2020 Virtual NASA Aerospace Battery Workshop

OCI Vacuum Microengineering Inc.

A new method for evaluating Li-ion battery anode materials based on surface compositional and structural characterization of Li thermal diffusion

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November 18th, 2020

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A new method for evaluating Li-ion battery anode materials based on surface compositional and structural characterization of Li thermal diffusion

Outline

- Company Roots
- Addressing the problems
- Solution – concept description
- Fundamentals of LEED and AES
- Results: HOPG (Graphite), Si(111), SiC-6H
- Results: Diamond CVD, Si (100), Si(211) and $LiNbO_3$ – Mg doped
- Conclusions
- Possible application of this method

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Company Roots

OCI Vacuum Microengineering was created in 1990 to commercialize Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES) instrumentation

Results of my previous work:
- University of Wroclaw, Poland, 1979-1984
- University of Claustahal-Zellerfeld, Germany, 1984-1986
- University of Western Ontario, Canada, 1986-1989

Today, OCI Vacuum Microengineering, Inc. is a world-wide leader in the manufacturing of LEED-AES instrumentation and operates with a strong commitment to materials research. Our focus is in applications to energy storage, solar harvesting, advanced substrates for microelectronics using Molecular Beam Epitaxy (MBE) of 2D materials. Company is also active in space plasma analyzers.

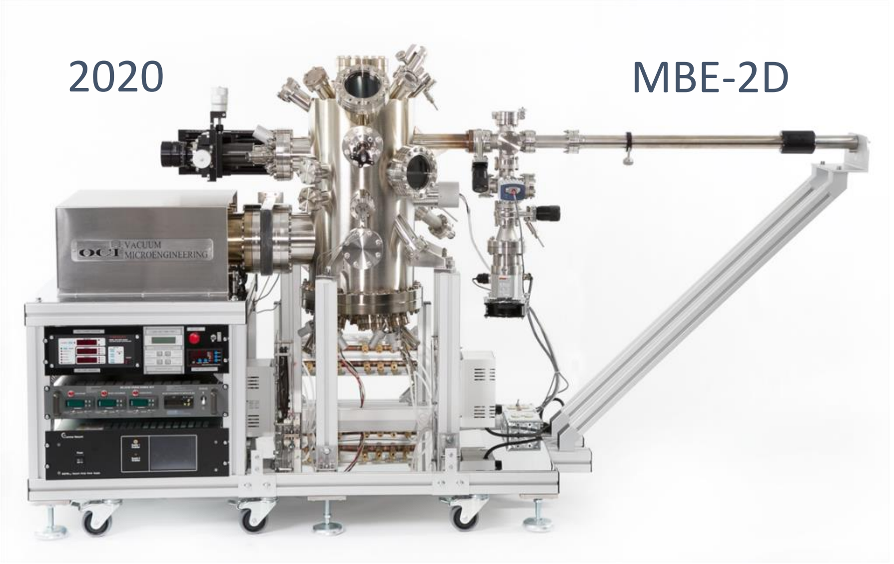
LEED-AES

1980

1990

2020

MBE-2D



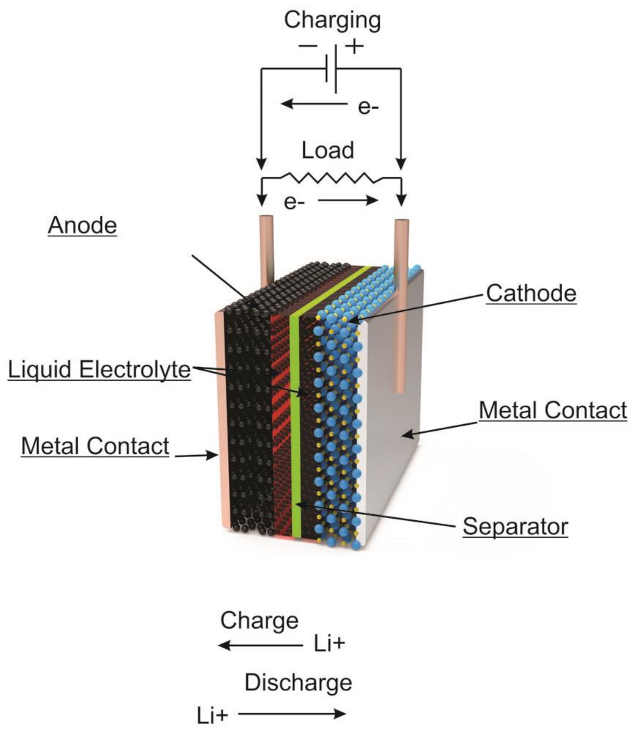
Problem: *Key properties of electrode materials are not tested before battery cell assembly*

- Li diffusion in electrode material is a key factor for battery performance
- There are no Li diffusion tests on battery electrodes prior to complete cell fabrication

Nanoscale material problems (structural and compositional) can have an effect on:

- Lost battery capacity
- Reduced cycle life
- Dendrite growth

Liquid Electrolyte Battery Cell



Solution: *Testing of Li thermal diffusion on designated material for Li battery*

Objective: probing Li atoms interaction with surface crystalline structure at nanoscale

Material forms:

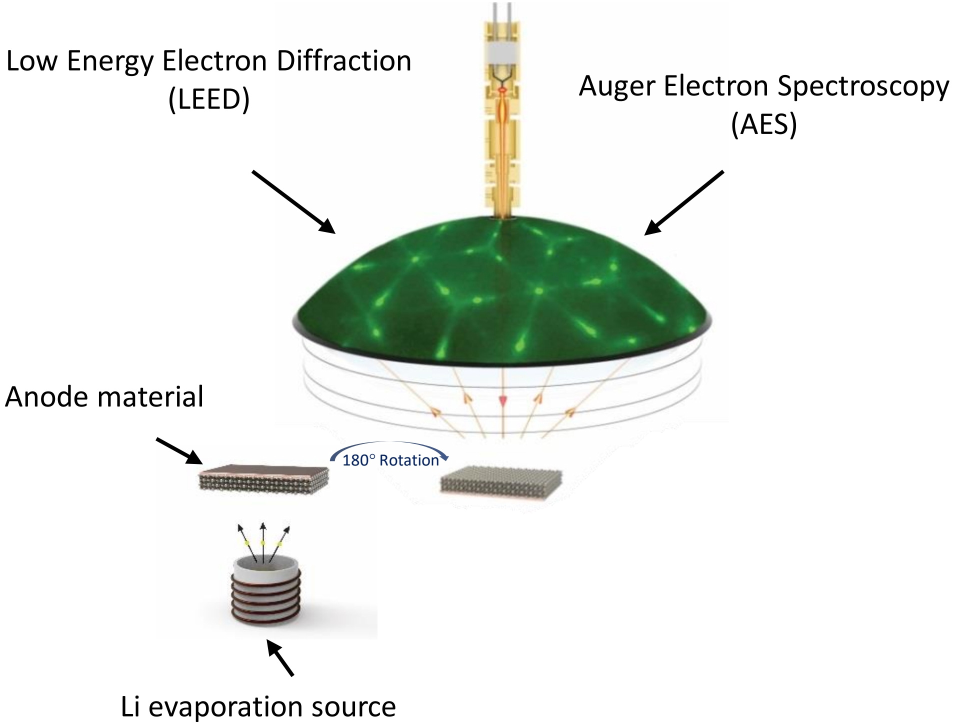
- Single crystals – LEED and AES
- Epitaxial films - LEED and AES
- Polycrystalline and amorphous – only AES

Method:

Ultra-thin film of Li is evaporated on the tested battery material, and measurements of Li diffusion with Auger spectroscopy and electron diffraction are performed

Experimental Set-up

Probing Depth: few nanometers



LEED Fundamentals

History

- 1897 - “Discovery” of electron beams (J.J. Thomson)
- 1924 - Wave nature of electrons postulated (L. de Broglie)

$$\lambda = h/p \qquad \lambda = \sqrt{150.4/E}\ (eV)$$

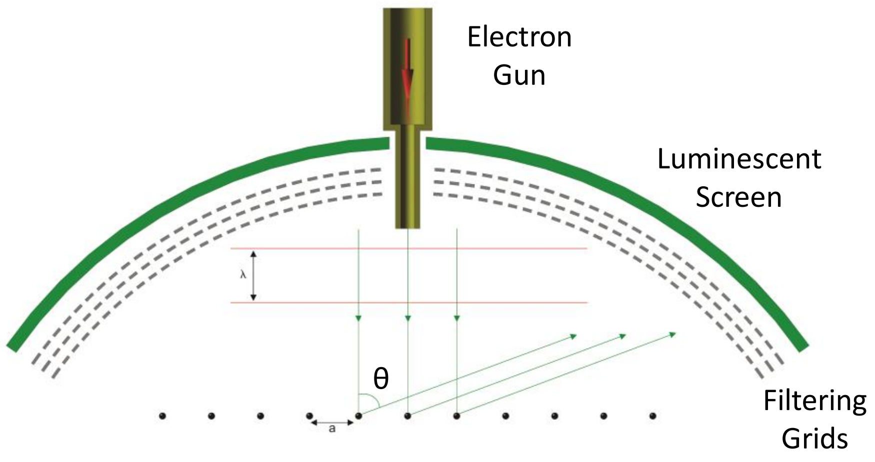
- 1927 - Proof of electron diffraction at an atomic lattice (Ni(111)-surface)
- 1937 - Nobel Prize for Physics awarded to G.P. Davisson (collaboration with L.H. Germer)

Physics

- Wavelength of the electrons is comparable to the lattice spacing of the crystal (a condition for electron diffraction)
- Electrons scattered back from the crystal at certain angles must have maximum intensity

Since 1960 - there are further significant developments and new applications...

LEED Optics



Constructive interference
Enhancement of intensity only in certain directions:
$a \sin\Theta = n\lambda$

Electron Energy (E)	Wavelength (λ)
150eV	1.0Å
100eV	1.4Å
20eV	2.7Å

$1\text{Å} = 10^{-10}\text{m}$

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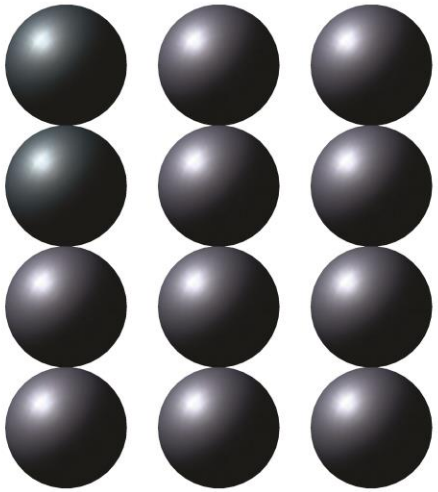
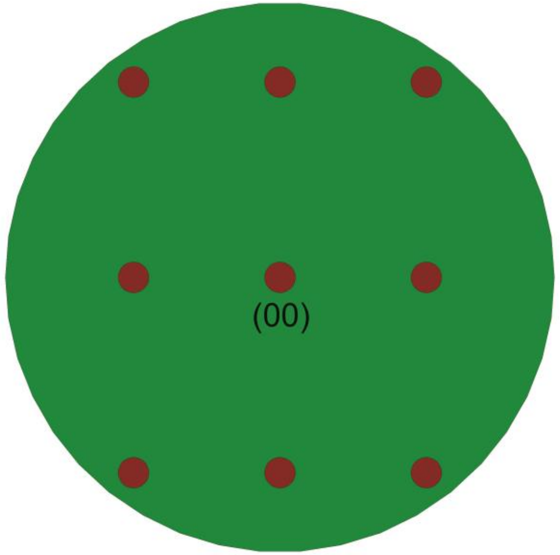
LEED Fundamentals

- LEED mainly provides information on 2D atomic structure of a surface
- Surface atomic structure can be measured with high accuracy

Rectangular symmetry FCC (100)



Real Atomic Space
FCC (110) surface



Diffraction Pattern
LEED

Symmetry of LEED pattern
⇕
Symmetry of real surface atomic structure

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AES Fundamentals

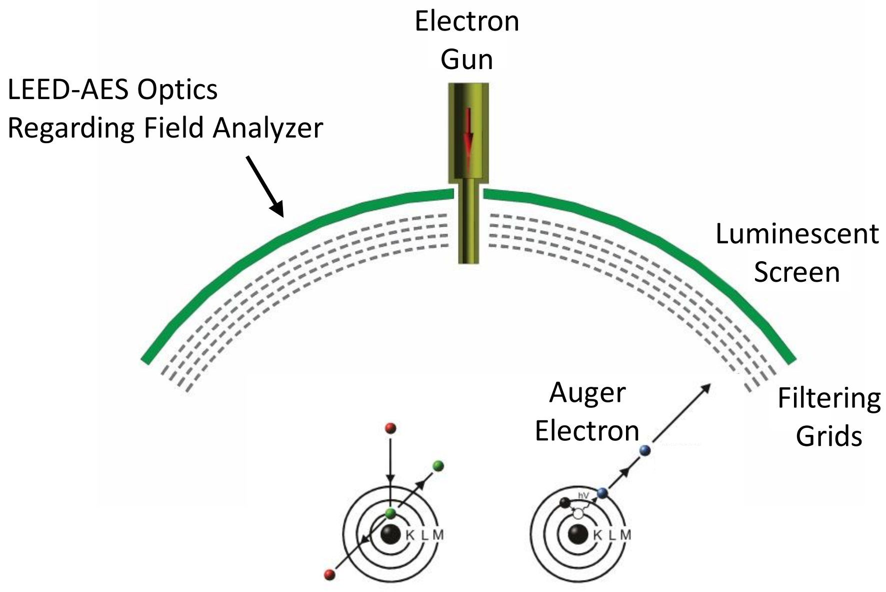
Auger effect – discovered in 1922 by Lise Meitner and Pierre Auger

- Primary electron beam excitation of an atom by removing an electron from core shells
- Empty hole forces another electron to fill the remaining hole
- The released energy causes an electron from the closest outer shell to be emitted from the atom as the Auger electron

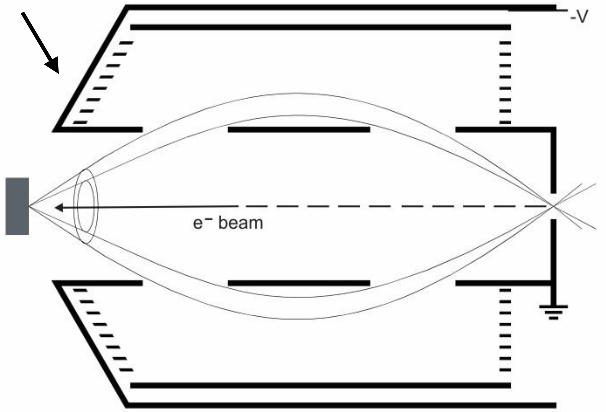
Auger electrons are characteristic for atoms of a specific element due to unique orbital energies

Auger peak energy corresponds to the element on the surface and the intensity of the peak to the element concentration

Lithium atomic number- 3 is limiting use of Energy Dispersive Spectroscopy (EDS) which is coupled with SEM



Cylindrical Mirror Analyzer (CMA)



Auger peaks
Li – 49 eV
C – 272 eV
Si – 92 eV

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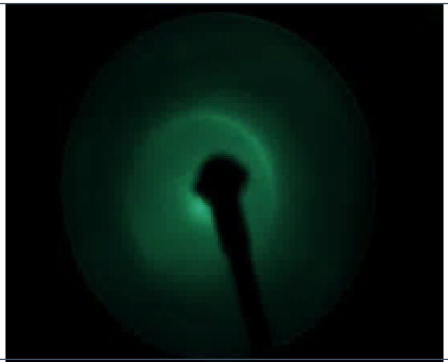
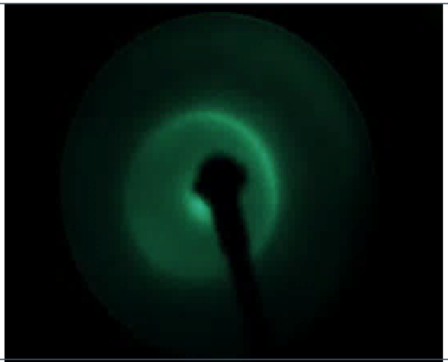
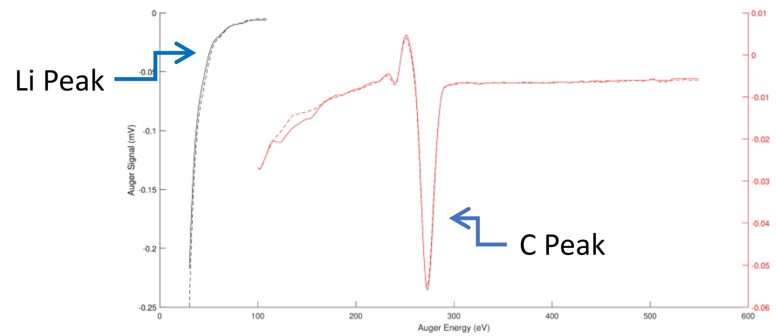
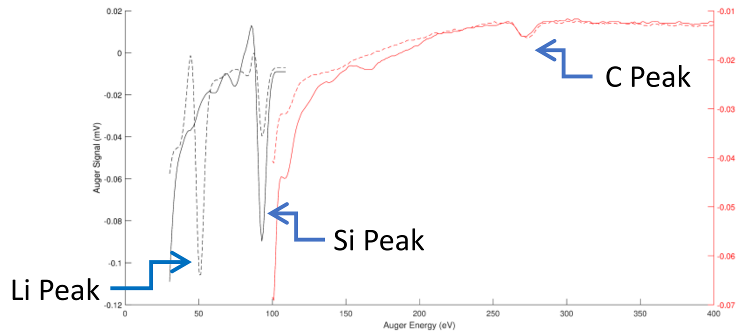
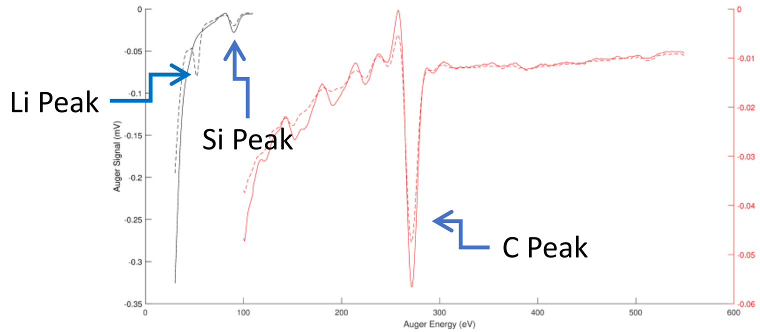
<table>
<tr><th>Substrate and Comments</th><th>LEED – Clean</th><th>LEED - 5Å Lithium</th><th>AES Spectrum (Before/After Evaporation)</th></tr>
<tr><td>HOPG (Graphite)
Strong Li diffusion, no change to surface crystalline structure (25°C)</td><td></td><td></td><td>
</td></tr>
<tr><td>Si(111)
No Li diffusion, drastic change to surface crystalline structure (25°C)</td><td></td><td></td><td>
</td></tr>
<tr><td>SiC-6H
Some Li diffusion, small effect on surface crystalline structure (25°C)</td><td></td><td></td><td>
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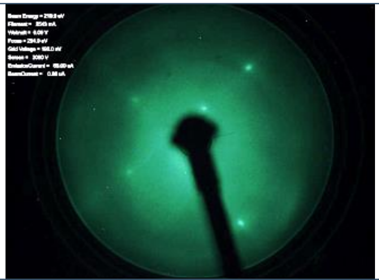
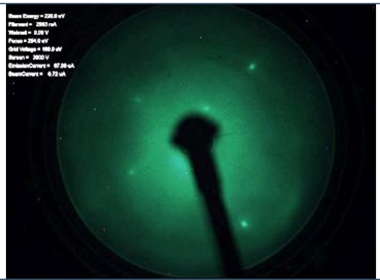
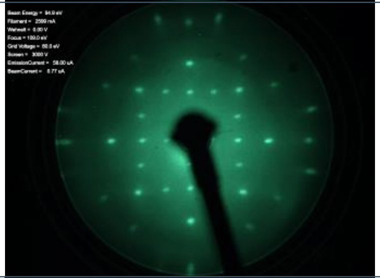
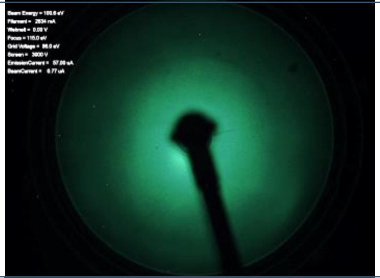
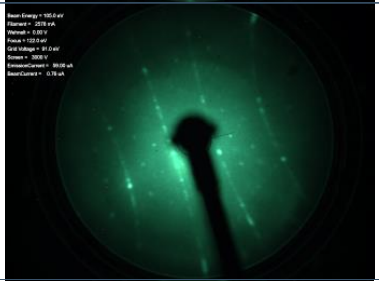
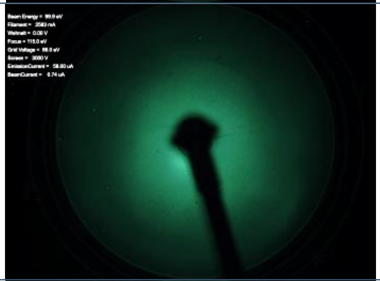
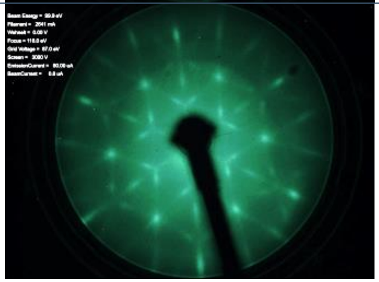
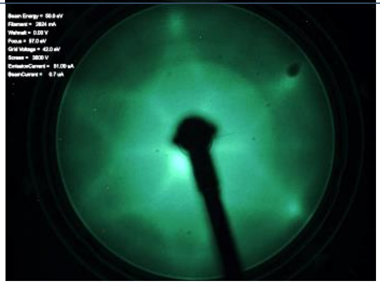
Substrate and Comments	LEED – Clean	LEED - 5Å Lithium	AES (After Evaporation)
Diamond (100) CVD (25°C) Li diffusion, no change			Small Li peak detected: 4 mV
Si (100) (25°C) no Li diffusion, change			Large Li peak: 70 mV
Si (211) (25°C) no Li diffusion, change			Large Li peak: 66 mV
$LiNbO_3$ – Mg Doped (25°C) Li diffusion, some change			No Li peak detected

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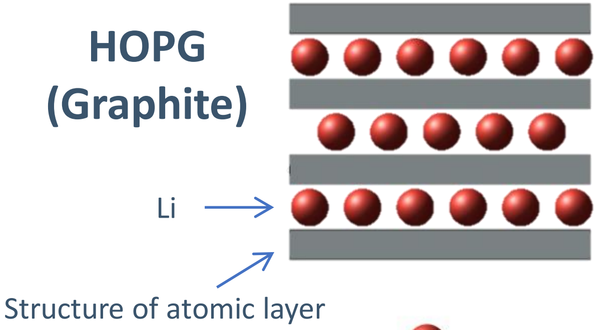
Conclusions

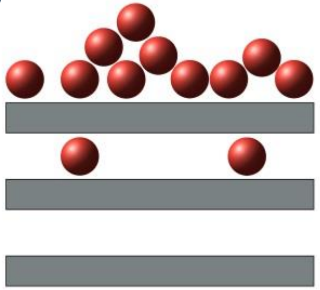
We identified 3 categories of the materials that can be used for the Li battery anode:

HOPG (Graphite)



"Graphite - like" : Materials with "native" rapid Li diffusion properties and no effect on structural order
Similar: LiNbO3-Mg doped

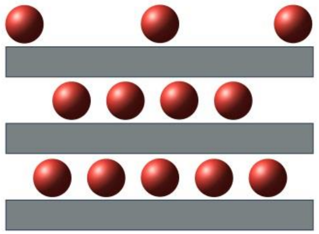
Si(111)



"Silicon - like" : Materials with no "native" Li diffusion and strong effect on structural order – polycrystalization or amorphization
Similar: Si(100), Si(211)

Silicon requires nano-engineering process to create the Li diffusion path

SiC-6H



"Silicon carbide - like" : Materials that have good "native" Li diffusion and low effect on structural order
Similar: Diamond CVD

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Summary

- Our data suggest high correlation between Li thermal diffusion and lithiation process in the battery cell
- Presented data confirms existing knowledge for Li diffusion on Graphite and Silicon
- Lithiation process in the battery cell is very difficult to measure at the nanoscale level and we offer measurements of Li thermal diffusion as a complementary method
- Li diffusion from ultra-thin film is a good practical method to perform initial investigations of next generation battery materials
- This novel method and classification shows very attractive properties of SiC or $LiNbO_3$ to be next generation battery anodes
- Using single crystal material for Li diffusion, experimental modeling is a very sensitive method to probe nanoscale Li interactions
  - Problems when making some complex oxides in single crystal form can be reduced by using epitaxial films from magnetron sputtering process
- The most desired material for the high energy density:
  - Strong "native" Li diffusion properties or intercalation
  - High bonding capacity of the electrode atom to several Li atoms – similar to silicon

Techniques:

- Auger electron spectroscopy (AES) demonstrates a very good sensitivity to detect Lithium and is suitable for all single crystal, polycrystalline and amorphous materials
- Low energy electron diffraction (LEED) is a powerful technique to probe Li diffusion but it is limited to the single crystals and epitaxial thin films

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Summary – Possible Applications

Next generation battery materials for Li-ion and solid electrolyte as an early indication of future battery performance and classification

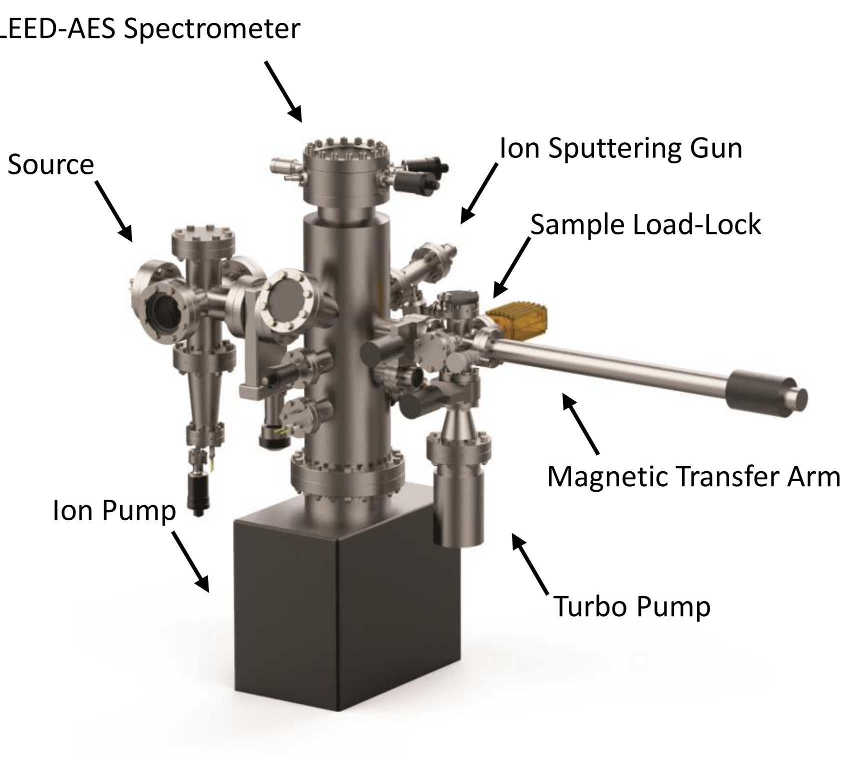
Processes that can impact Li thermal diffusion:

- Annealing in vacuum or gas atmosphere
- Deposited films as a buffer layer
- Exposure to liquid electrolyte
- Exposure to various gases and water vapour
- Plasma treatment

Additional capability: Depth profiling of Li diffusion

Cathode materials: future plans but require creation of Li deficiency

Lithium Diffusion Tester



https://events.techconnect.org/DTCFall/awards.html

Thank you for your time and attention

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Project financed by OCI R&D Funds

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