Lithium Diffusion and Surface Oxidation on Battery Materials at Room Temperature Characterized by AES and LEED

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Introduction

Next-generation clean energy storage needs high-quality materials, interfaces, and stabilizing compounds to enhance the performance of the existing Li-based technology.

There is also strong interest in new materials that will accumulate more Li atoms in the crystalline structure with high Li ion mobility, stable charge cycling and log life.

Existing Li ion based technology is a proved successful but still is bearing low energy density, capacity degradation and dendrite growth.

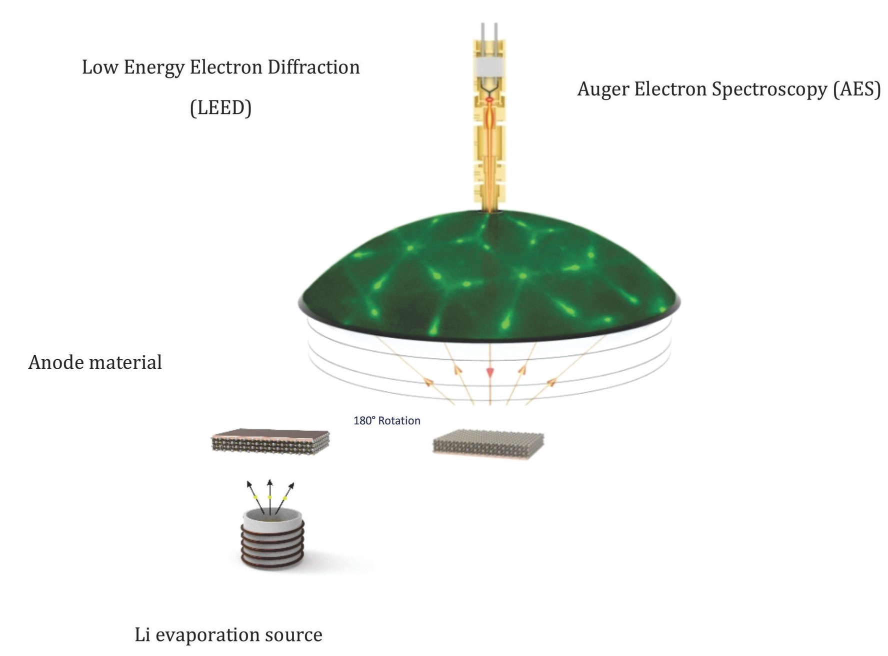
Those factors require a wider spectrum of advanced tools for the battery materials characterization and our method is addressing that field.

Li transport properties are the key factor for the battery's performance.

Li passive diffusion is defined as the process of Li atoms/ions migration under a concentration gradient and activated by thermal energy from atomic vibrations of the host structure.

This process of passive Li diffusion is strongly correspond to the active Li diffusion processes where external energy component such electrical potential is applied. It is expected that materials that exhibit good Li passive diffusion will perform much better under the external electrical potential.

Experimental Set-up



Sample preparation and characterisation:

- Single crystal is cleaned by thermal annealing after loading to UHV system

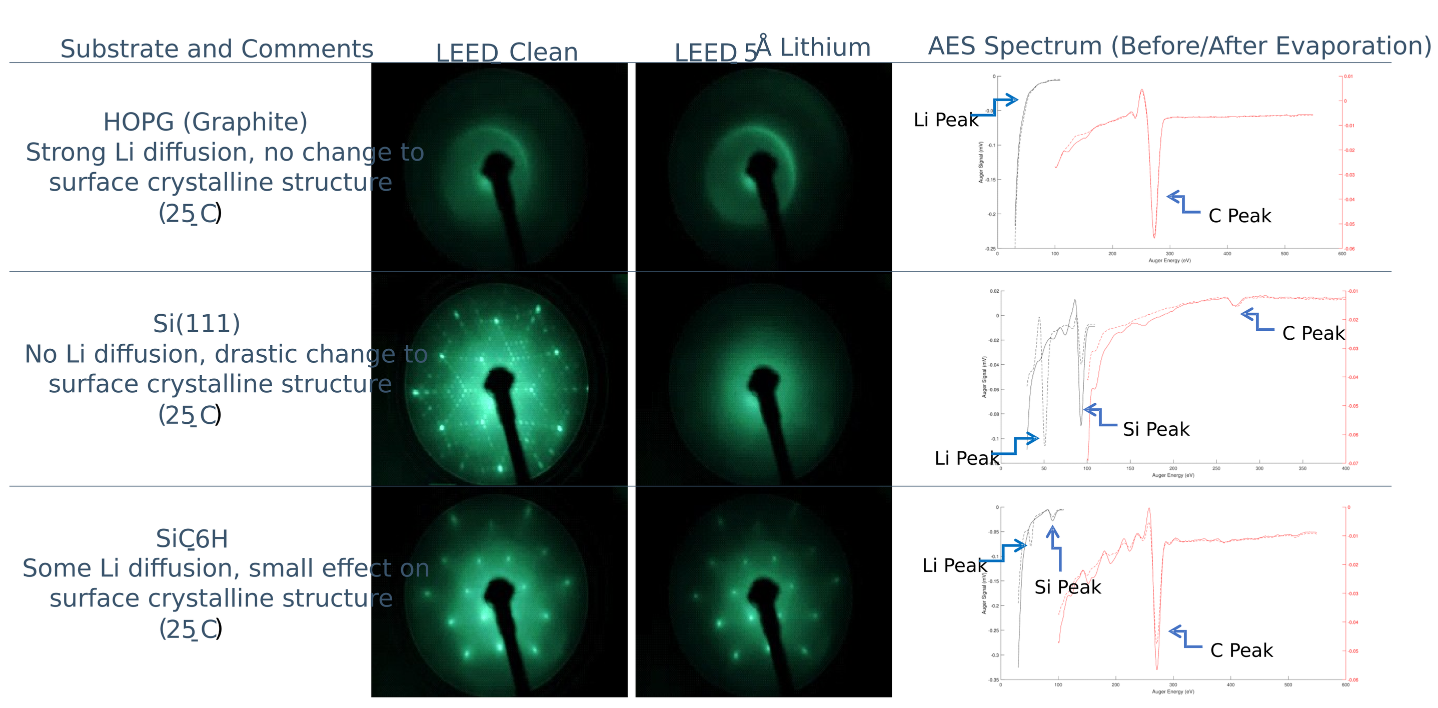
- Thin film of Li is evaporated under UHV conditions

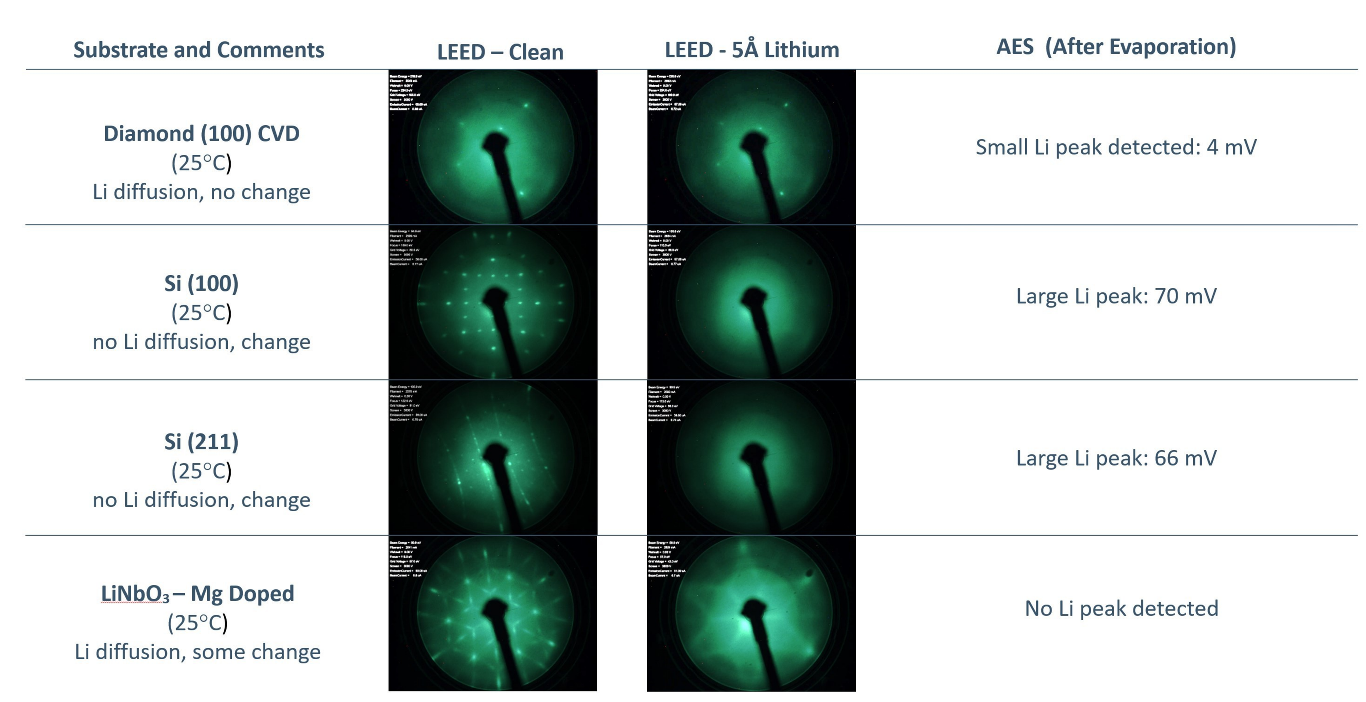
- Surface crystallography with LEED

- Measurements of Li peak at 52 eV with AES and other peaks depending on the substrate composition

- Li deposition thickness is monitored with Quarts Crystal Microbalance

Results - Li Diffusion





Results - Li Oxidation

Comparison of AES data for SiC single crystal and polycrystalline samples
All experiments at Room Temperature

Process	SiC 6H Si face	SiC CVD Si present on surface
After UV cleaning	Si 92eV: 32.5 mV	Si 92eV: 20 mV
After 100 A of Li evaporation	Si 92eV: 0 mV Li 51 eV: 70 mV	Si 92eV: 0 mV Li 51 eV: 25.8 mV

Process	SiC 6H C face	SiC Recrystallized, very lo Si present on the surface
After UV cleaning	Si 92eV: 0 mV	Si 92eV: spectrum is "bent"
After 100 A of Li evaporation	Si 92eV: 0 mV Li 51 eV: 4 mV	Si 92eV: 0 mV Li 51 eV: 6.6 mV

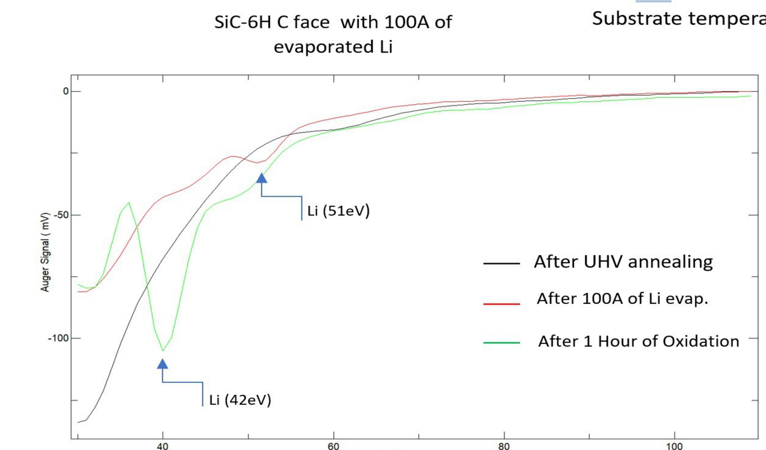
The presence of Si atoms on the surface limits Li diffusion into bulk

Li diffusion into a single crystal structure is more preferential than diffusion into grain boundaries
Substrate temperature: 300K

Oxygen exposure of SiC with an evaporated dose of Li -100 Angstrom

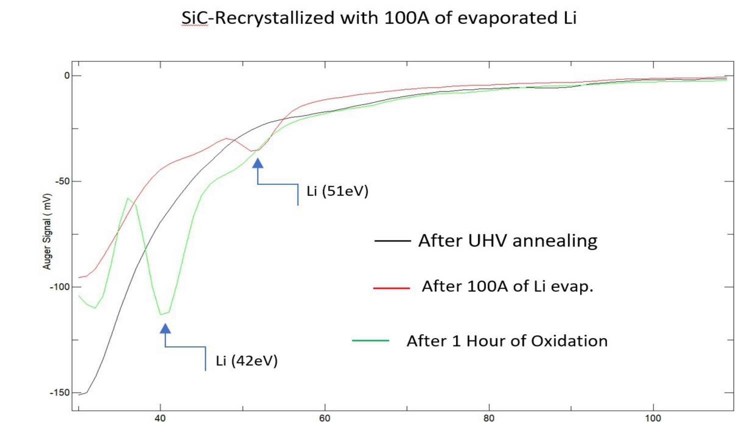
Oxygen pressure: 5x 10-6 Torr
AES measurements
Substrate temperature: 300K

SiC-6H C face with 100A of evaporated Li



Li Auger peak is 19 times larger after oxidation, and energy is shifted to 42 eV Substrate during oxidation temperature: 300K

SiC-Recrystallized with 100A of evaporated Li

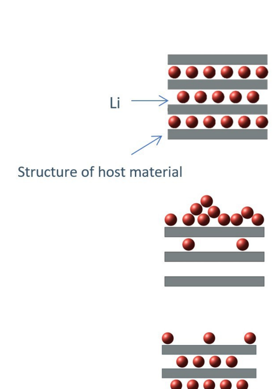


Li Auger peak is 8 times larger after oxidation, and energy is shifted to 42 eV Substrate during oxidation temperature: 300K

Discussion

Classification of the tested materials

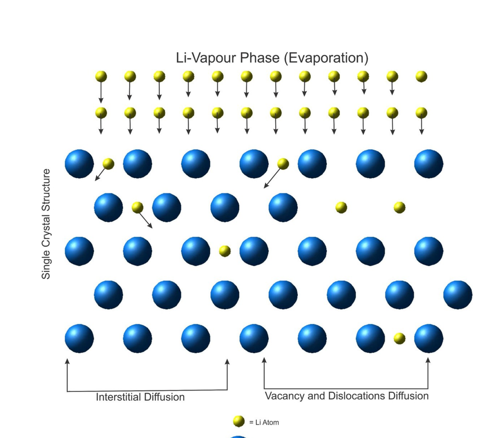
We identified 3 categories of characterized materials:

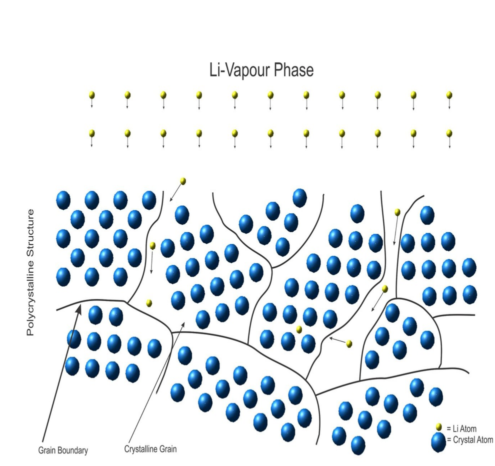


"Rapid lattice diffusion": Materials with passive rapid Li diffusion in lattice structure: HOPG and no effect on the long-range structural order

"No lattice diffusion": Materials with no passive Li diffusion and a strong effect on long-range structural order – polycrystalization or amorphization
Si(100), Si(211), SrTiO2, Ga2O3
Silicon requires a nano-engineering process to create the Li diffusion path

"Moderate lattice diffusion": Materials that have moderate passive Li diffusion and some effect on the long-range structural order
SiC, CVD Diamond, SiO2/Si(001), LiNb2O3, TiO2, TiO2/Si(111), CdS, InP





This approach offers a unique method to measure transport of Li atoms/ions into the solid structure and simplify the understanding of diffusion processes especially if the single-crystal structures are used. The single structures are free from grain boundaries. This approach allows for classification of the materials that are attractive to Lithium diffusion based on the pure lattice component.

The conditions which limit Li diffusion such as lithium oxidation, lithium plating and the role fo grain boundaries can be investigated selectively and independently of other factors.

Conclusions

- There is a large group of materials with moderate Li diffusion at room temperature: SiC, SiO2/Si(001), Diamond CVD, LiNbO3, TiO2, CdS and InP.

- These materials can be used as a thin film interface at the electrode-electrolite interface of Li-based batteries reducing plating, dendrite growth or capacity degradation

-Silicon lattice is presenting the barrier for Li diffusion. Silicon is very atractive material because of its high capacity for bonding with Li.
However, the lack of lattice diffusion require to develop special nano-structural paths allowing migration of Li ions.

- Ga2O3 is the case that possibly unsaturated oxygen atoms on the surface are "trapping" Li atoms. Layered structure of Ga2O3 is not helping with that.

- SiC demonstrate the case that Li lattice diffusion is more preferential than grain boundary diffusion

- Li oxidation reaction on the surface is more preferential than Li diffusion Li atoms are diffusing from bulk to surface to get oxidized
- Oxidation reation on Lithiated single crystal is 2 times faster than on Lithiated polycrystalline SiC