Graphite Degradation in Molten FLiNaK – *Role of Salt Impurities*

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Graphite – Molten Salt Interactions Workshop - ORNL

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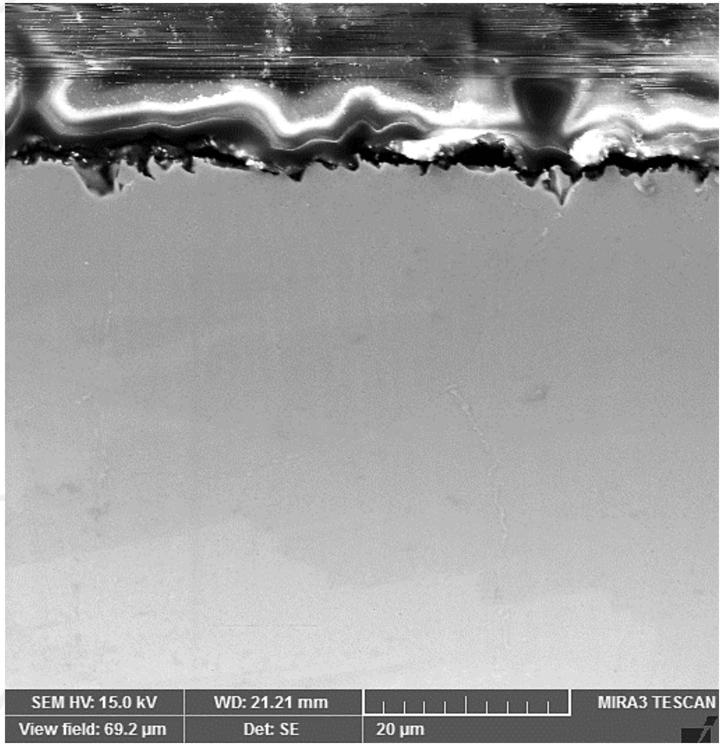
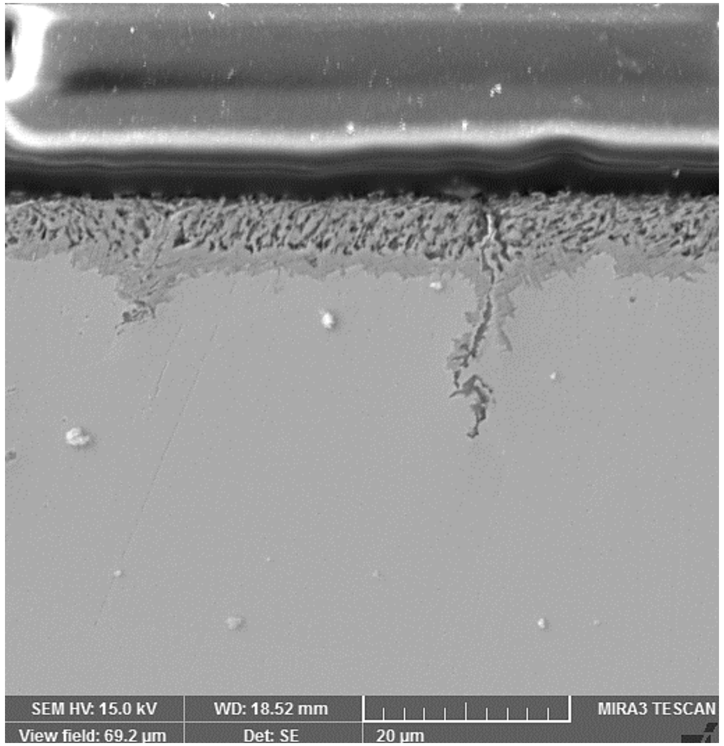
Background

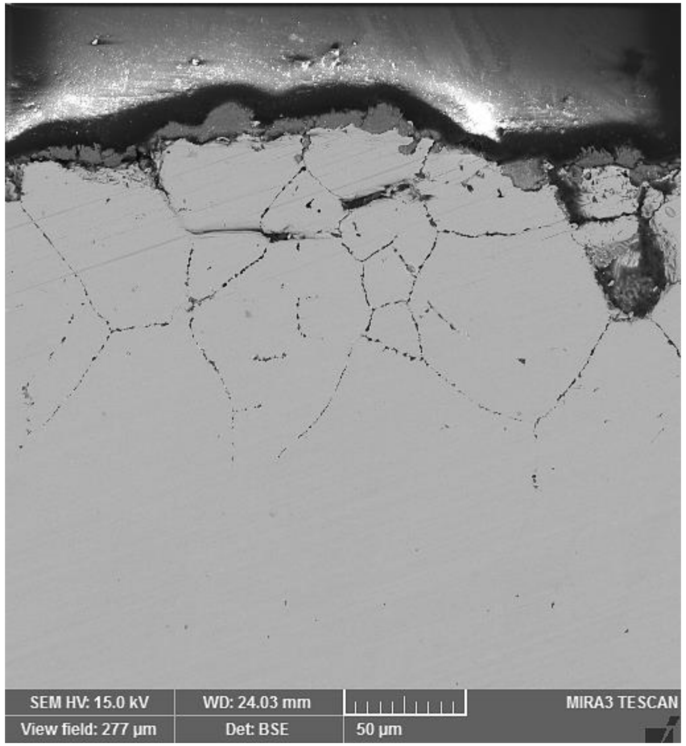
- ***Our research focus - metallic corrosion in halide salts for MSRs and CSP***
  - ***Measurement and Control of Salt Redox – effect on alloy corrosion***
  - ***Effect of Added Impurities on Corrosion in FLiNaK***



SS316H exposed to FLiNaK



SS316H exposed to FLiNaK +0.5 wt.% Li_2O



SS316H exposed to FLiNaK + 0.5 wt.% NiO

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Graphite – Molten Fluoride Interaction

- **Solidified FLiNaK-puck was more difficult to remove from graphite crucibles when certain oxide or fluoride impurities were intentionally added to the salt**
  - **Wetting behavior of FLiNaK changed with impurities**
- **Some oxide impurities lead to “leak” of FLiNak in the graphite crucible**
- ***We decided to systematically study the effect of salt impurities on graphite “wetting” or impregnation***

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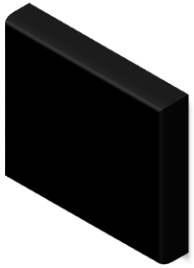
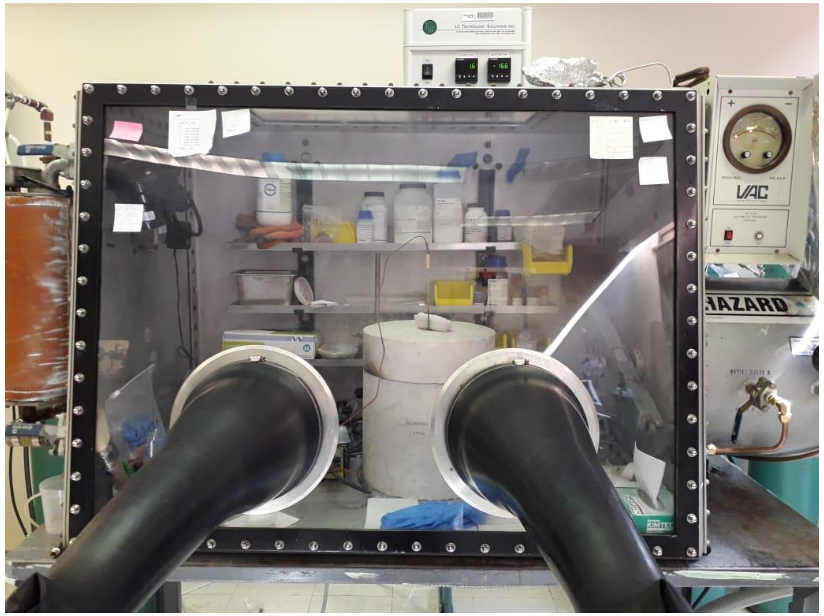
Experimental Methods



Graphite
Sample



- Graphite “fired” in glovebox by heating the sample at 900 °C in Ar-4%H_2 gas environment - to remove moisture and other impurities
- Tests conducted at 700^{o}C for 100 hours in Nickel crucibles
- IG-110 High Purity Graphite *(Ash content <5ppm)*

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Graphite Testing Conditions

- **Graphite Samples were Exposed to molten FLiNaK salt** *(46.5-11.5-42 mol % LiF-NaF-KF)*
- **At 700^{o}C for 100 hours in Nickel crucibles**

Graphite Fired/Not Fired	Salt Environment
Fired	Purified FLiNaK
Not Fired	Purified FLiNaK
Fired	FLiNaK + 0.5 wt.% Li_2O
Fired	FLiNaK + 0.5 wt.% Cr_2O_3
Fired	FLiNaK + 0.5 wt.% NiO
Fired	FLiNaK + 0.5 wt.% CrF_3
Fired	FLiNaK + 0.2 wt.% Li
Fired	FLiNaK + 2 wt.% Li

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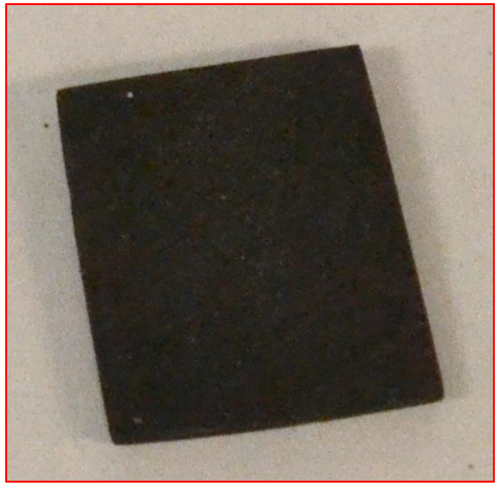
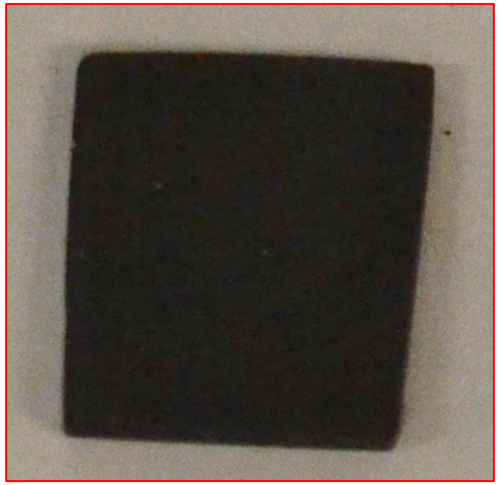
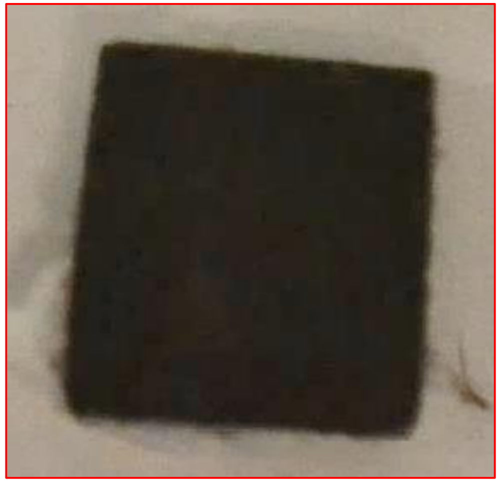
Organic Impurities and Moisture in Graphite

Graphite Samples “Fired” at 900°C in Ar-4%H_2 Environment

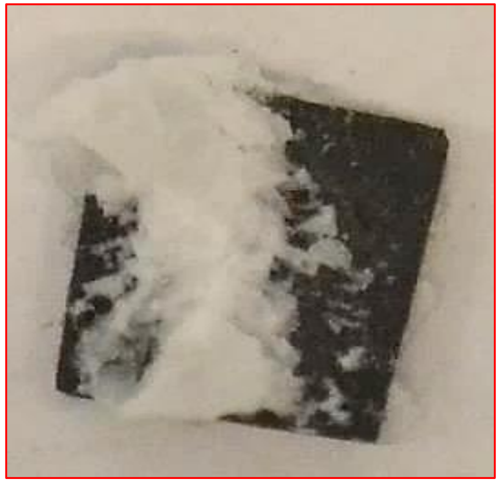




Sample *(Fired)*
No mass gain or loss after test



TOP



BOTTOM

Graphite Sample *(Not Fired)*

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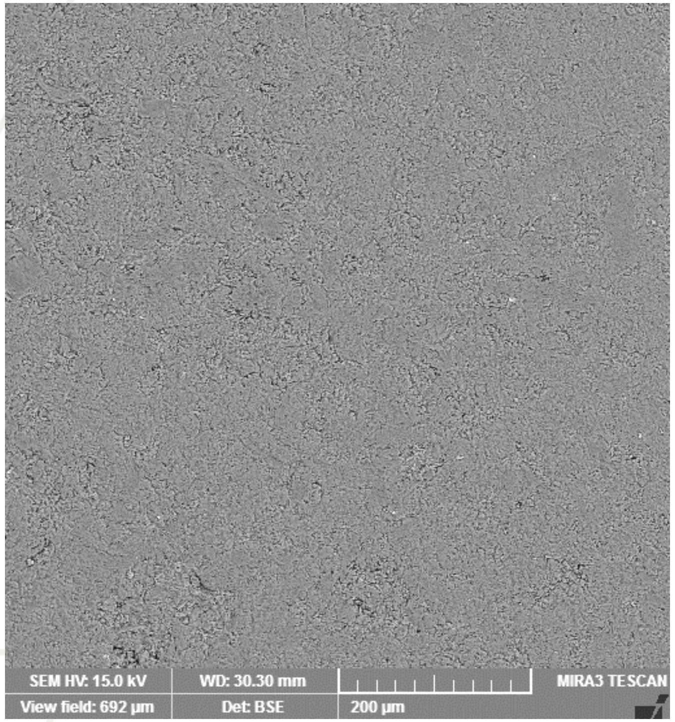
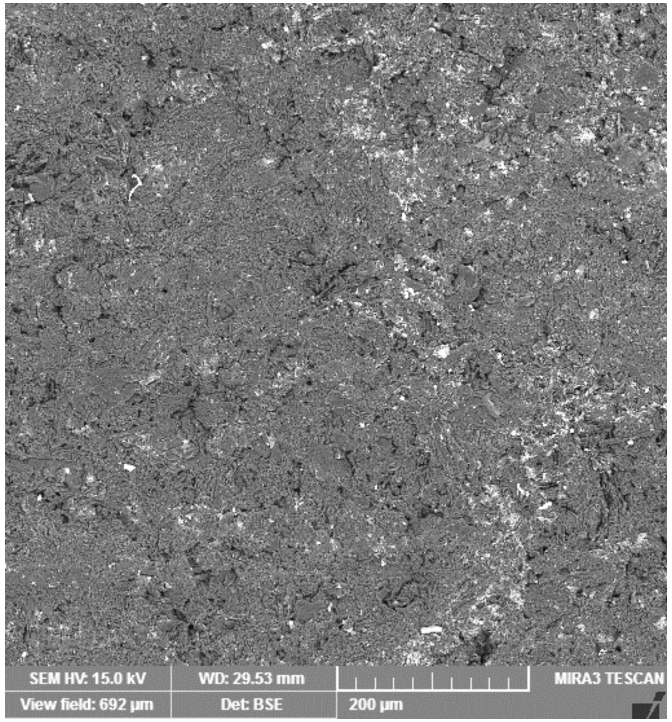
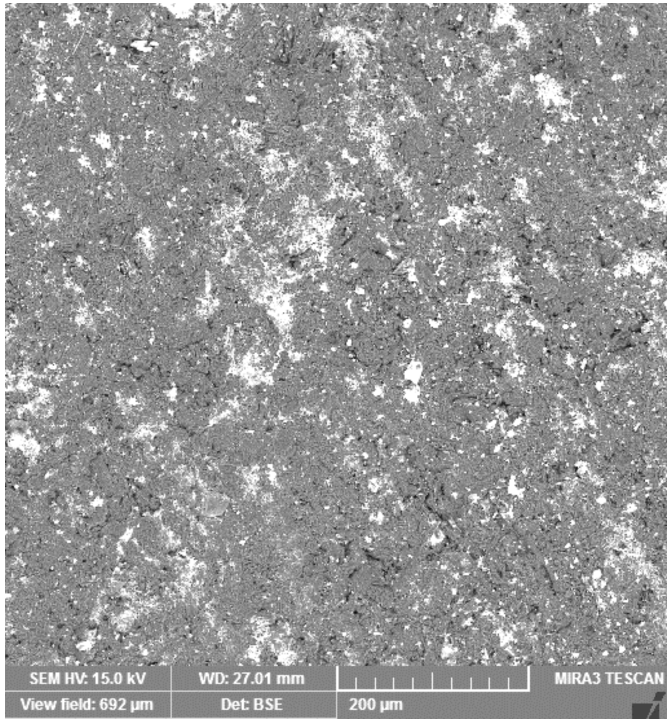
Salt at the Surface of Graphite - *Wetting*



Untested Graphite IG-110



Graphite (Fired) in Molten FLiNaK - Top



Graphite (Not Fired) in Molten FLiNaK - Top

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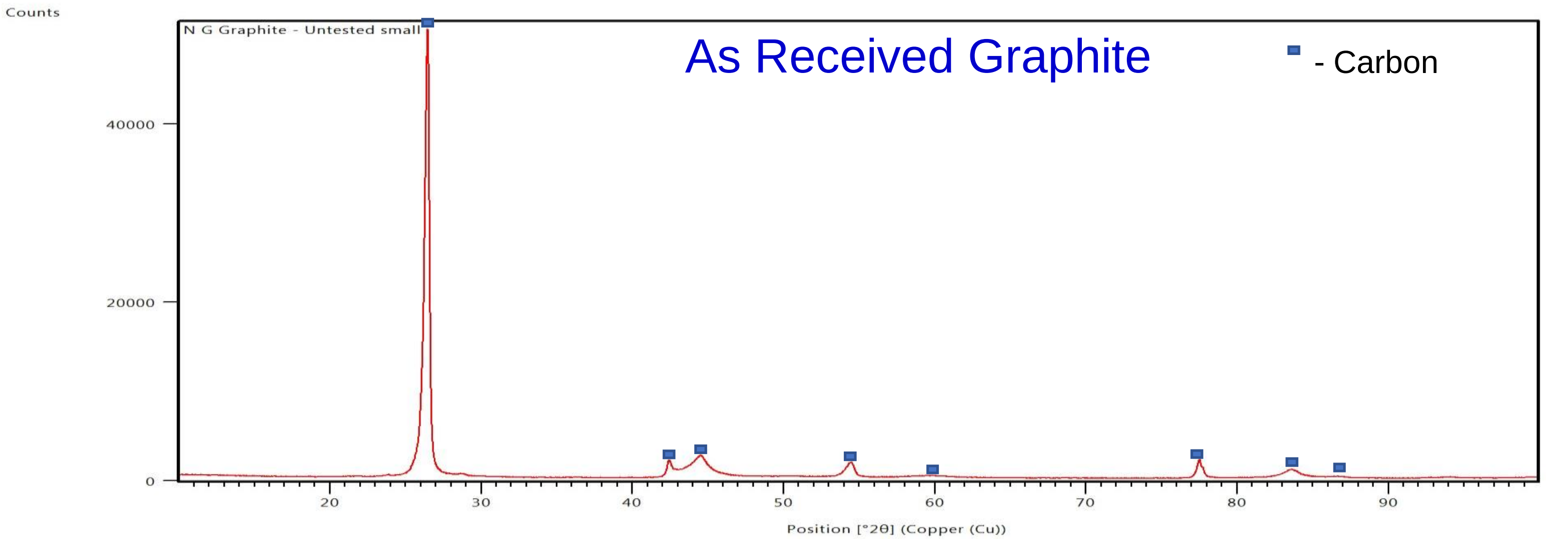
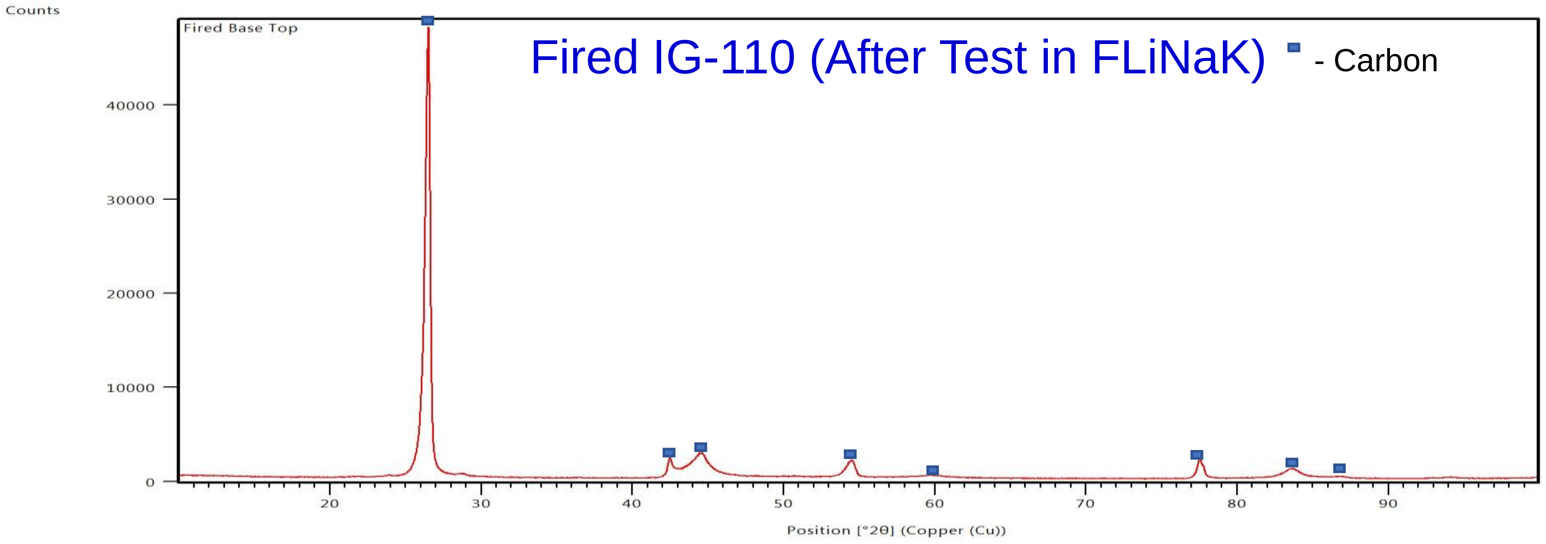
XRD of IG-110 Graphite Samples





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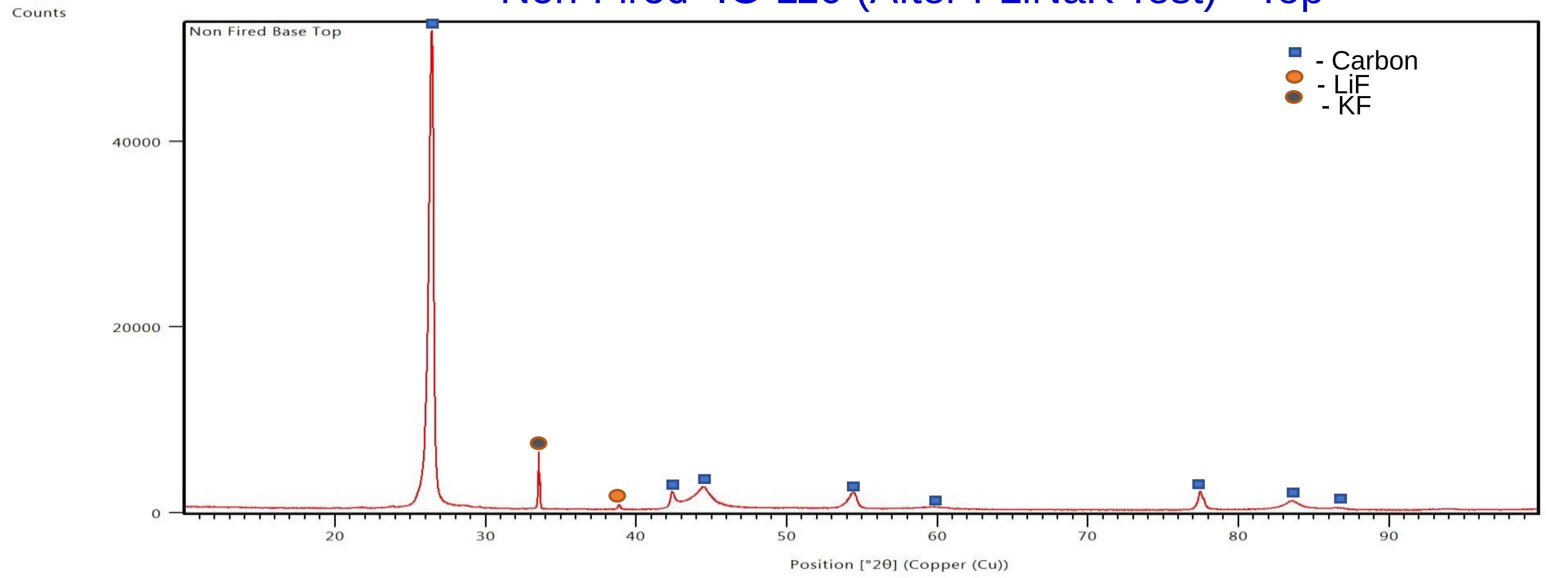
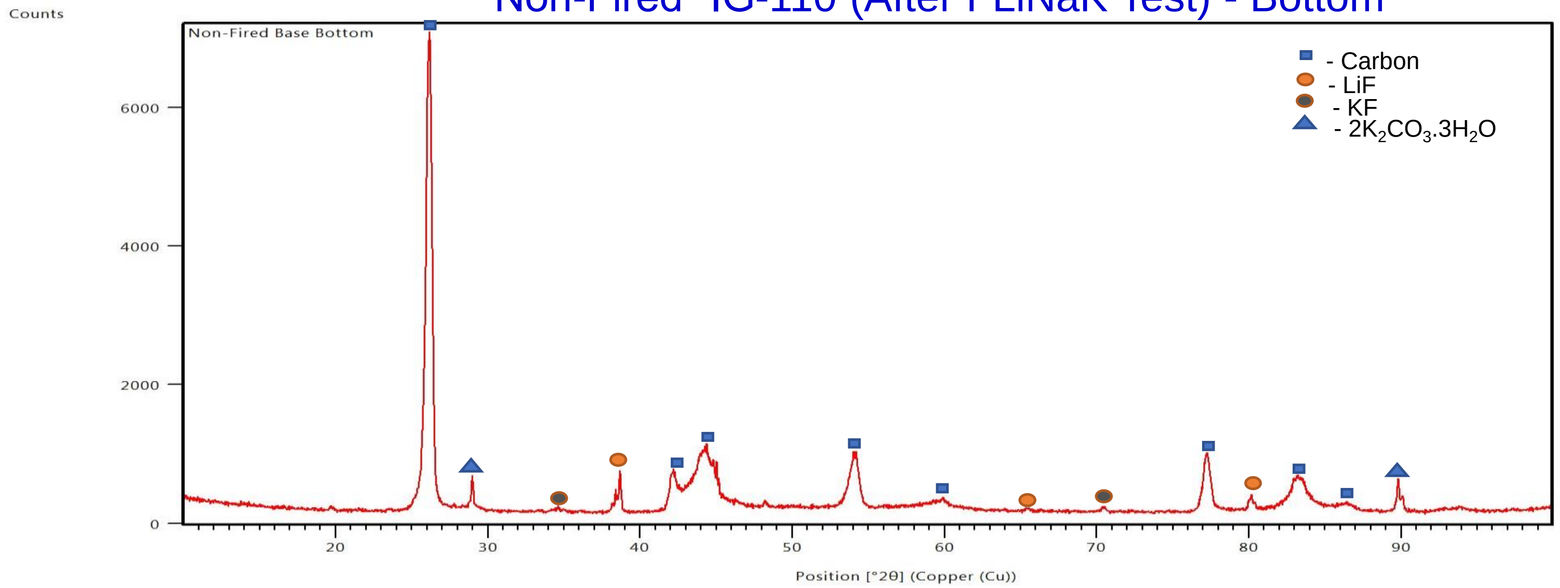
XRD of “Non-Fired” IG-110 Graphite Samples

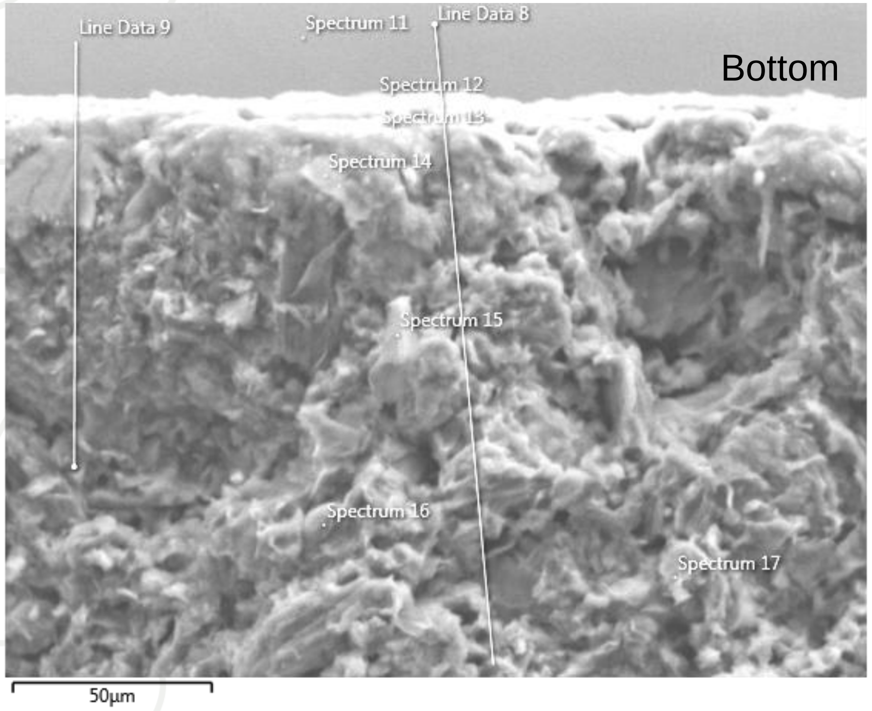
“Non-Fired” IG-110 (After FLiNaK Test) - Top

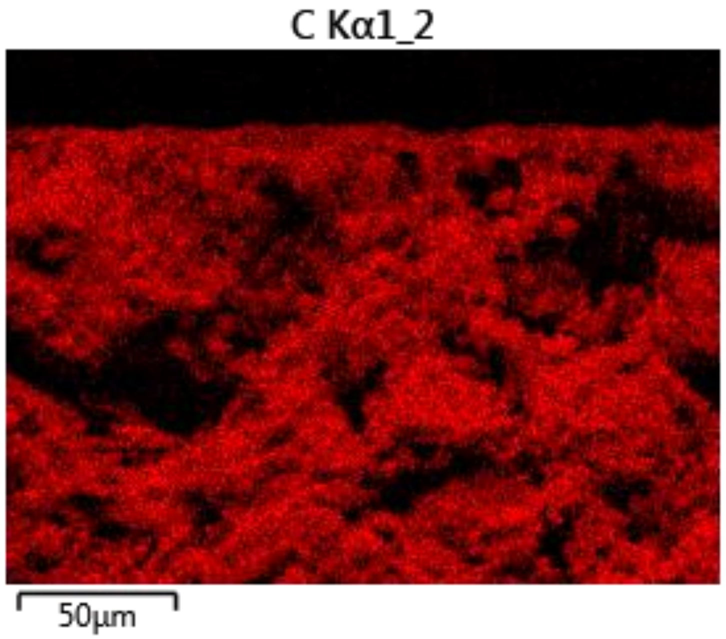


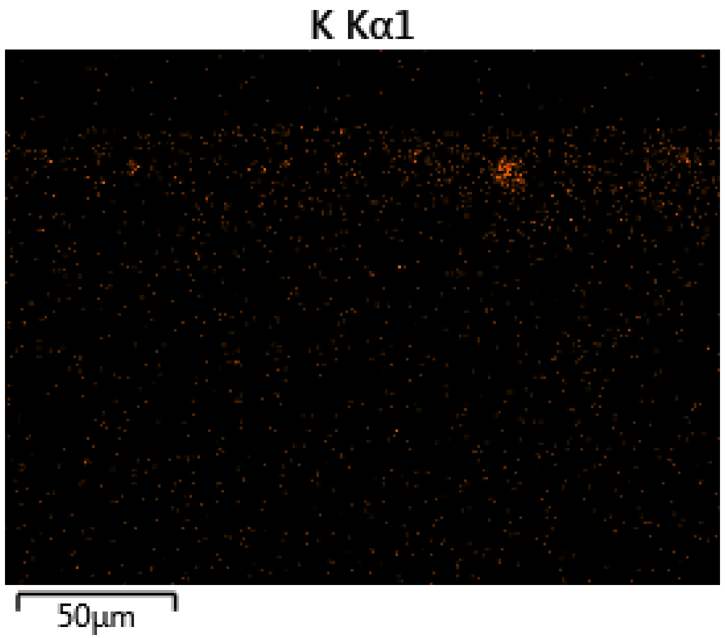
“Non-Fired” IG-110 (After FLiNaK Test) - Bottom



EDS - *Fractured "Fired" Graphite Sample After FLiNaK Exposure*







- **SEM images of cross-section of tested Graphite specimens**
- **Cross-sectioning performed by breaking the sample without cutting it with a saw to avoid salt contamination**

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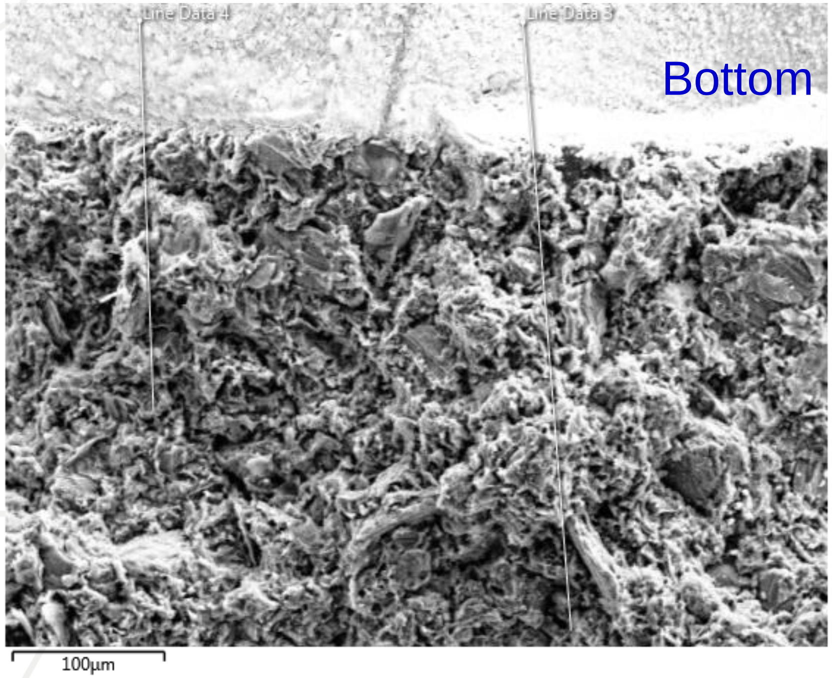
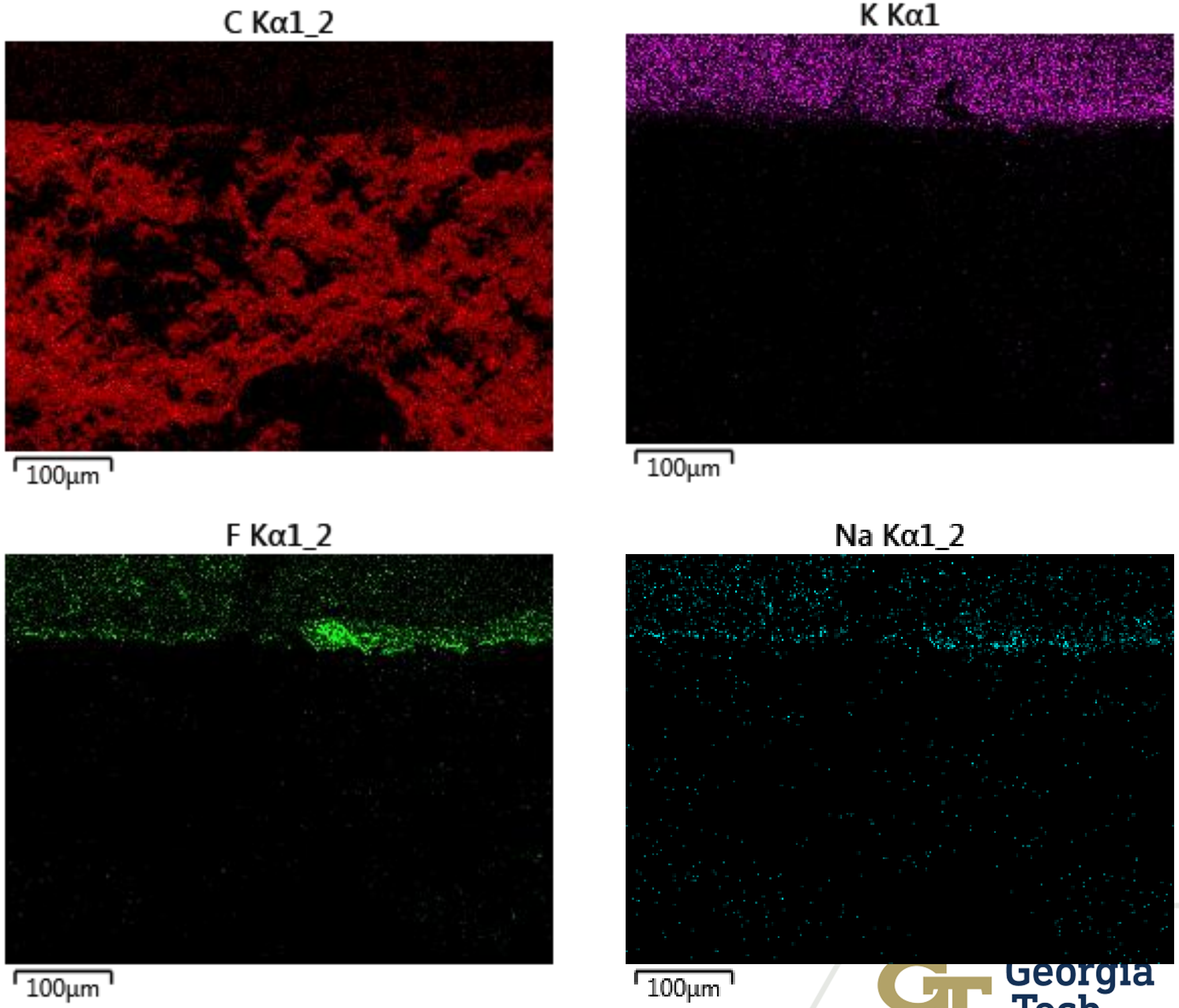
EDS - *Fractured “Not Fired” Graphite Sample after FLiNaK Exposure*





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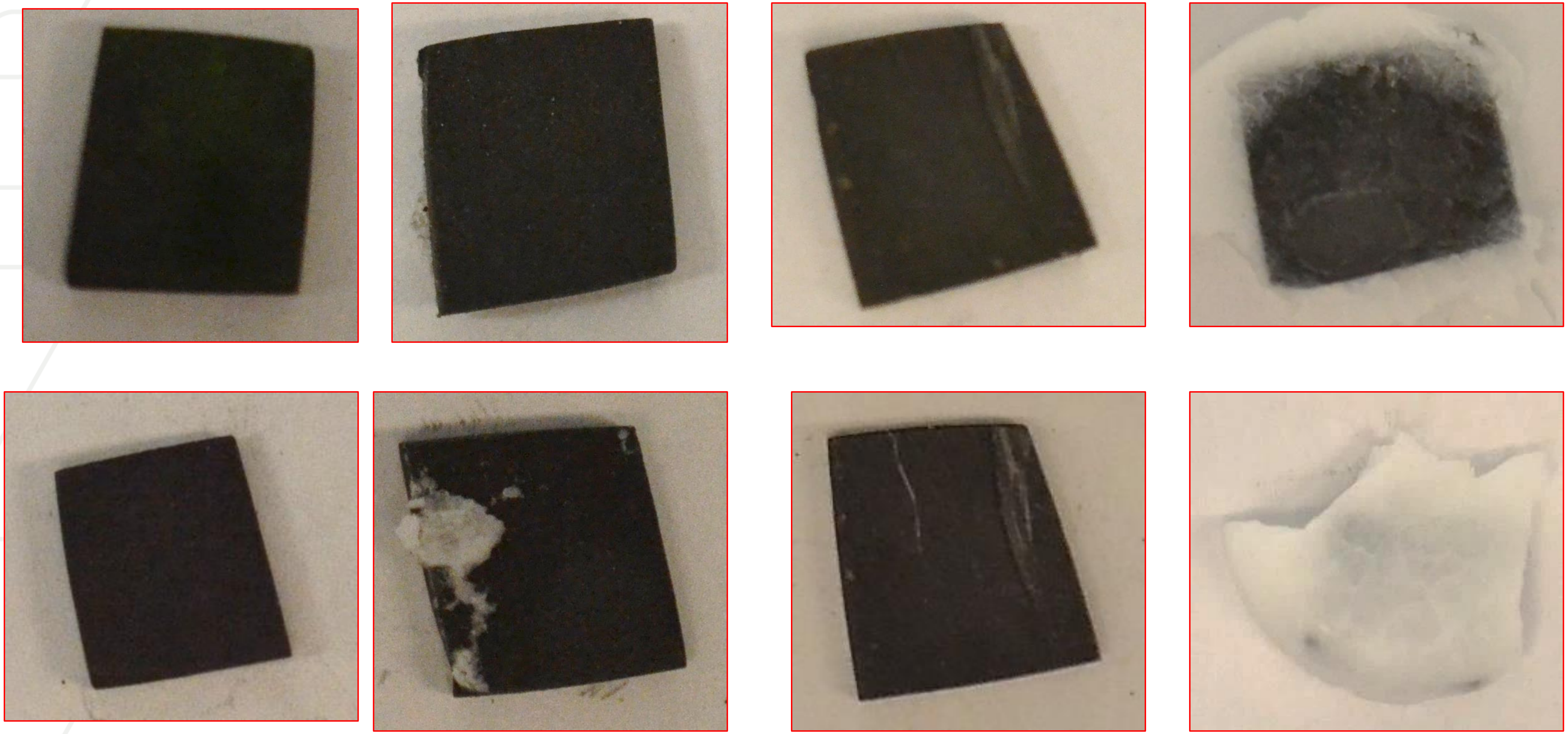
Graphite (Fired) in Molten FLiNak with Impurities



TOP

BOTTOM

FLiNaK + 0.5 wt.% CrF_3	FLiNaK + 0.5 wt.% NiO	FLiNaK + 0.5 wt.% Cr_2O_3	FLiNaK + 0.5 wt.% Li_2O

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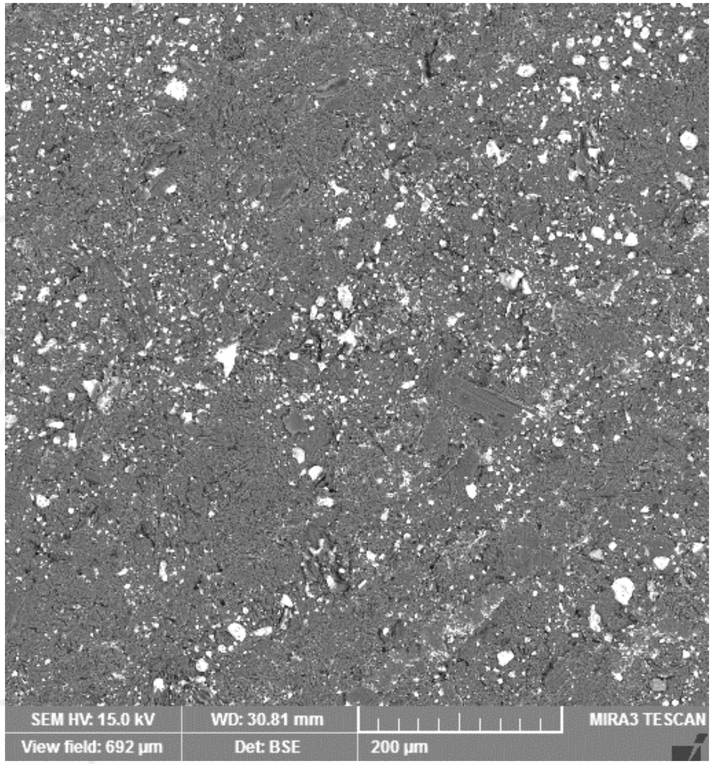
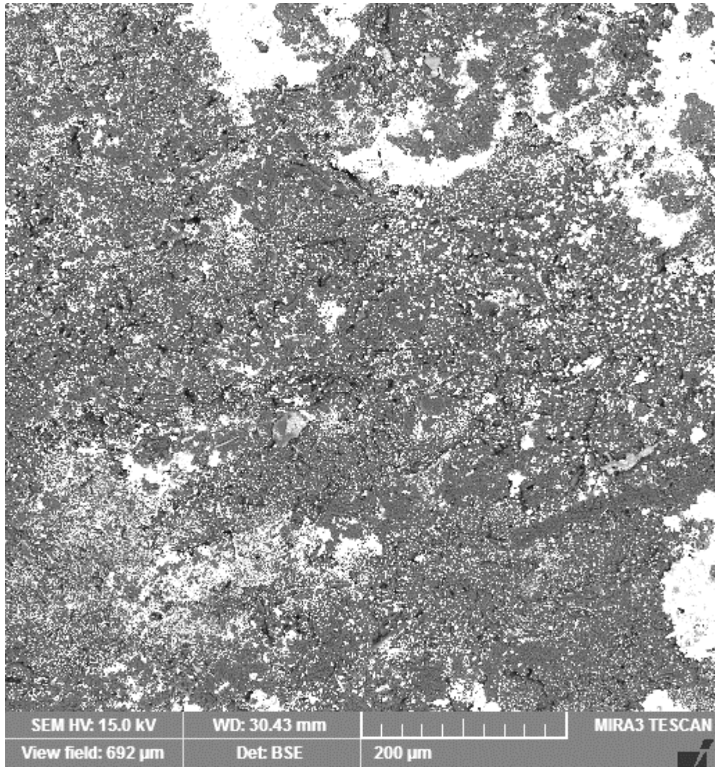
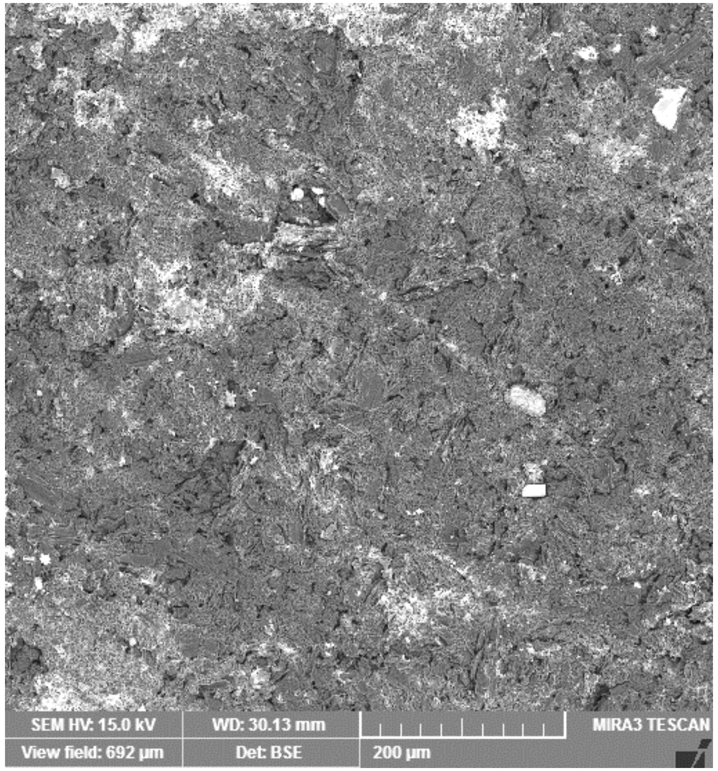
Surface of Tested Graphite Samples



Graphite (Fired) in Molten FLiNaK with added Cr_2O_3 - Top



Graphite (Fired) in Molten FLiNaK with added CrF_3 - Top



Graphite (Fired) in Molten FLiNaK with added NiO - Top

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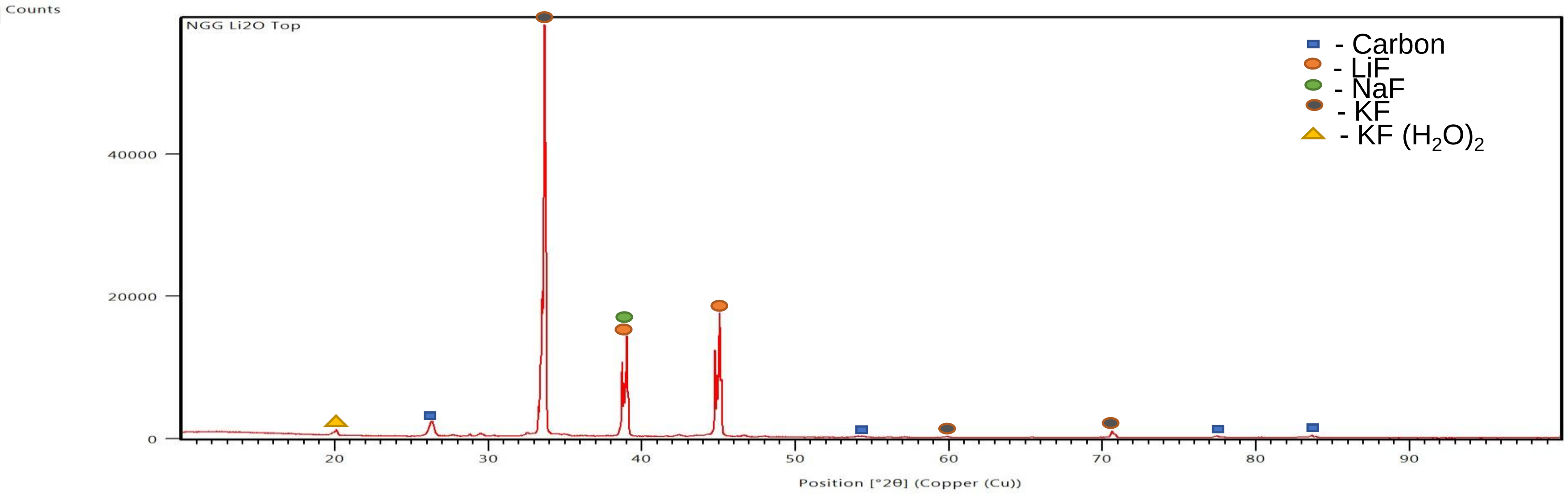
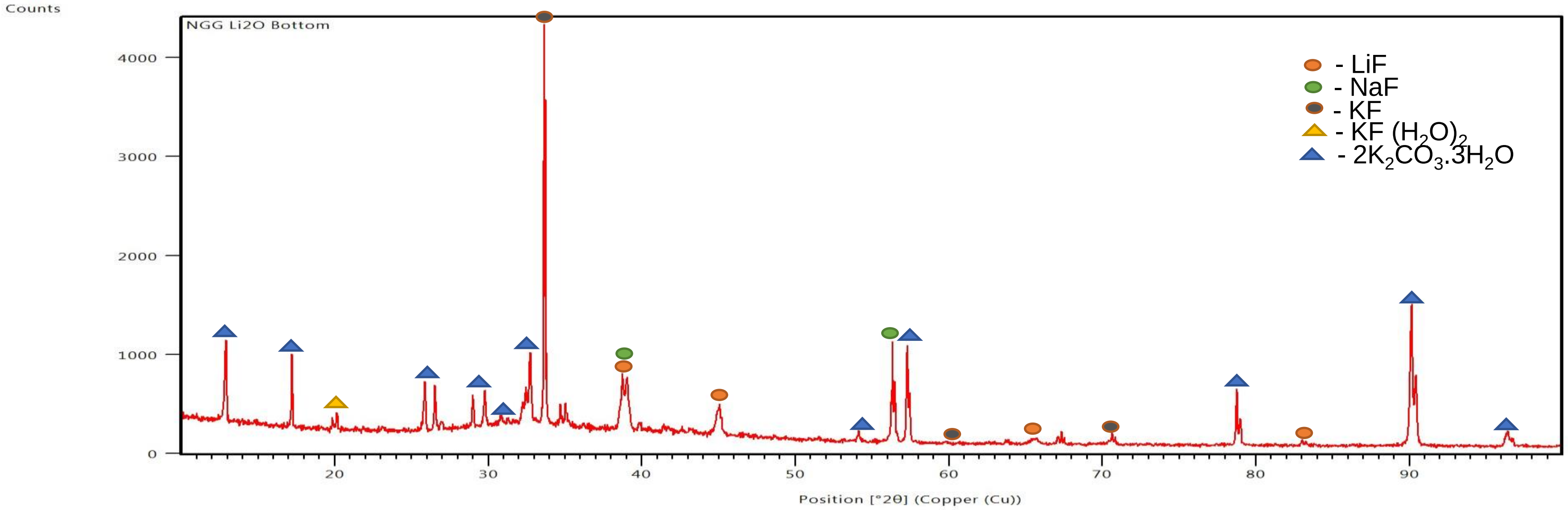
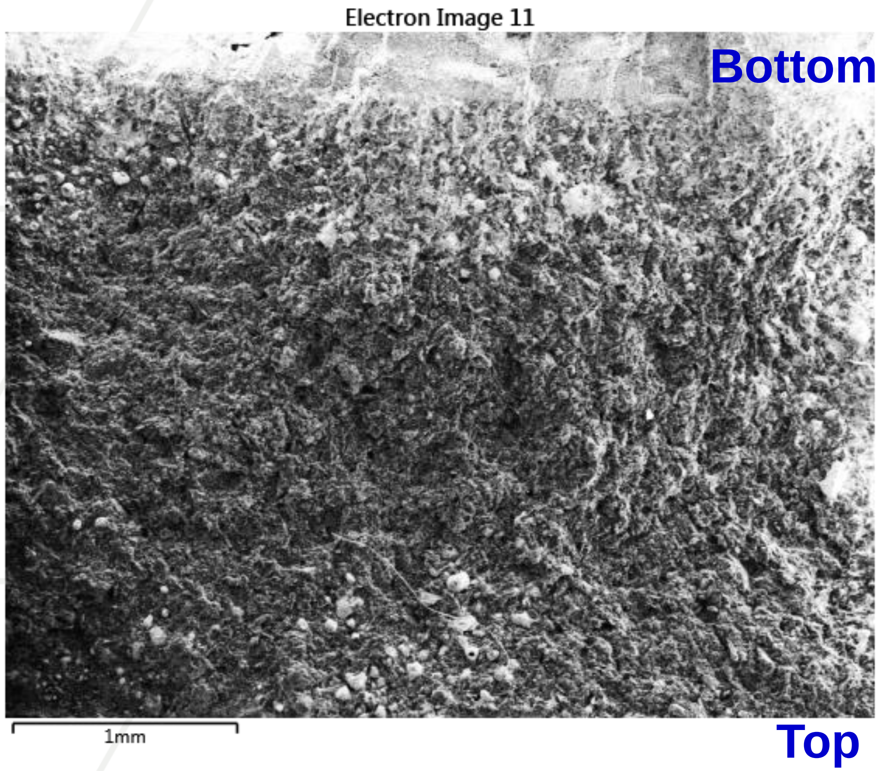
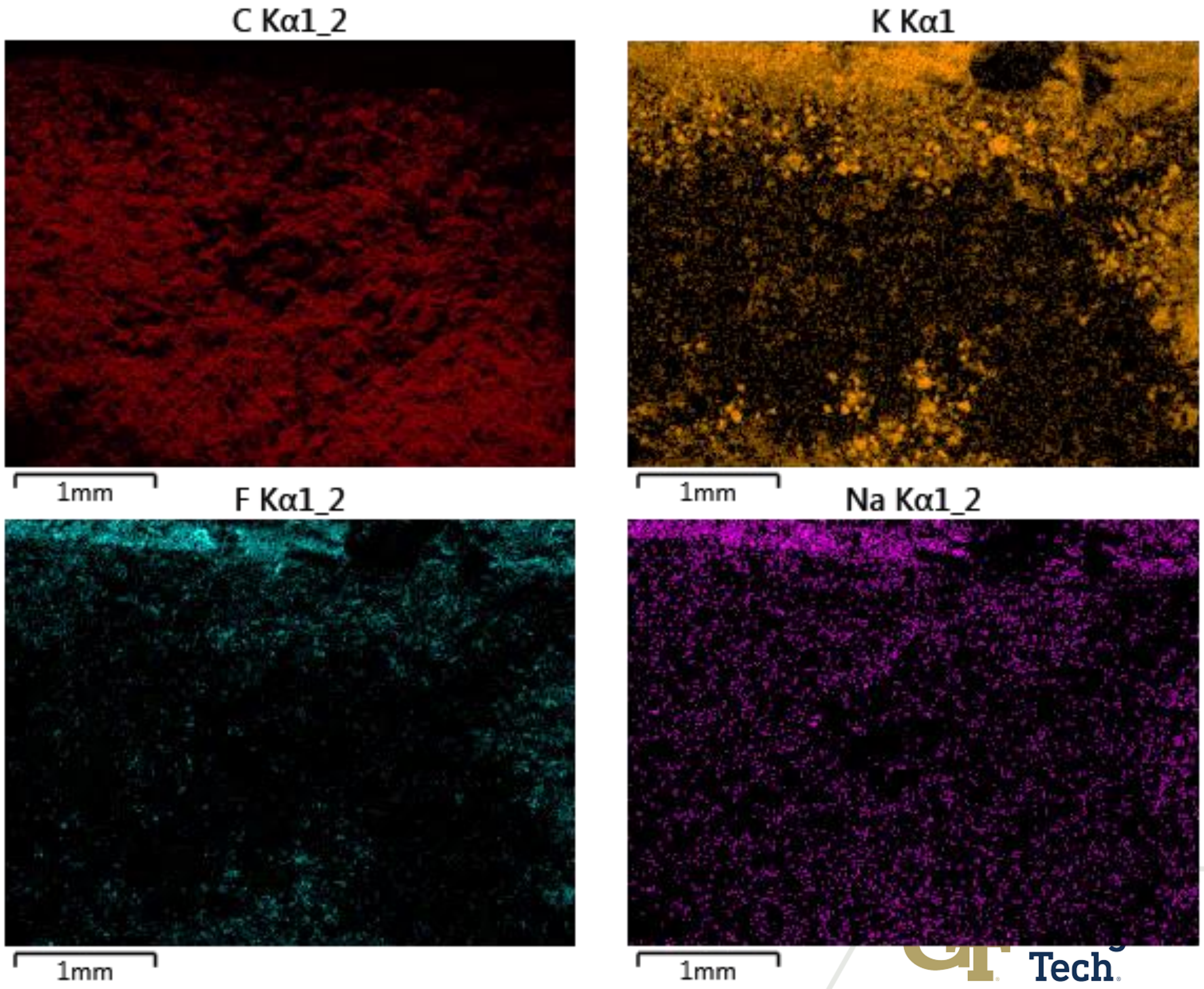
Samples Tested with Li_2O Impurities





EDS - Fractured Graphite Sample (Fired) - FLiNaK + Li_2O

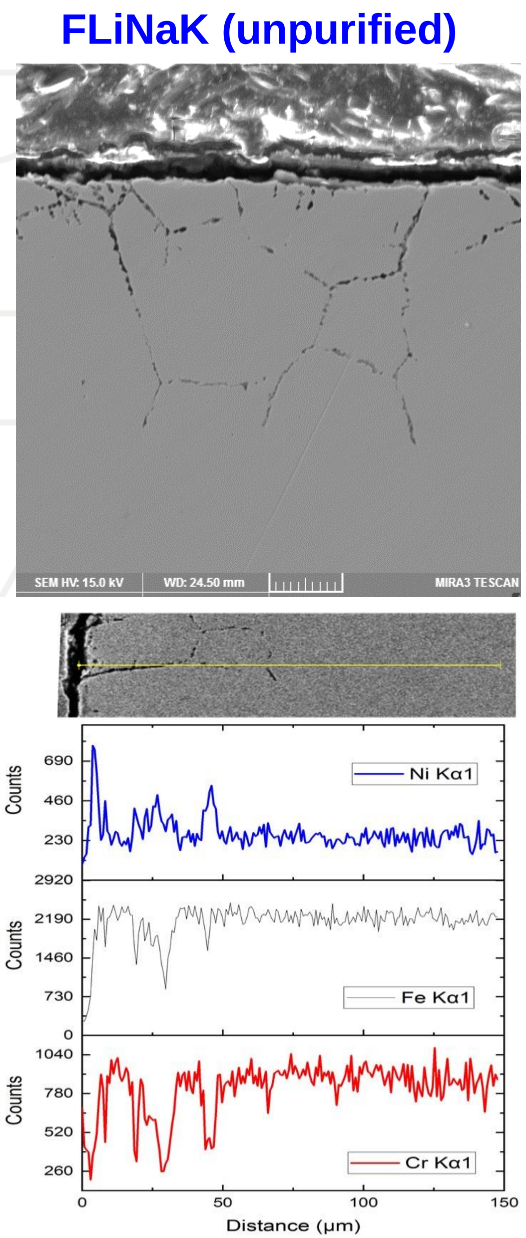


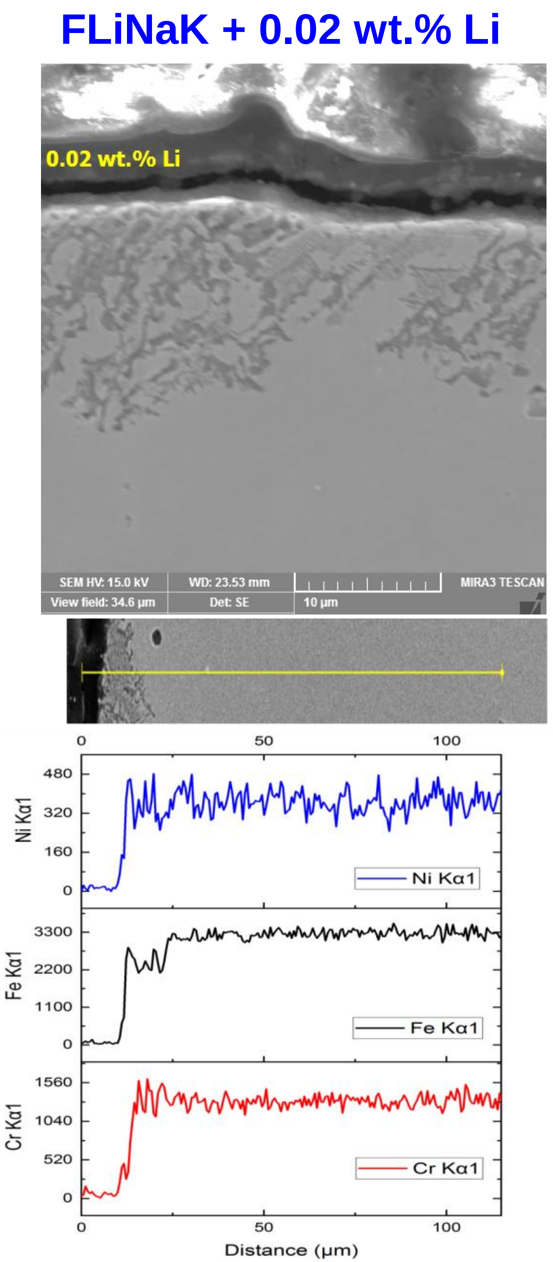


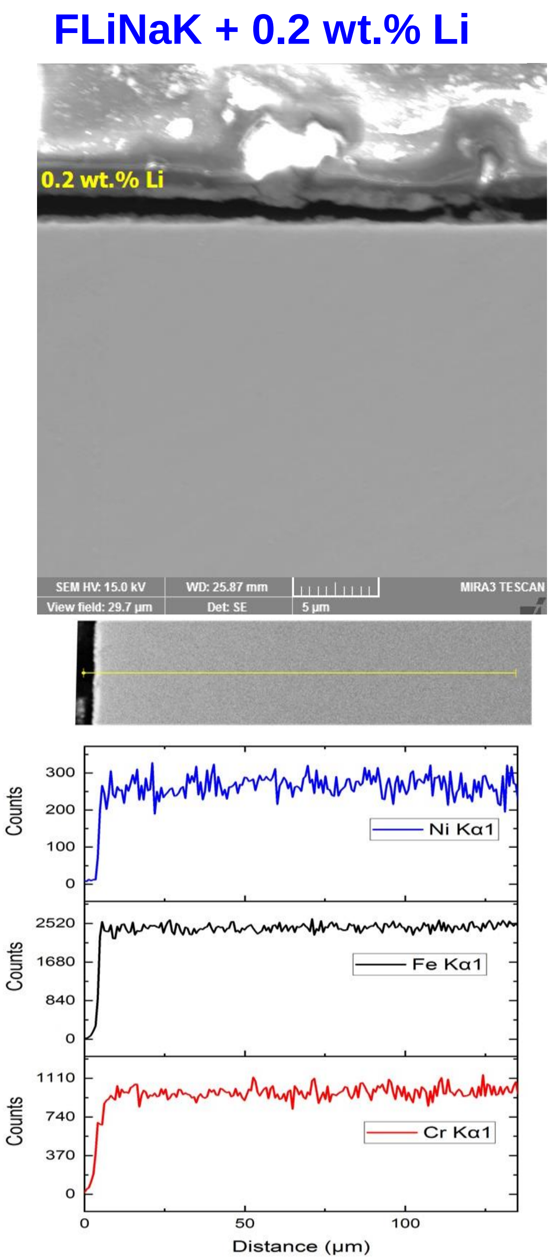
Use of Active Metals *(Be, Li, or others)* to Control Redox Potential and Corrosion of Structural Alloys in FLiBe or FLiNaK

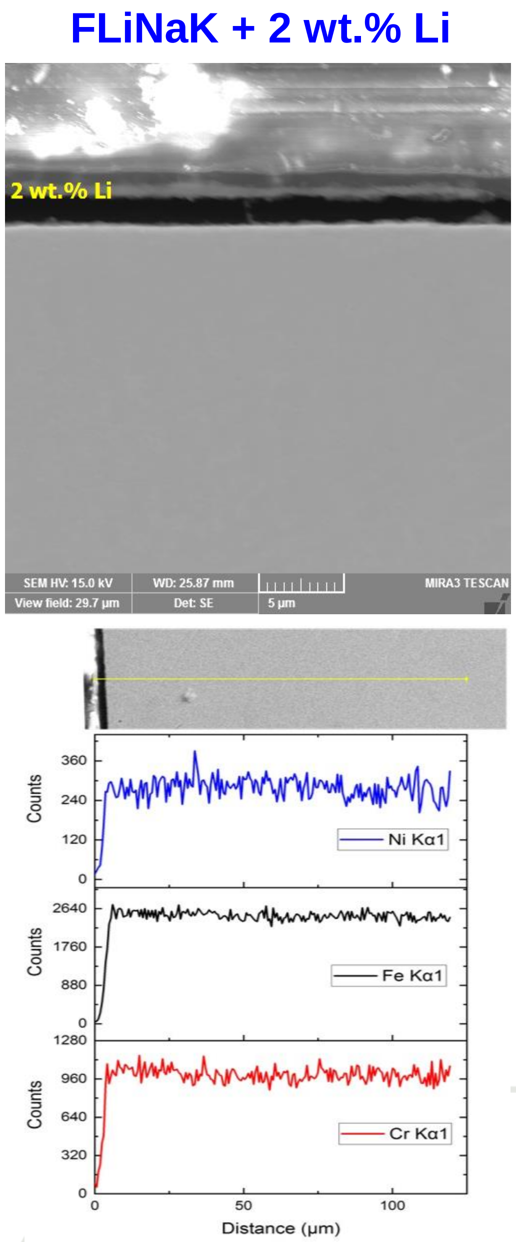
Can "*excess*" *active metal in molten salt affect Graphite?*

Effect of Li addition of Corrosion of 316H SS in Molten FLiNaK









Graphite (Fired) in Molten FLiNaK + Li

Tests conducted at 700°C for 100 hours in Nickel crucibles

TOP

BOTTOM

FLiNaK + 0.2 wt.% Li

FLiNaK + 2 wt.% Li

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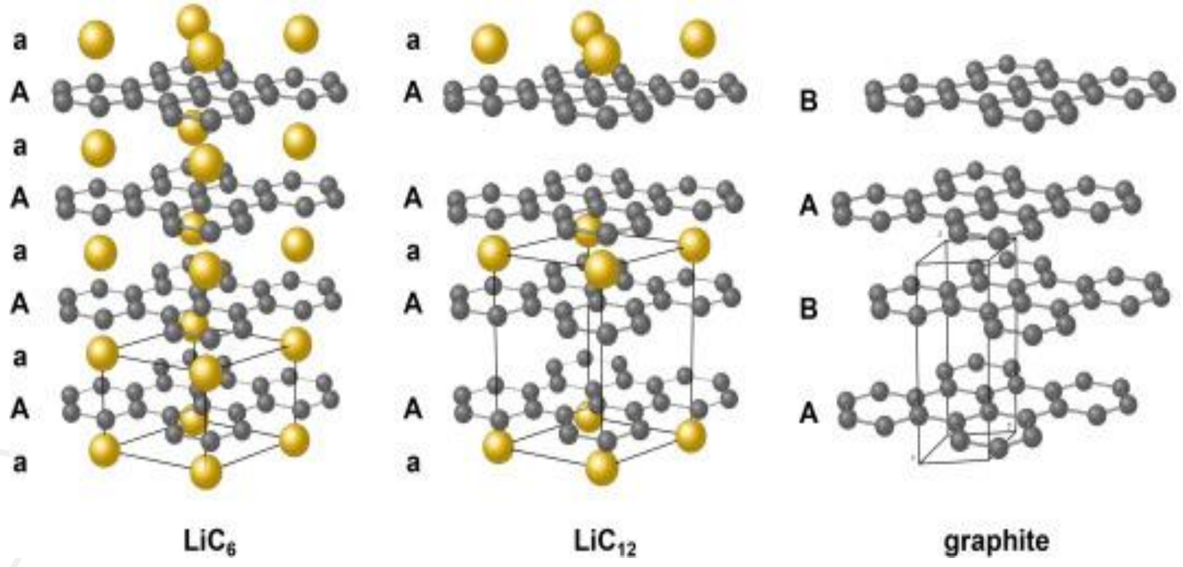
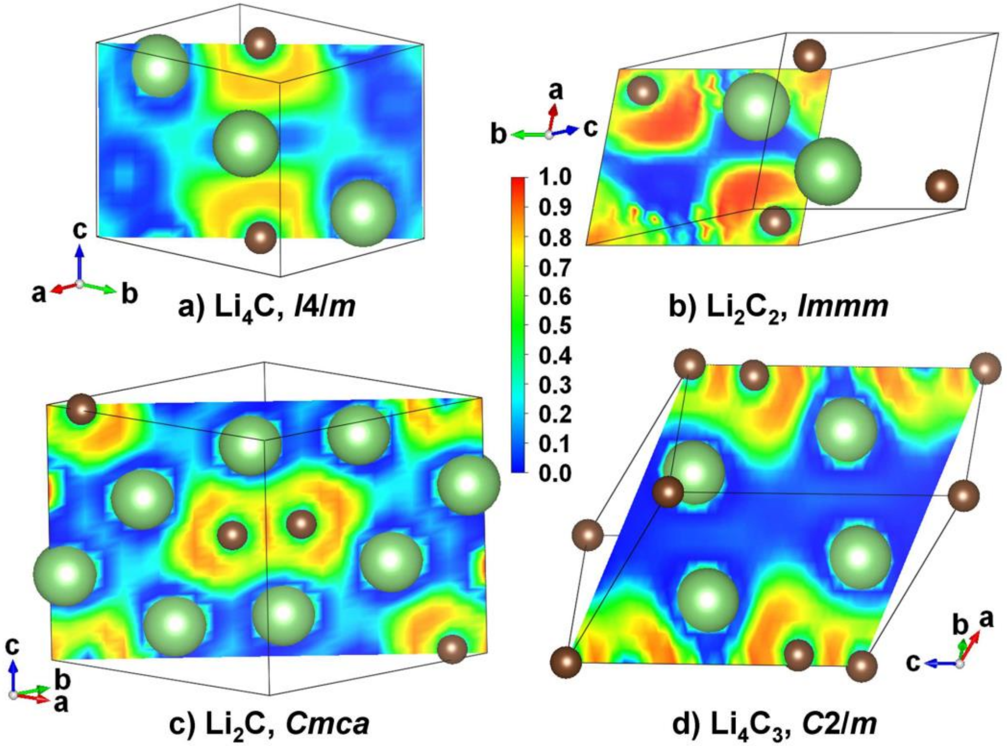
Intercalated Li in Graphite – *Formation of Lithium Carbides*

2Li + 2C = Li2C2 *ΔG = -10.7Kcal/mol at 700°C (HSC data)*

Li_4C_3, Li_2C_2 and LiC_{12} are Thermodynamically Stable - *ab initio* DFT Calculations



Toshiyuki et. al, Comprehensive elucidation of crystal structures of lithium intercalated graphite; Carbon, Volume 142, February 2019, Pages 513-517



Yangzheng Lin, Timothy A. Strobel, and R. E. Cohen; Structural Diversity in Lithium Carbides *Phys. Rev. B 92, 214106 – Published 11 December 2015*

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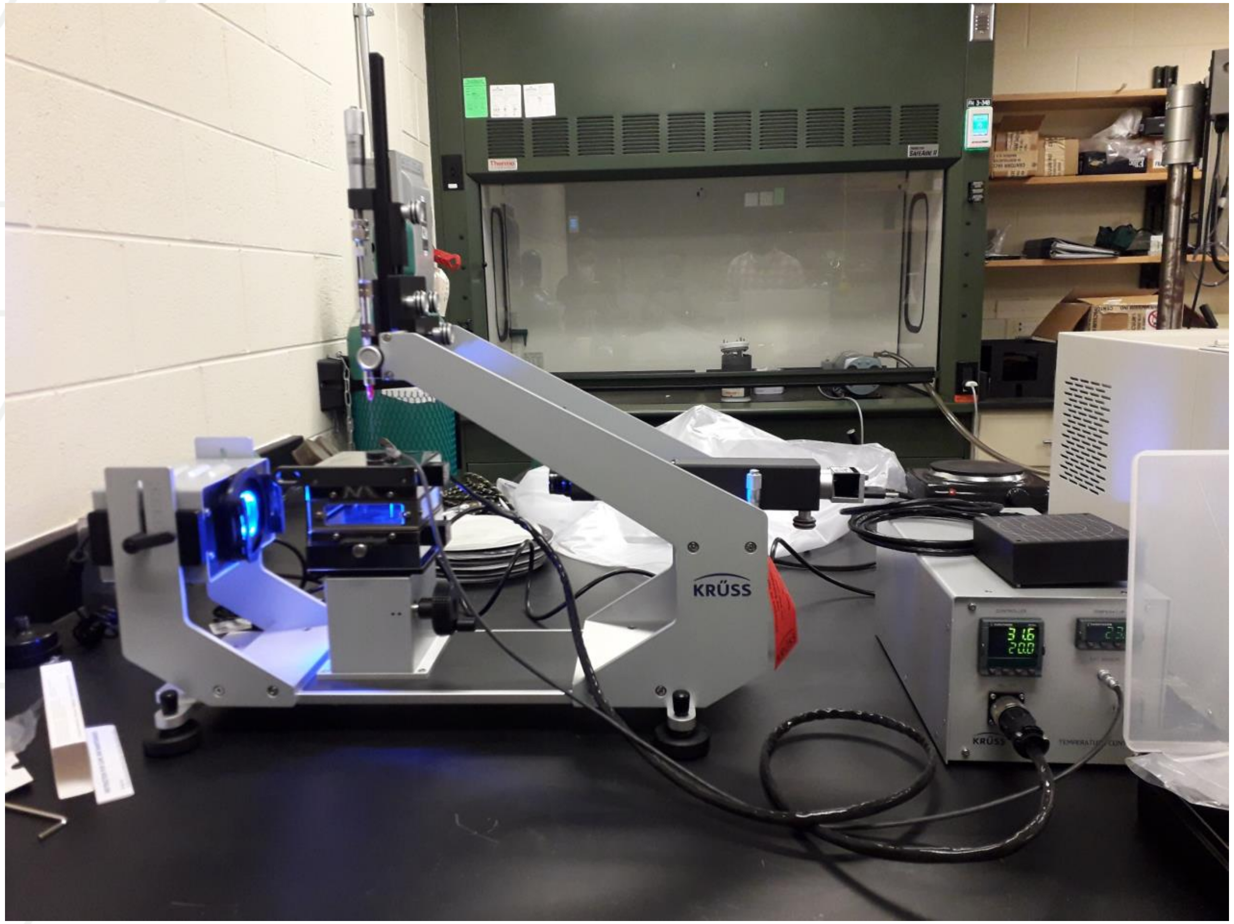
Planned Work

Contact Angle Measurements – *Effect of Impurities*



Setting up contact angle measurements inside glove box – *to study effect of FLiNaK impurities on graphite wetting*

Summary

- **Graphite firing to remove moisture and volatile impurities decreases wetting of IG-110 graphite in molten FLiNaK salt**
- **Presence of impurities in the salt can change the wetting behavior and salt impregnation of IG-110 graphite in molten FLiNaK**
  - **Depends on impurity type and amount**
  - **Type and Surface Conditions of Graphite**
- **Presence of excess lithium metal can cause "lithiation" of graphite and formation of lithium carbides.**
  - **May result in mechanical degradation *(Cracking)* of IG-110 graphite**
- ***What about excess beryllium? – Beryllium Carbide*** *(Be_2C)* ***is also thermodynamically stable under MSR operating conditions***

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Acknowledgements

- DOE NEUP Grant – DE-NE0008749
- Sandia National Laboratories (LDRD) Funding
- Toyo Tanso for Graphite Samples
- Prof. Derek Hass (University of Texas)
- Prof. Chaitanya Deo (Georgia Tech)
- Dr. Kevin Chan (now at Kairos Power)

QUESTIONS?

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