SAND2015-6687C

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Monitoring of CoS_2 reactions using high temperature XRD coupled with Gas Chromatography (GC)

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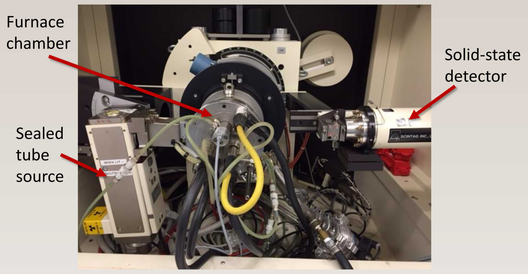
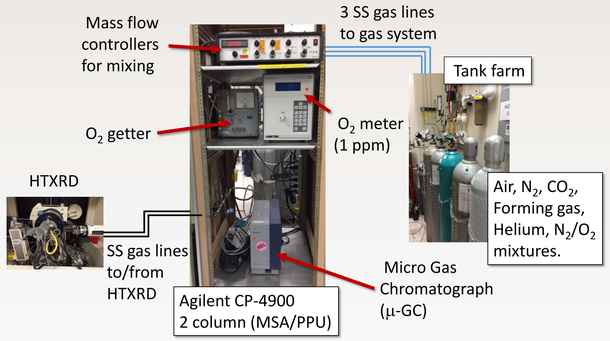
Introduction

- We desire to have a science-based understanding of the decomposition of CoS_2 cathode material.
- Our approach:
  - 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 CoS_2 reaction in air.

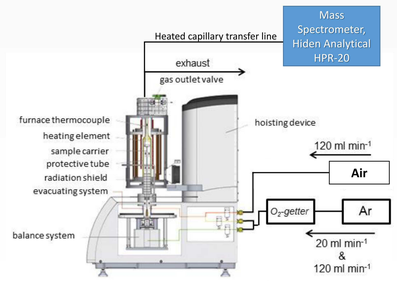
Our Scintag PAD X_1 XRD system was employed for the CoS_2 reaction experiments



The Gas-handling system is equipped for a variety of configurations including mixtures and is now configured with a μ-GC to monitor the gas exiting the Rx chamber

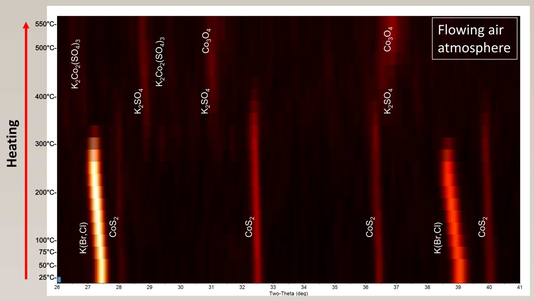


Thermal analysis schematic

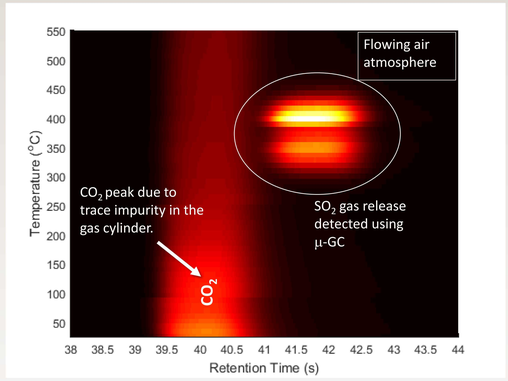


Netzsch STA 409-CD TGA/DSC

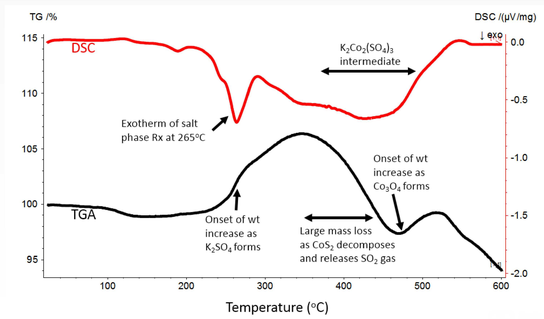
High temperature XRD analysis of CoS_2 cathode in an air atmosphere shows significant reactions occurring after the decomposition of K(Br,Cl) salt phase.



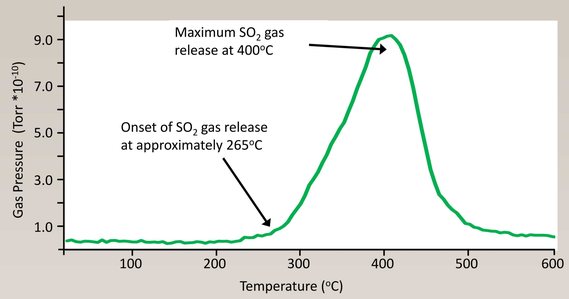
Concurrent Gas Chromotography (GC) measurements made on the gas stream from HTXRD reaction chamber confirmed the release of SO_2 gas in the 300-450°C temperature range.



Independent thermal analysis (DSC/TGA) of the CoS_2 cathode showed consistent thermal response to observed reactions in the HTXRD data. **Most notable is the exothermic reaction of the salt phase at 265°C to form K_2SO_4.**

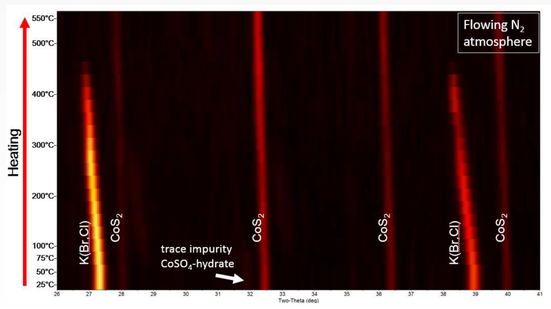


Mass Spectroscopy (MS) results from DSC/TGA analysis confirm SO_2 gas release with an onset of SO_2 formation at 265°C when the salt phase starts to react to form K_2SO_4.

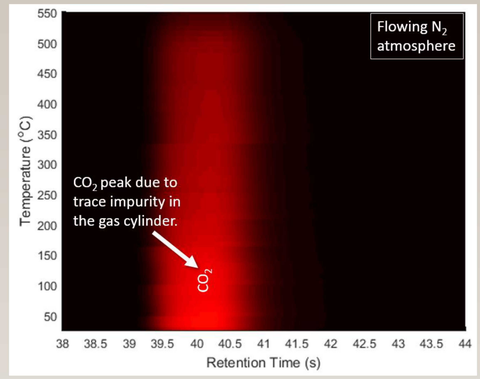


Emerging picture of CoS_2 decomposition reactions in air atmosphere.

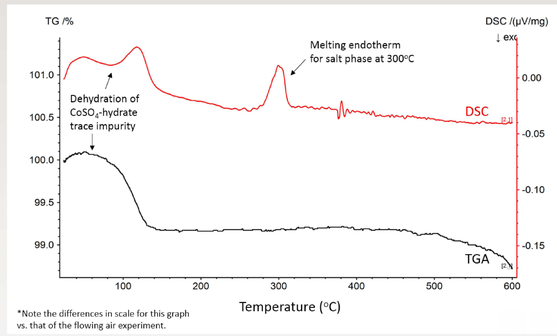
High temperature XRD analysis of CoS_2 cathode in flowing N_2 gas shows little change to the CoS_2 phase and the onset of the decay of the K(Br,Cl) signal (due to melting) is delayed until above 300°C.



Concurrent Gas Chromotography (GC) measurements made on the gas stream from HTXRD reaction chamber under inert (flowing N_2 gas) conditions showed no SO_2 gas release.



Independent thermal analysis (DSC/TGA) of the CoS_2 cathode under inert gas conditions (Ar) reveals a true melting endotherm for the K(Br,Cl) phase at ~300°C with no significant changes* in sample mass between 100 and 550°C.



*Note the differences in scale for this graph vs. that of the flowing air experiment.

Summary

- We have successfully integrated the use of GC with simultaneous HTXRD analysis for characterization of CoS_2 based cathodes.
- In an air environment, oxidation of the salt phase in the cathode leads to the formation of K_2SO_4 which subsequently reacts with CoS_2, leading to the decomposition of the CoS_2 phase.
- Independent thermal analysis experiments augment the in-situ XRD results and support the overall picture of CoS_2 decomposition.

Acknowledgment

The authors are grateful to Christine White for selecting and preparing the samples and to Marshall Reviere for his assistance with the HTXRD experiments.