

Monitoring of FeS_2 reactions using high temperature XRD coupled with Gas Chromatography (GC)

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Introduction

Thermally activated batteries require high levels of reliability, both in longevity and electrical stability. FeS_2 cathode materials are employed in thermal battery builds, and while aspects of empirical performance of their cathode materials have been evaluated during discharge, little is known about the scientific aspects of cathode behavior at temperature. We have investigated the thermal decomposition of the FeS_2 material under differing atmospheric conditions in the presence of LiCl and KCl electrolytes. Our approach is twofold:

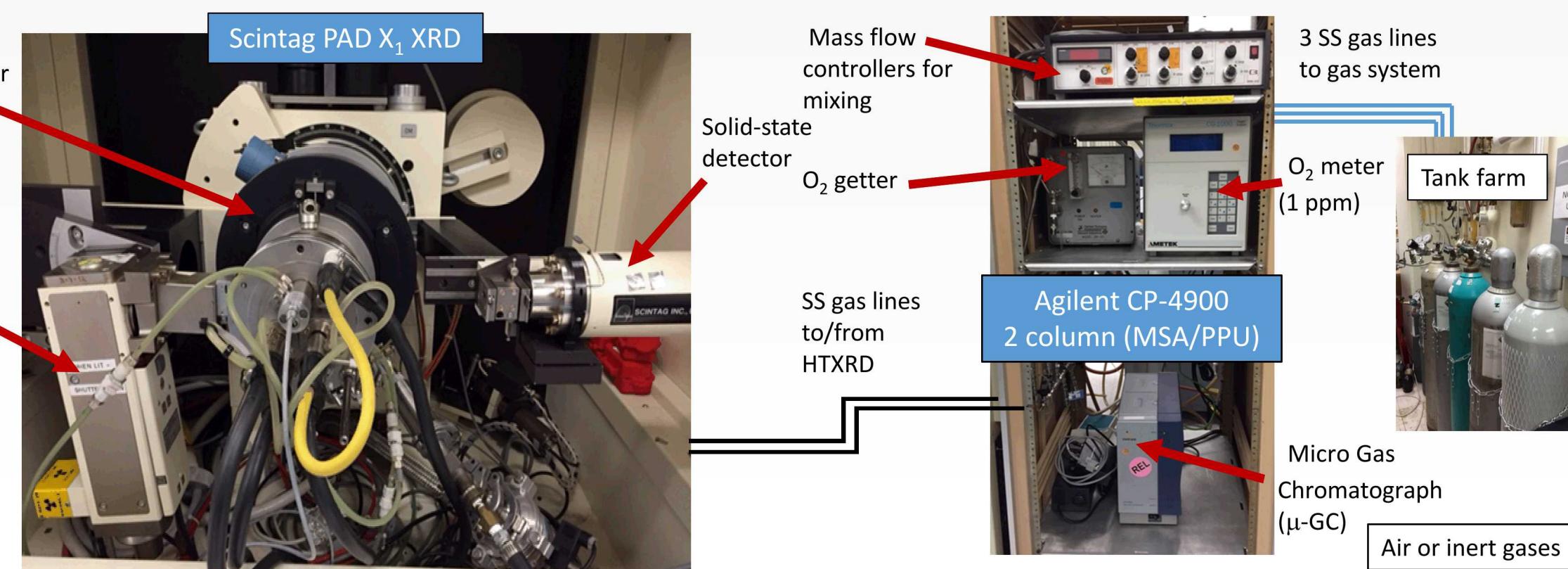
- In-situ High Temperature X-ray Diffraction (HTXRD) coupled with concurrent Gas Chromatography (GC)
- Analysis is augmented by Differential Scanning Calorimetry and Thermogravimetric Analysis (DSC/TGA) coupled with Mass Spectroscopy (MS)

Synergy of these multiple analysis techniques yields valuable insight into the FeS_2 reaction in air, as well as to the impact of thermal decomposition on the ultimate functionality of a fabricated thermal cell.



Experimental

1. High Temperature X-Ray Diffraction with Gas Chromatography



Powder samples were dispersed in a methanol solution, deposited onto an alumina substrate, and sealed into the furnace chamber.

XRD Parameters:

- Step size (2θ): 0.04°
- Scan range (2θ): 26° to 41°
- Dwell (s): 1.0

Temperature Parameters:

- Heat increments ($^\circ\text{C}$): 10
- Ramp Rate ($^\circ\text{C}/\text{min}$): 50
- Temperature Range ($^\circ\text{C}$): 25 to 550

*Gas composition analysis via GC was continuous throughout the XRD run.

2. Simultaneous Thermal Analysis

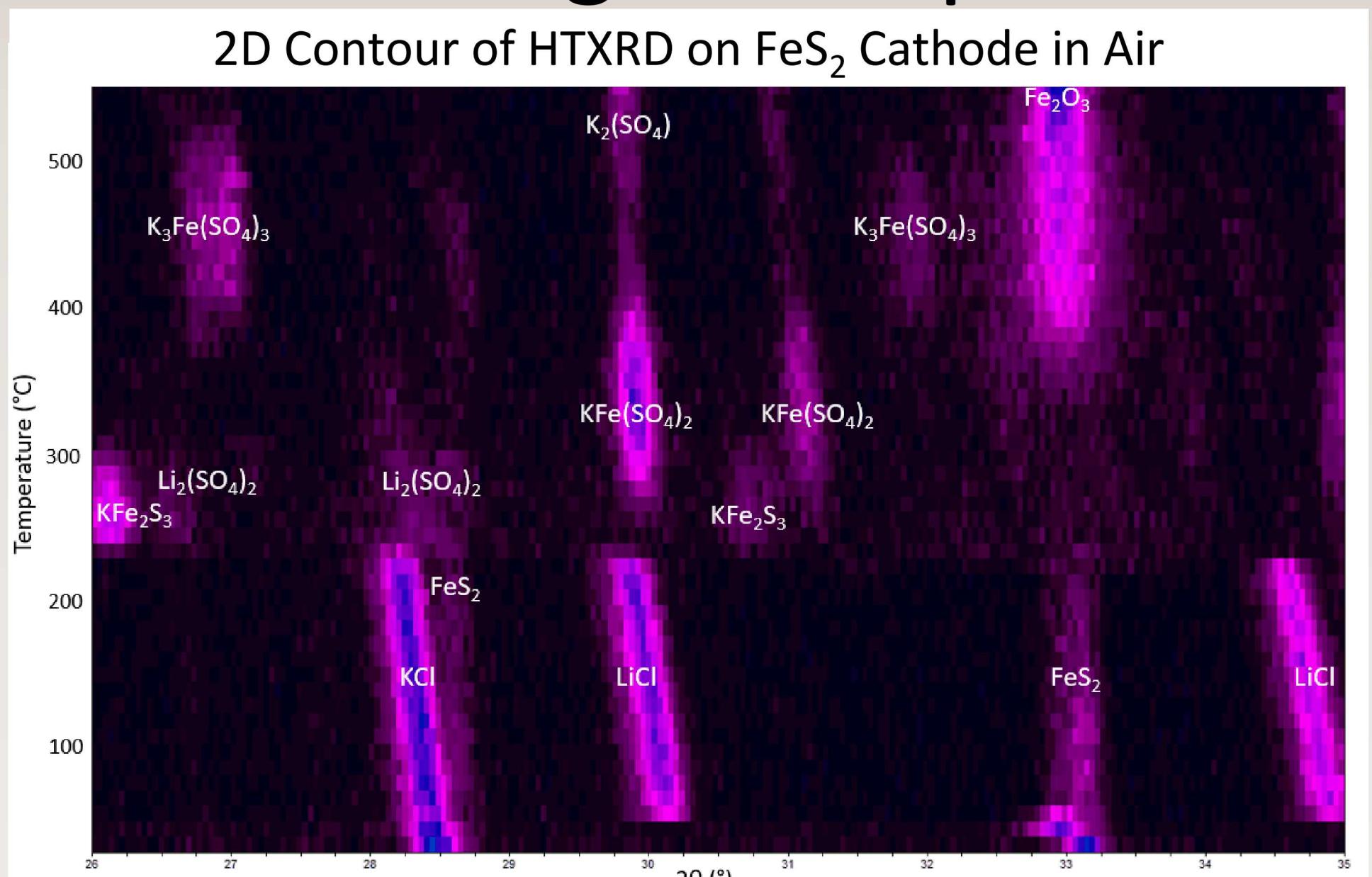
Specimens were loaded into an cup and placed in the STA while minimizing air exposure.

STA Parameters:

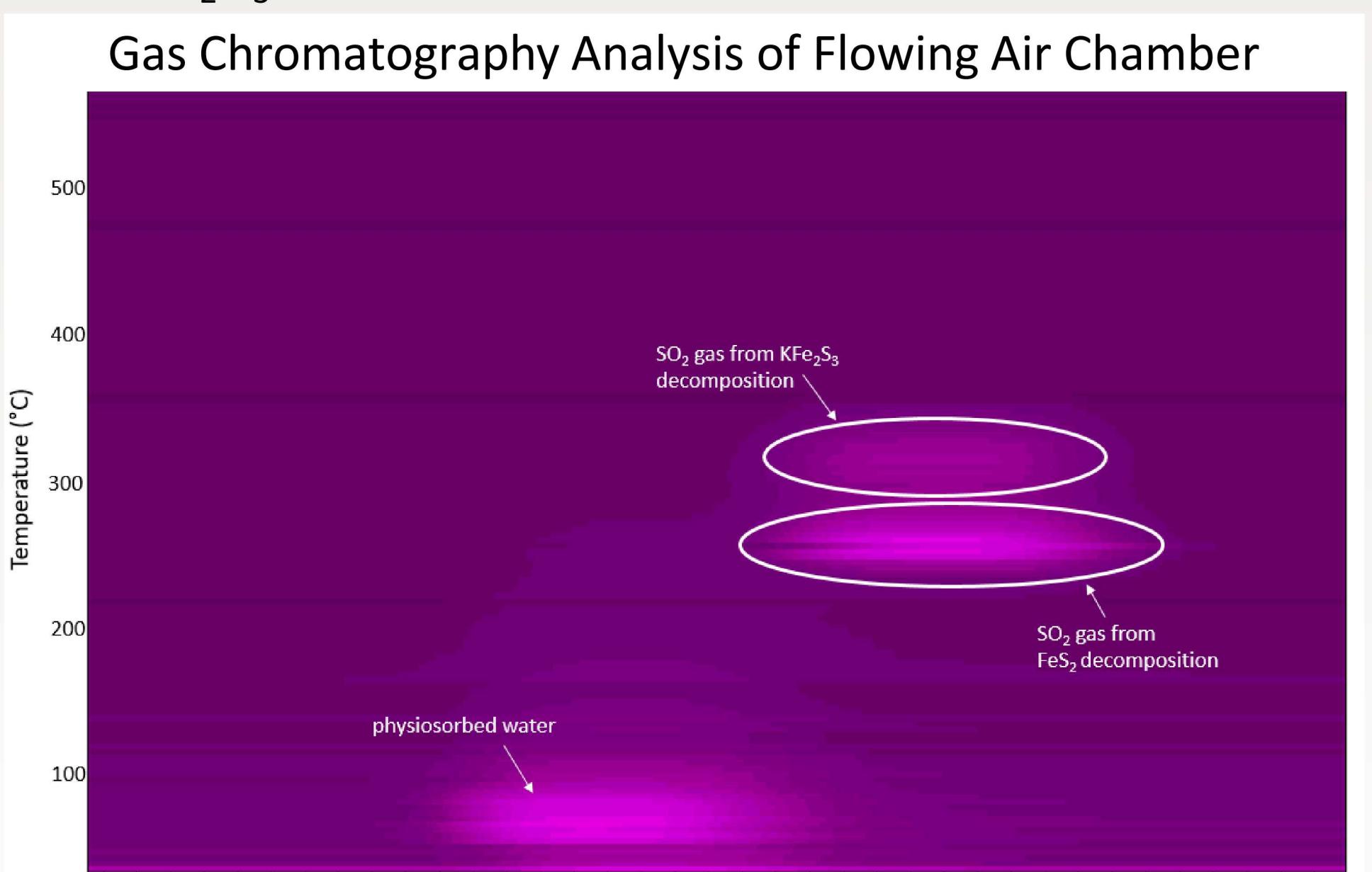
- Heating rate ($^\circ\text{C}/\text{min}$): 5
- Temperature range ($^\circ\text{C}$): 30 to 550

*Gas composition analysis via mass spectro was continuous throughout the STA run.

Oxidizing Atmosphere

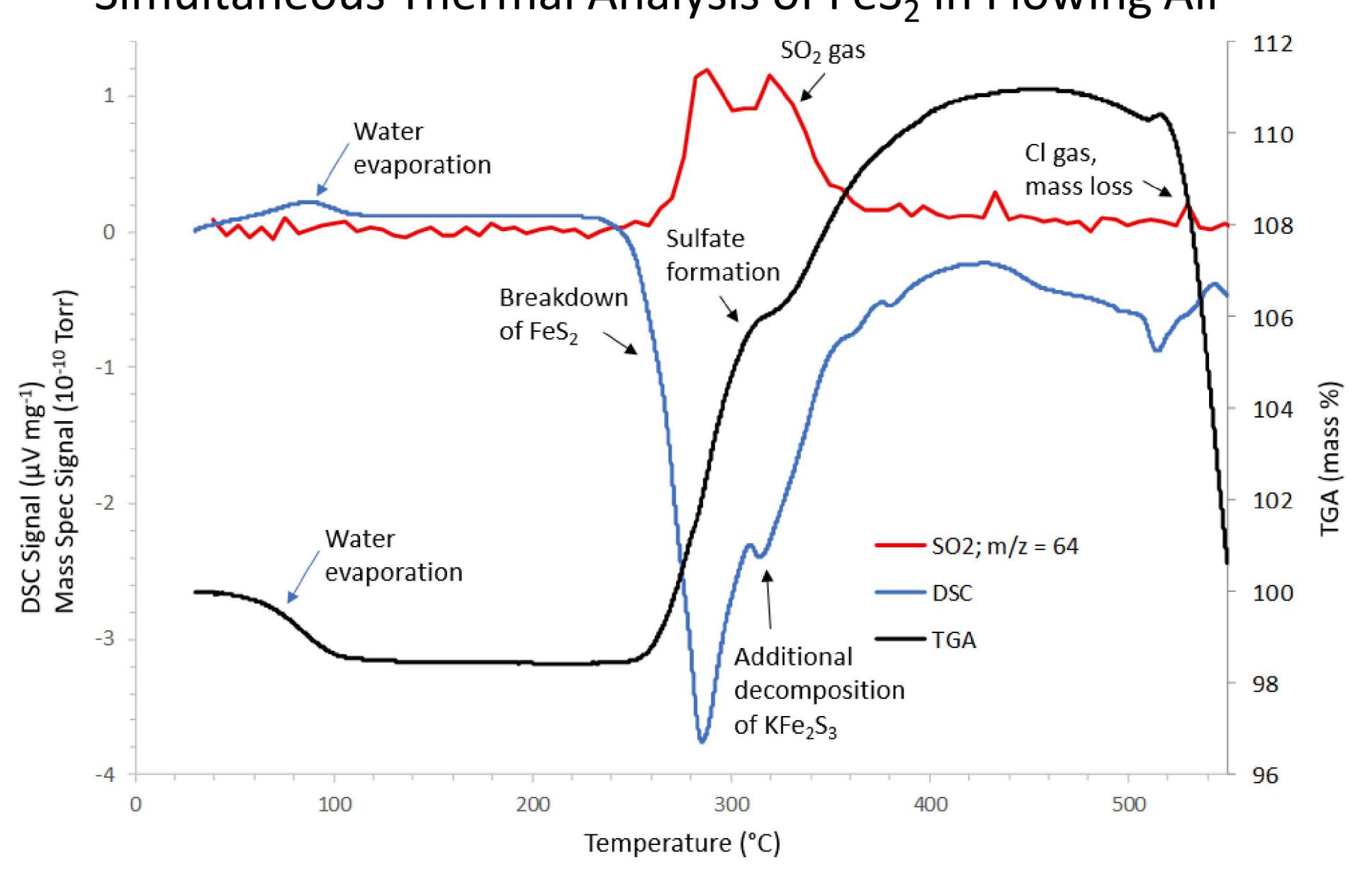


A significant chemical reaction with decomposing KCl and LiCl salt phases is observed at 240°C . Additional heating results in the formation and decomposition of intermediate sulfates, while Fe_2O_3 persists through 550°C .



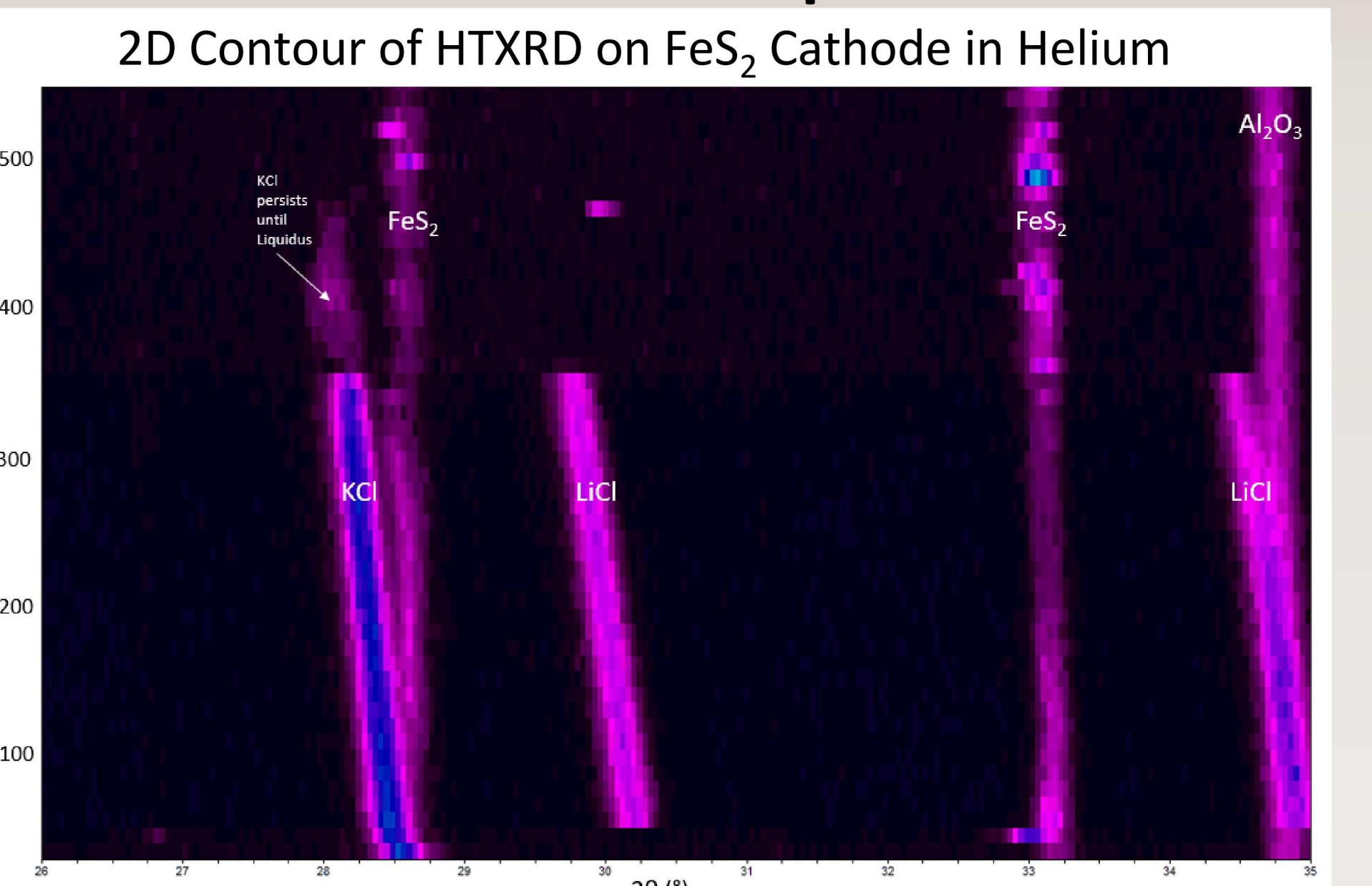
Concurrent GC measurements made on the gas output stream from the HTXRD reaction chamber detected the release of SO_2 gas in two distinct temperature ranges, confirming formation and decomposition of the sulfates during heating.

Simultaneous Thermal Analysis of FeS_2 in Flowing Air

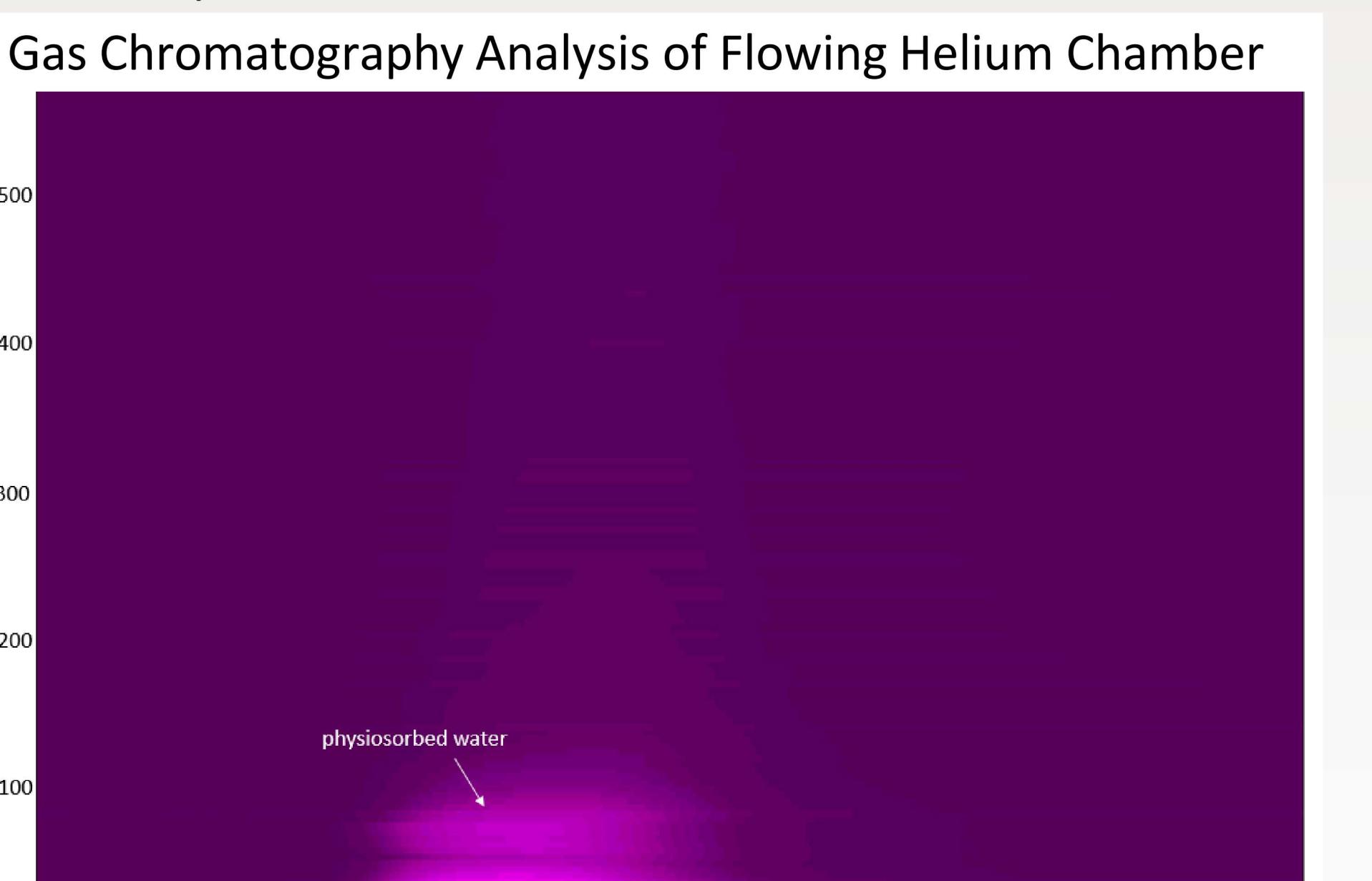


Independent thermal analysis of the cathode showed consistent thermal response to observed reactions in the HTXRD data. Most notable is the exothermic reaction of the salt phase at 280°C to form additional intermediate sulfates. MS detected two distinct SO_2 gas output, coincident with the decomposition of FeS_2 and KFe_2S_3 .

Inert Atmosphere

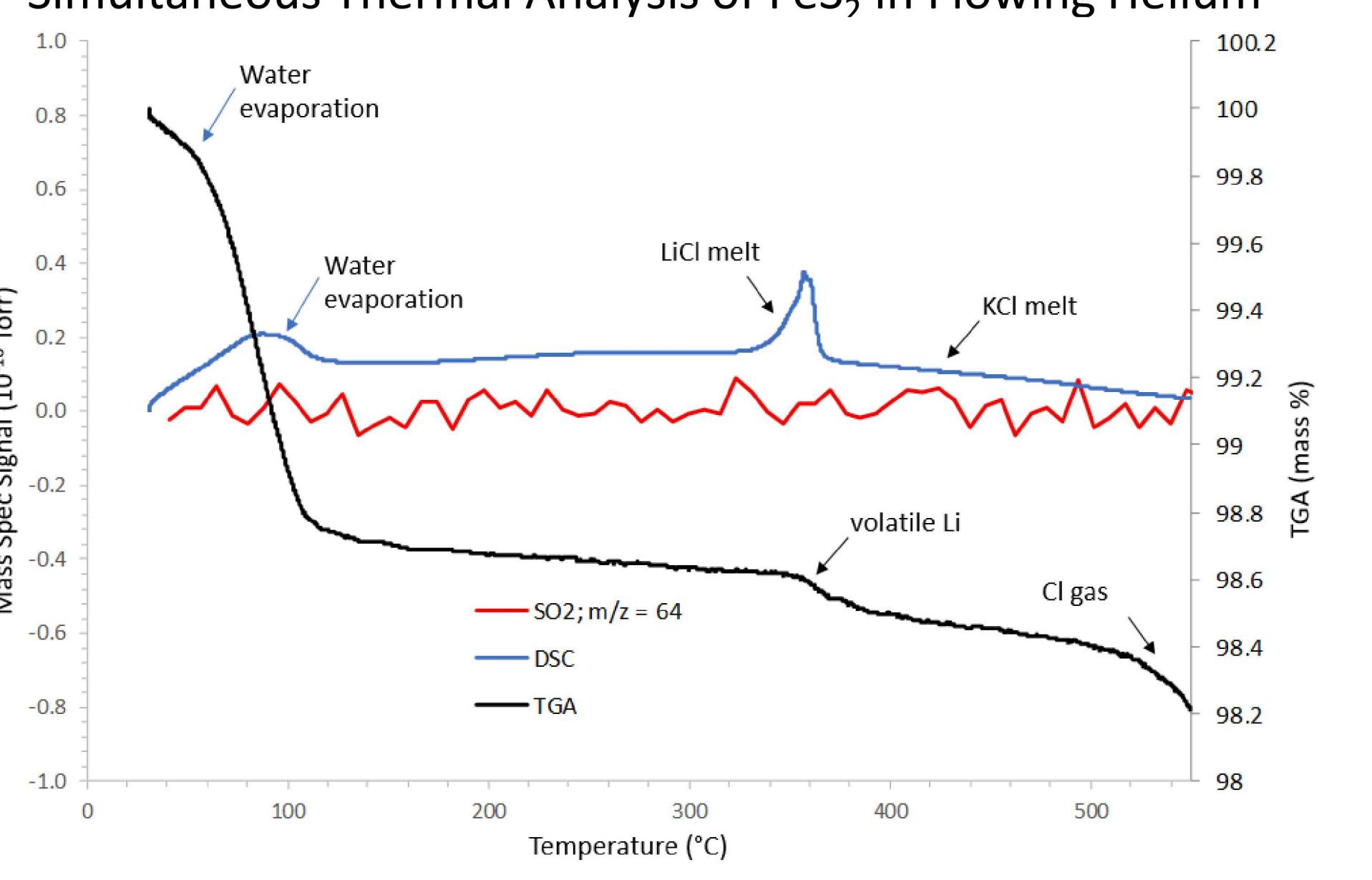


Heating the FeS_2 cathode in a Helium atmosphere shows little change to the pyrite phase. Characteristically, LiCl melts at 350°C while the full melt of KCl is delayed until 450°C . No additional phase transitions are observed.



Concurrent GC measurements made on the output gas stream from the HTXRD reaction chamber detected no release of SO_2 gas, only the release of physiosorbed water at low temperatures.

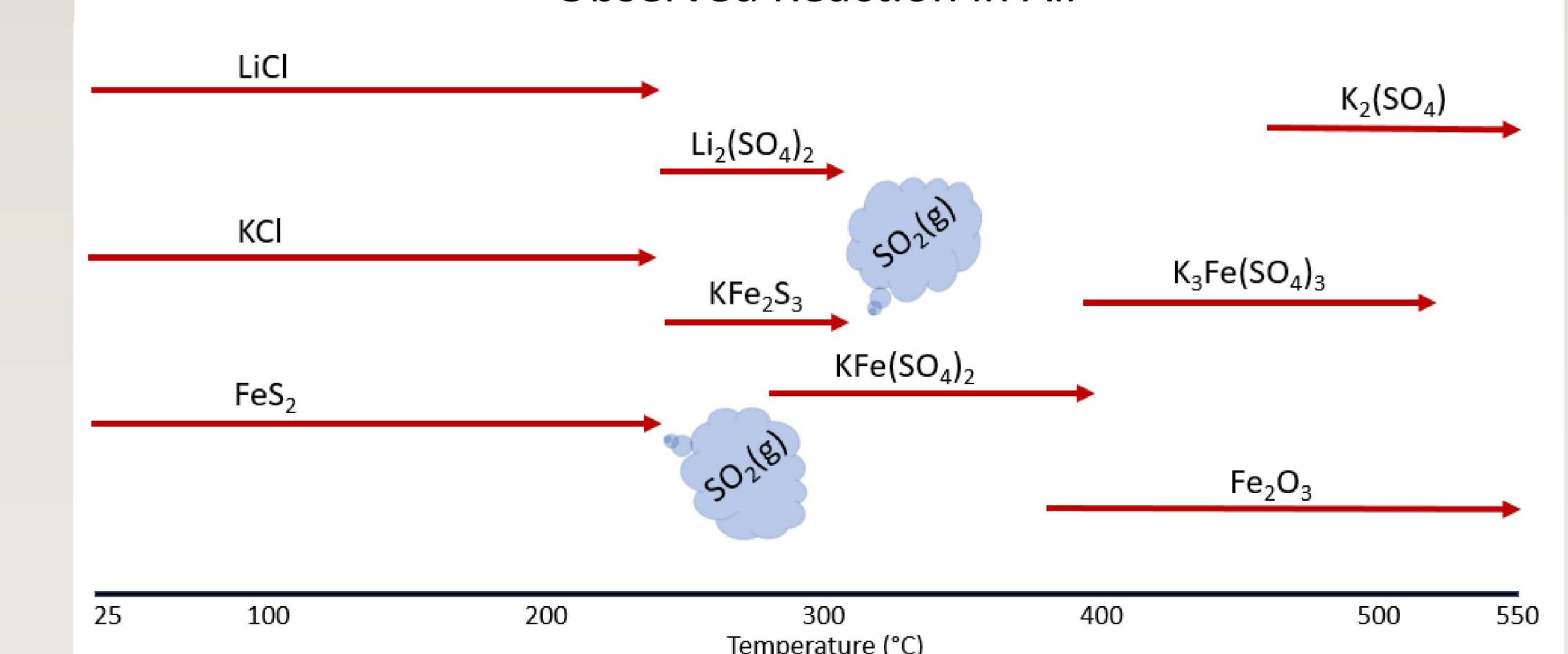
Simultaneous Thermal Analysis of FeS_2 in Flowing Helium



Additional independent thermal analysis of the cathode in inert conditions reveals a true melting endotherm for the LiCl phase at 350°C , with no significant release of SO_2 detected in MS analysis. This result is consistent with GC measurements. Cl gas released at 500°C is freed from the electrolyte melt but is not indicative of an additional reaction.

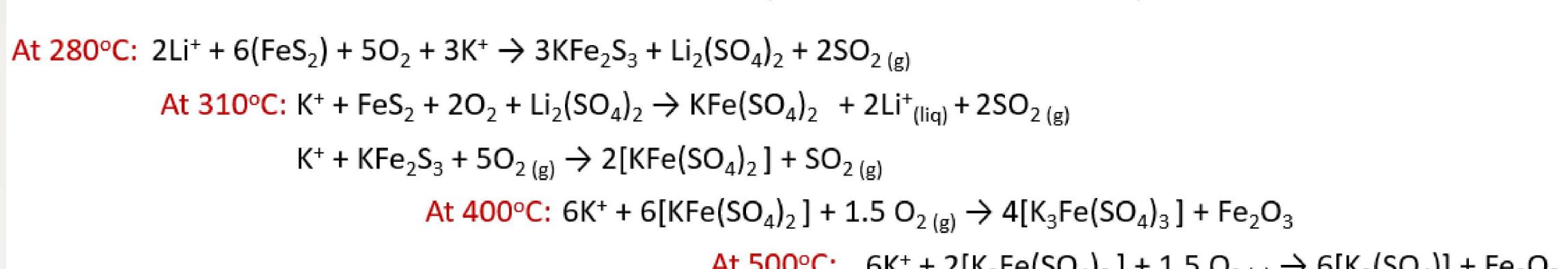
Reaction Sequence

Observed Reaction in Air



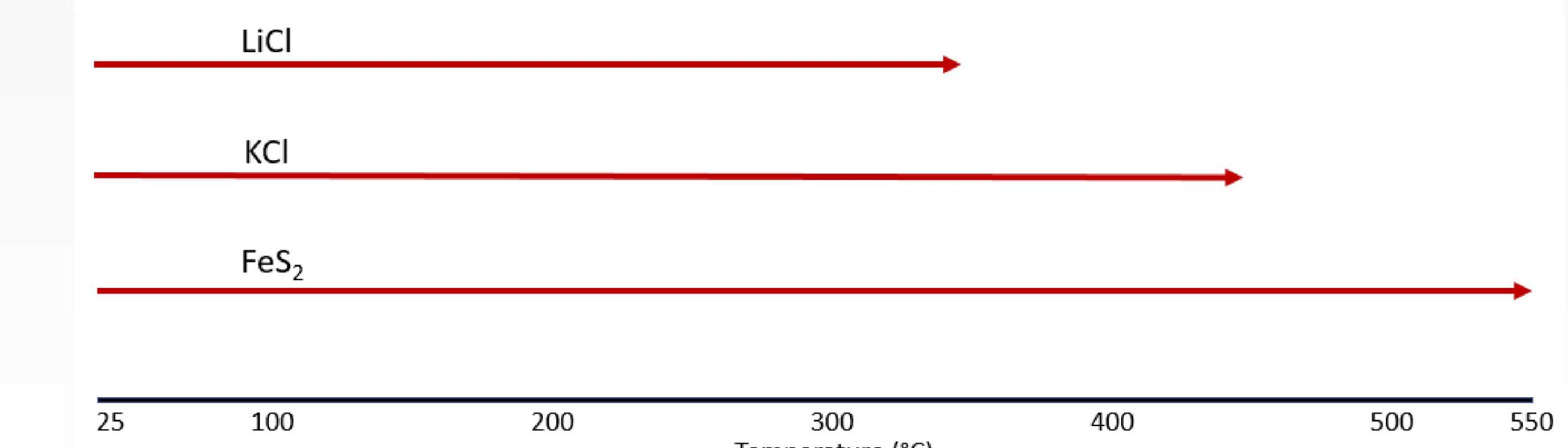
Notably, the final Fe_2O_3 phase formed has a cubic crystal structure similar to Yttria-stabilized Zirconia (YSZ) in the Ia-3 space group, and is not common rhombohedral Hematite. The Ia-3 defect Fe_2O_3 structure observed may have a proclivity for substitution, possibly incorporating available Li and K cations.

Cathode Decomposition Chemistry



The decomposition of initial KCl and LiCl salts at 240°C in the presence of an oxidizing agent triggers the onset of an irreversible chain reaction, resulting in the formation of the undesired compounds KFe_2S_3 and $\text{Li}_2(\text{SO}_4)_2$ which are not observed when heating in an inert atmosphere.

Observed Reaction in Helium



Here, KCl and LiCl dissipate into a liquidus phase indiscernible in XRD intensity.

Summary

- Under an air atmosphere, FeS_2 experiences an irreversible degradation at 280°C due to oxygen exposure resulting in impeded thermal battery performance
- Cathode degradation is characterized by generation of KFe_2S_3 , $\text{Li}_2(\text{SO}_4)_2$, and $\text{KFe}(\text{SO}_4)_2$ which cause a significant exothermic reaction and release of SO_2 gas during decomposition
- Independent thermal analysis experiments augment the in-situ XRD results and support the overall picture of FeS_2 decomposition
- Under an inert atmosphere, FeS_2 experiences no significant reaction and generates no gaseous output
- Detection of SO_2 gas presence provides a non-destructive criteria for determination of cathode viability
- Possible future work: Determining what percentage of oxygen exposure is detrimental to the cathode material