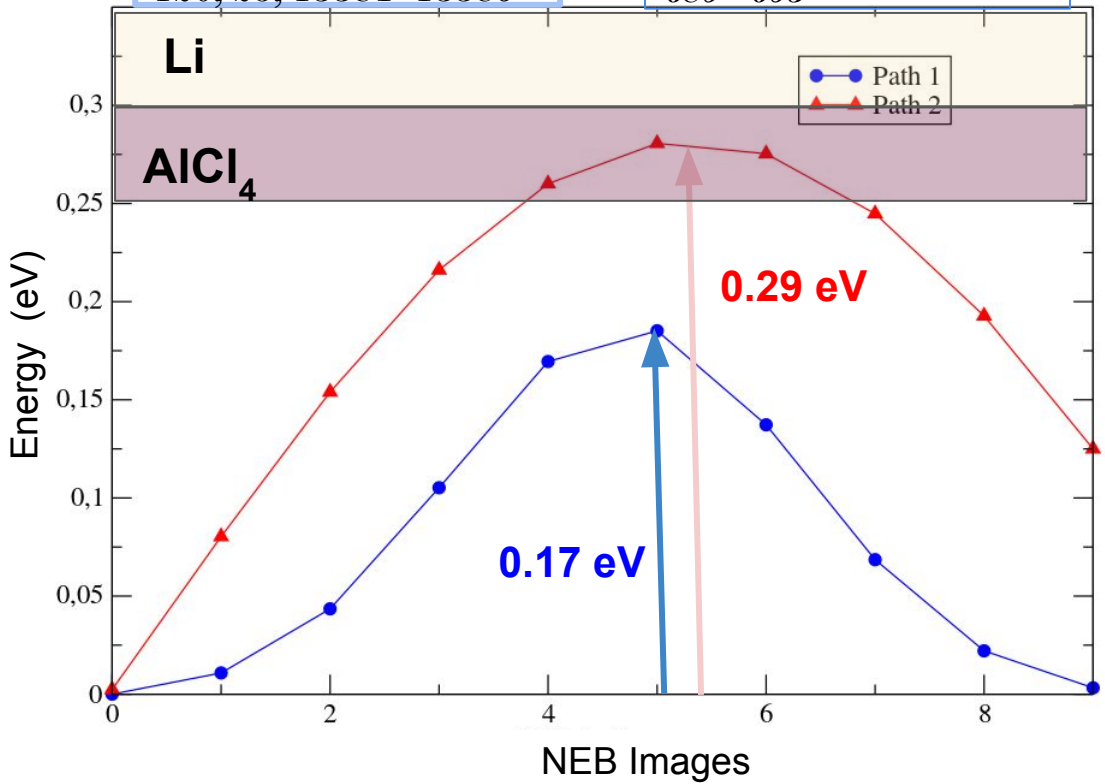
Results

2. Diffusion



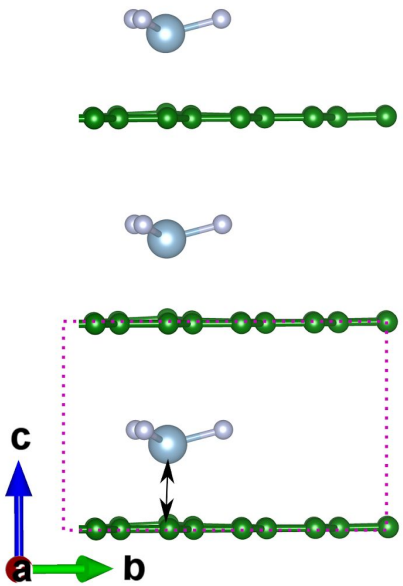
J. Phys. Chem. C 2016, 120, 25, 13384–13389

ACS Energy Lett. 2017, 2, 689–693



Conclusions for bulk intercalation

AlF_3



		AlF_3	$AlCl_4$	Li
Stability	Stage 1_1 Stage 2_1	-2.50 eV ↑ -2.06 eV ↑	-1.33 eV [1] -1.47 eV [1]	---
Voltage	Stage 1_1 Stage 2_1	3.4-3.5 V ↑ 2.4-3.6 V ↑	(2.00-2.3 V) [2]	3.7 V [2]
Barrier Energy	--- ---	0.17 eV ↓	0.25-0.30 eV [3]	0.30 eV [3]

[1] Phys. Chem. Chem. Phys., 2020, 22, 5969-5975
[2] ACS Energy Lett. 2017, 2, 689—693
[3] J. Phys. Chem. C 2016, 120, 25, 13384–13389

Is AlF_3 intercalated in graphite?

What happens to the graphite surface when AlF_3 is intercalated?

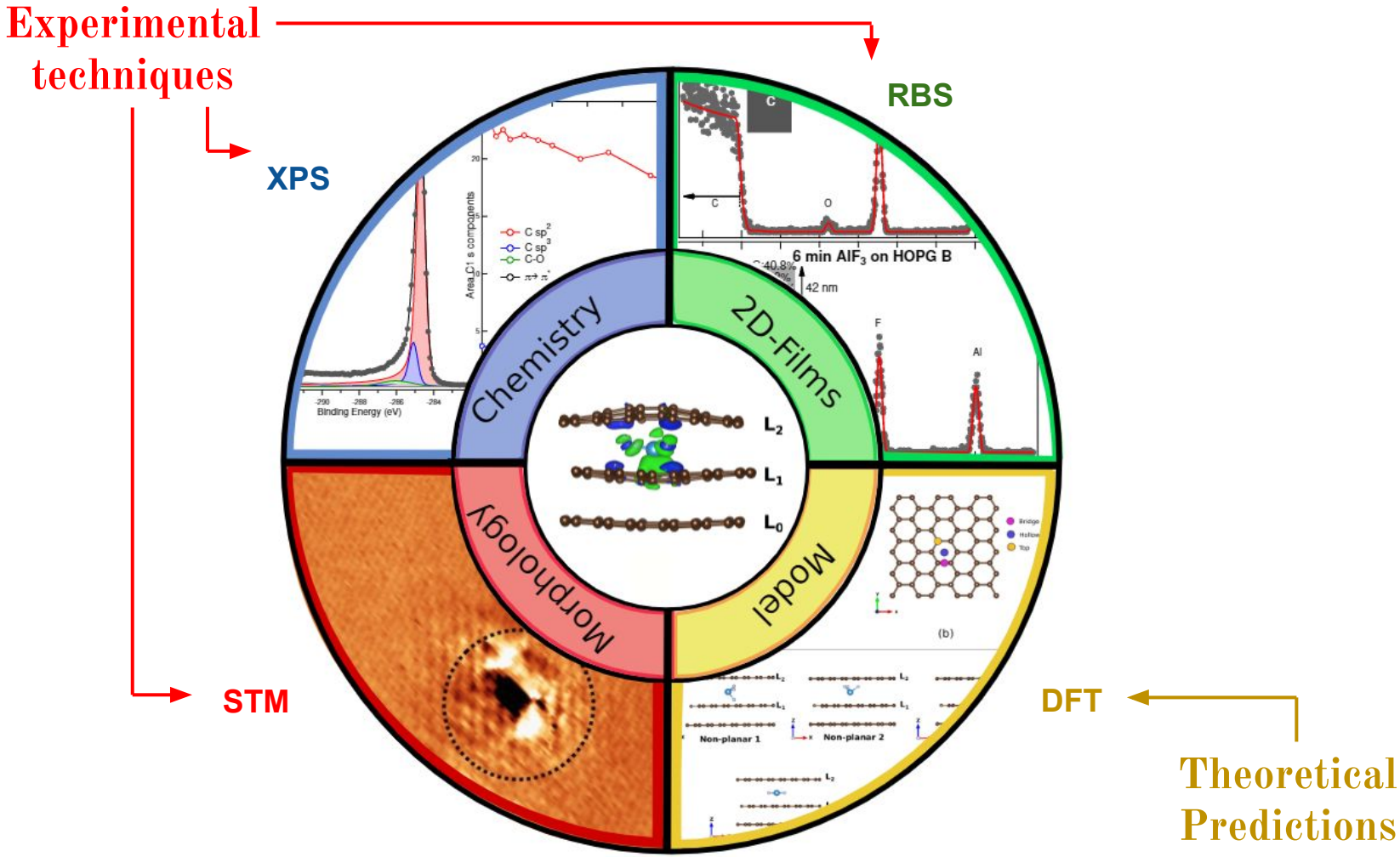
Carbon 186 (2022) 724–736

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Aluminum fluoride intercalation in graphite for rechargeable batteries design


Experimental techniques
XPS
RBS
STM
DFT
Theoretical Predictions
Chemistry
2D-Films
Morphology
Model
C sp2
C sp3
C-O
Binding Energy (eV)
6 min AlF3 on HOPG B
42 nm
F
Al
L2
L1
L0
(b)
Non-planar 1
Non-planar 2

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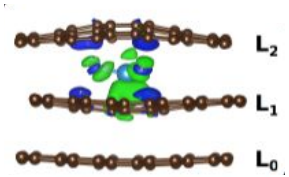
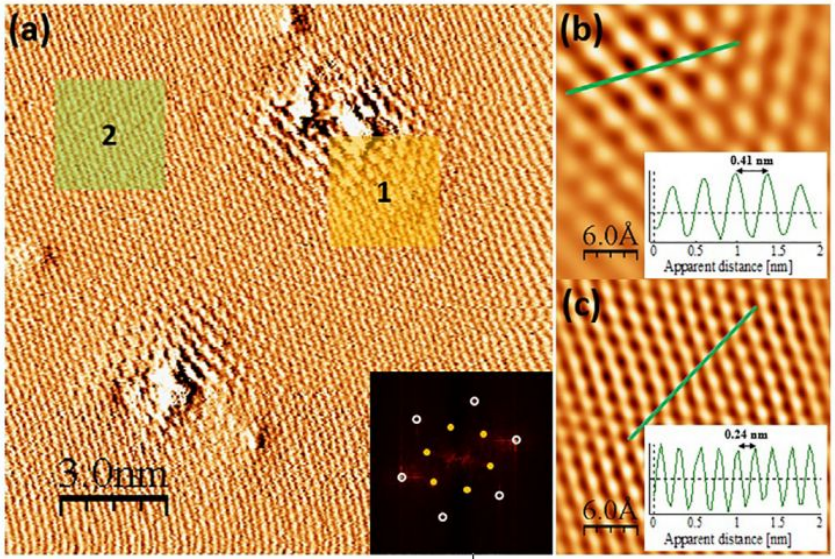
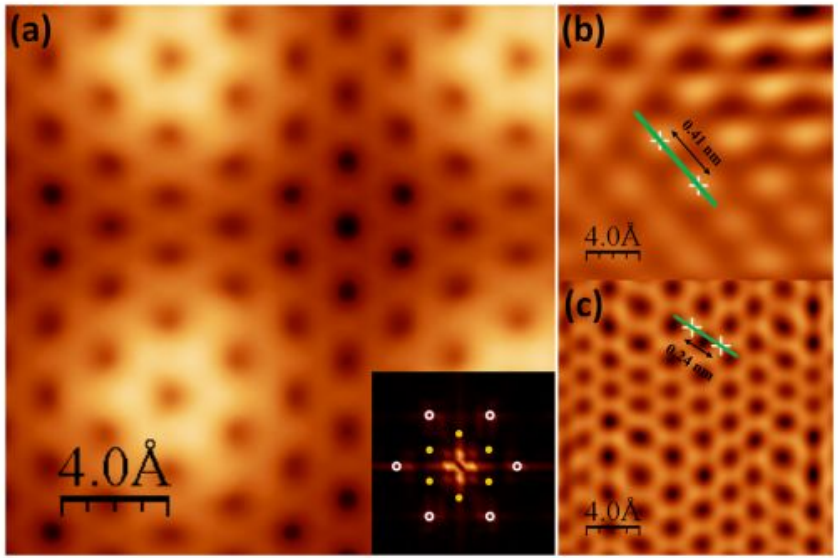


STM

DFT





2D Fast Fourier Transform (2D-FFT) spectrum

Tersoff-Hamann approximation

Conclusions for Surface

	Theory	Experimental
AlF_3 is intercalated into HOPG	✓	✓ STM RBS
Blisters formation between carbon layers	✓	✓ STM
No covalent bonding between AlF_3 and carbon	✓	✓ XPS
AlF_3 stoichiometry is maintained after intercalation	✓	✓ XPS

Thank you

Does anyone have any questions or comments?

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sindy.rodriguez@santafe-conicet.gov.ar