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32.2: Study of Cell Performance in Long-Life Thermal Battery Design Space

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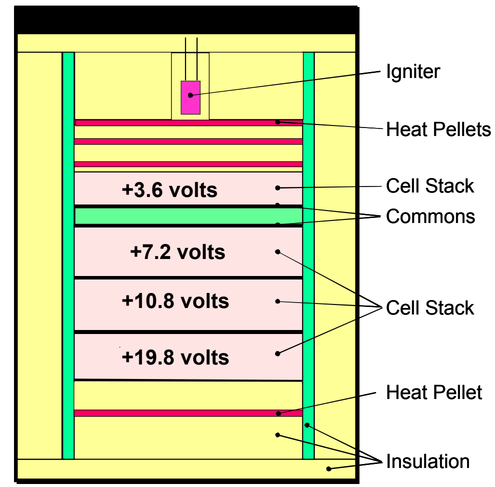
Electrochemistry alternatives for a long-life thermal battery

FeS_2-based batteries

$2FeS_2$ (Pyrite) $+3Li^+ + 3e^- \rightarrow Li_3Fe_2S_4$

- Natural material- low cost
- Details of discharge well known
- 1.9V against $Li_{13}Si_4$



CoS_2-based batteries

$3CoS_2$ (pyrite structure) $+ 4Li^+ + 4e^- \rightarrow Co_3S_4$ (spinel structure) $+ Li_2S$

- Synthetic material – excellent homogeneity
- Higher decomposition temperature
- Flatter voltage during discharge
- Lower capacity and voltage in first transition
- Details of discharge less well known

- DOE used to relate controllable variables to performance
- Analytical techniques developed to understand chemistry

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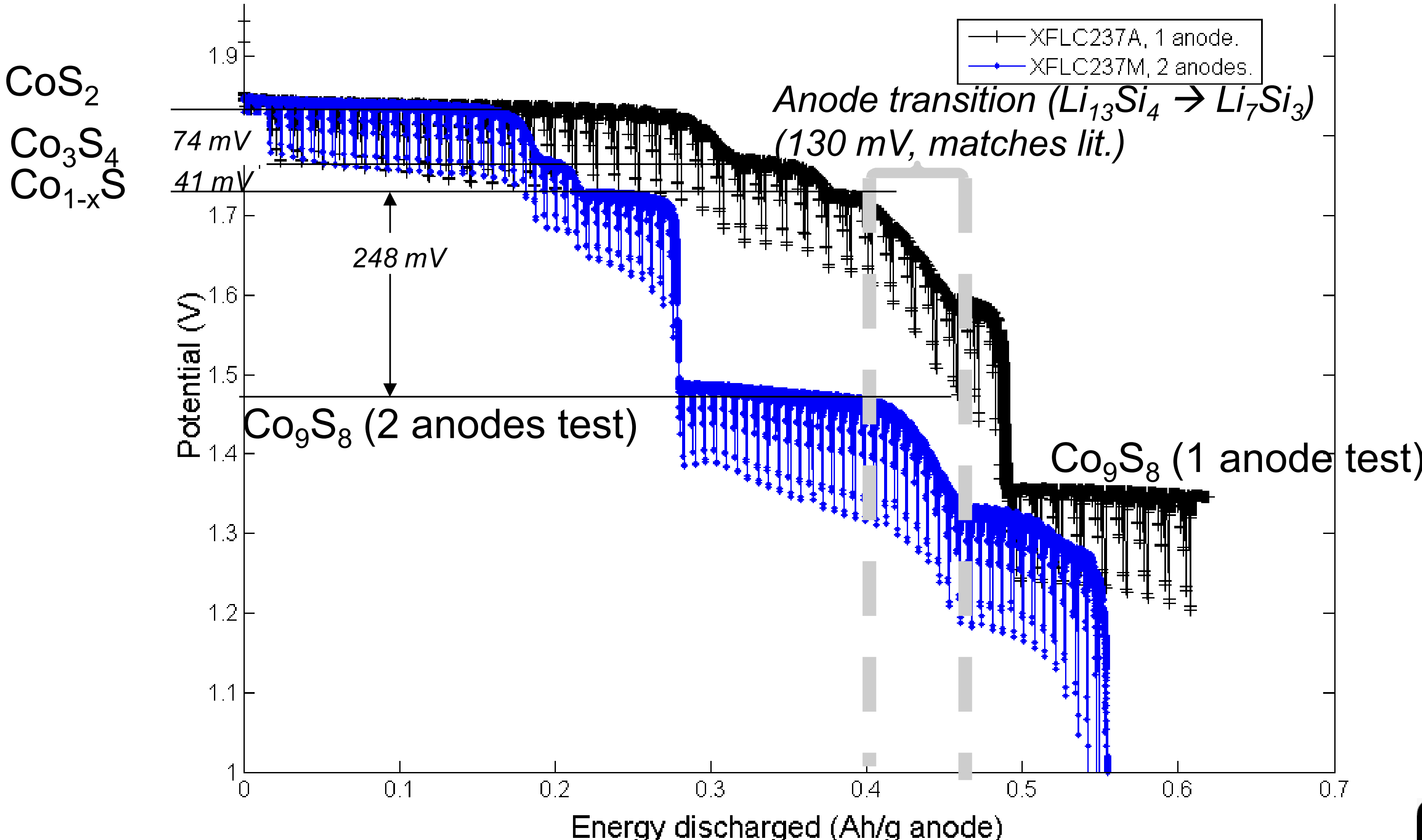
Overview of chemistry: CoS_2 / Li(Si) single cell discharge curves

Comparison of cells discharged at 500°C, 12 PSI



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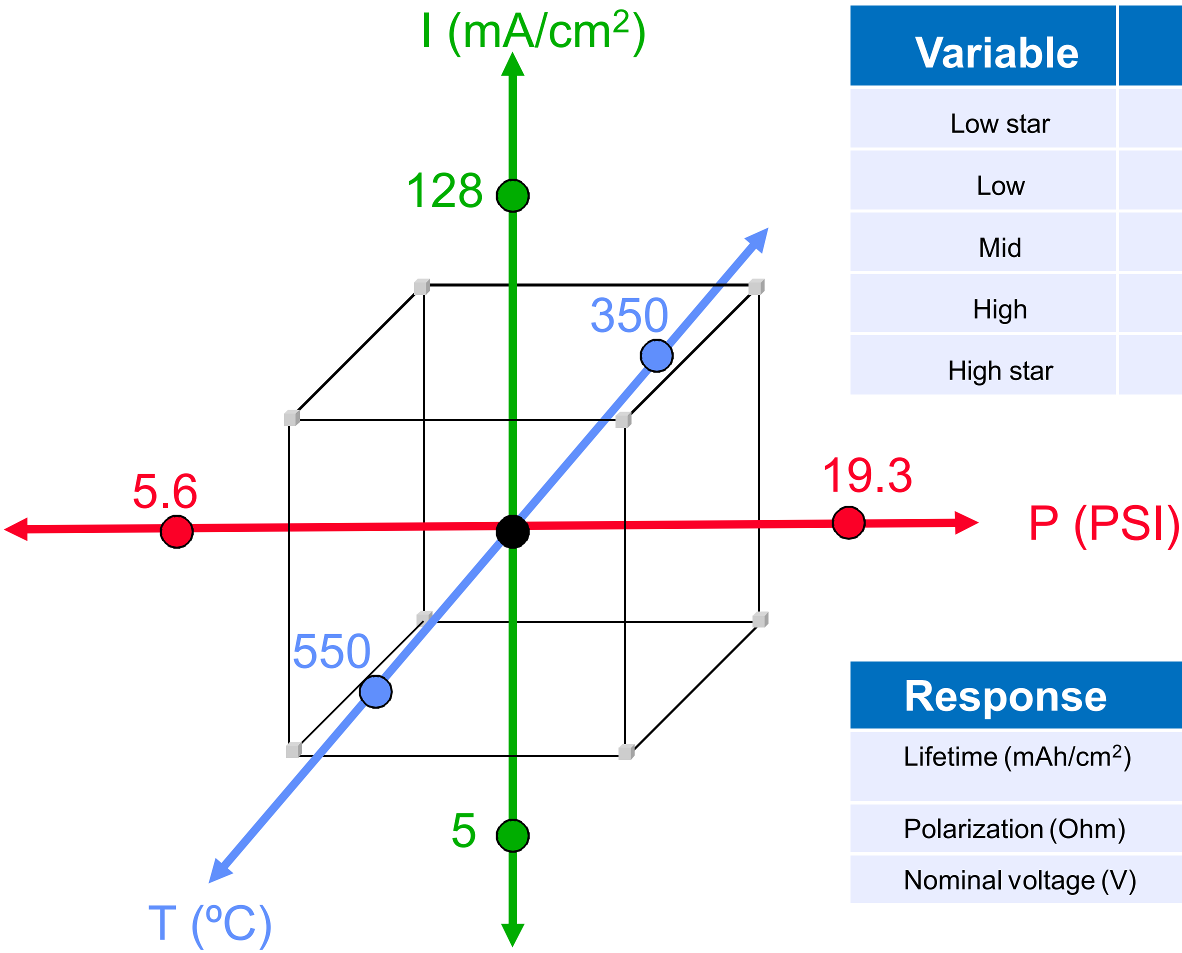
Description of cell performance found using CoS_2-based cell DOEx



Variable	Temp,T (ºC)	Pressure,P (PSI)	Current, I (mA/cm²)
Low star	350	5.55	5.12
Low	400	8.09	12.80
Mid	450	12.66	25.60
High	500	15.28	51.21
High star	550	19.33	128.02

Response	Criteria
Lifetime (mAh/cm²)	V < 1.63V
Polarization (Ohm)	
Nominal voltage (V)	V_{avg} for 5-10mAh/cm²

Galvanostatic discharge tests performed to a potential of < 1 V.

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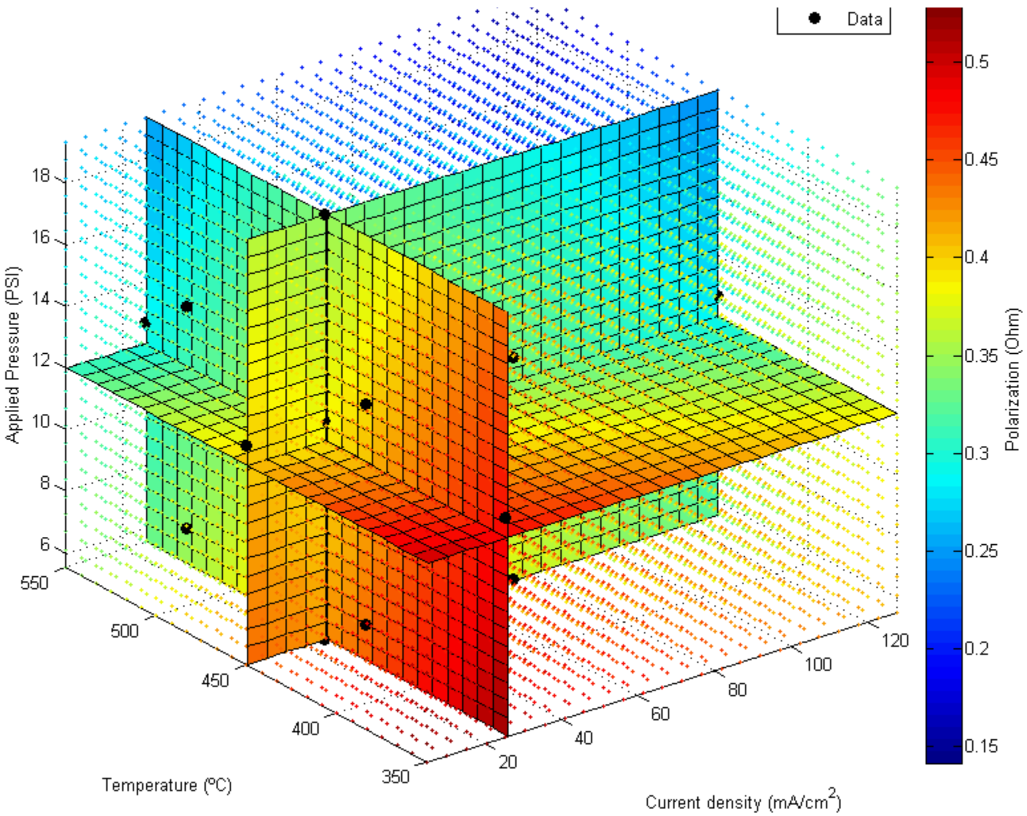
Regression modeling of cells

Cell polarization: 3 factor linear model



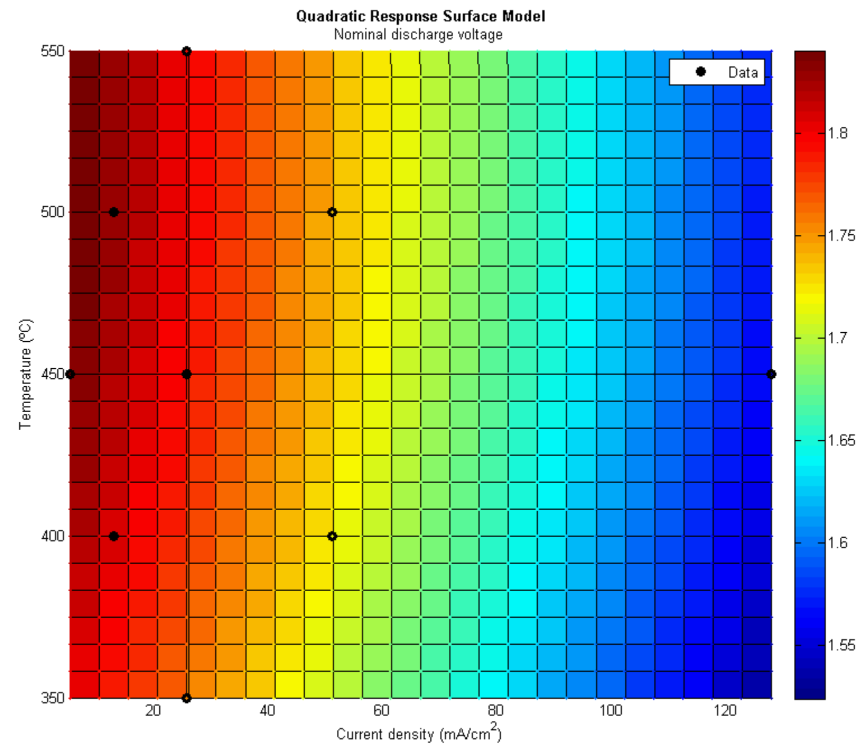
$$\hat{y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3$$

$R^2 = 0.80$

$p < 0.05$ for all coefficients

* Note: Cell lifetime was dependent only on current density, with poor predictive capability ($R^2 = 0.62$)

Cell voltage: 3 factor quadratic model



$$\hat{y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_8 {x_2}^2$$

x_2 = Temperature

x_1 = Current density

$R^2 = 0.99$

$p < 0.05$ for all coefficients

Significant effects from DOEx

Effect	Magnitude (Coefficient)	Units
I on Lifetime	**-60±30 (β_1)**	**mAh/A**
I on Voltage	**-2.3±1.2 (β_1)**	**mV/ºC**
T on Voltage	**1.3±0.6 (β_2)**	**mV/ºC**
T^2 on Voltage	**-1.3±0.7 (β_8)**	**μV/ºC²**
I on Pol.	**-0.99±0.61 (β_1)**	**Ohm/A**
T on Pol.	**-0.96±0.35 (β_2)**	**mOhm-cm²/ºC**
P on Pol.	**-5.8±4.89 (β_3)**	**mOhm-cm²/PSI**

$$\hat{y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \ldots$$
$$\beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 {x_1}^2 + \beta_8 {x_2}^2 + \beta_9 {x_3}^2$$

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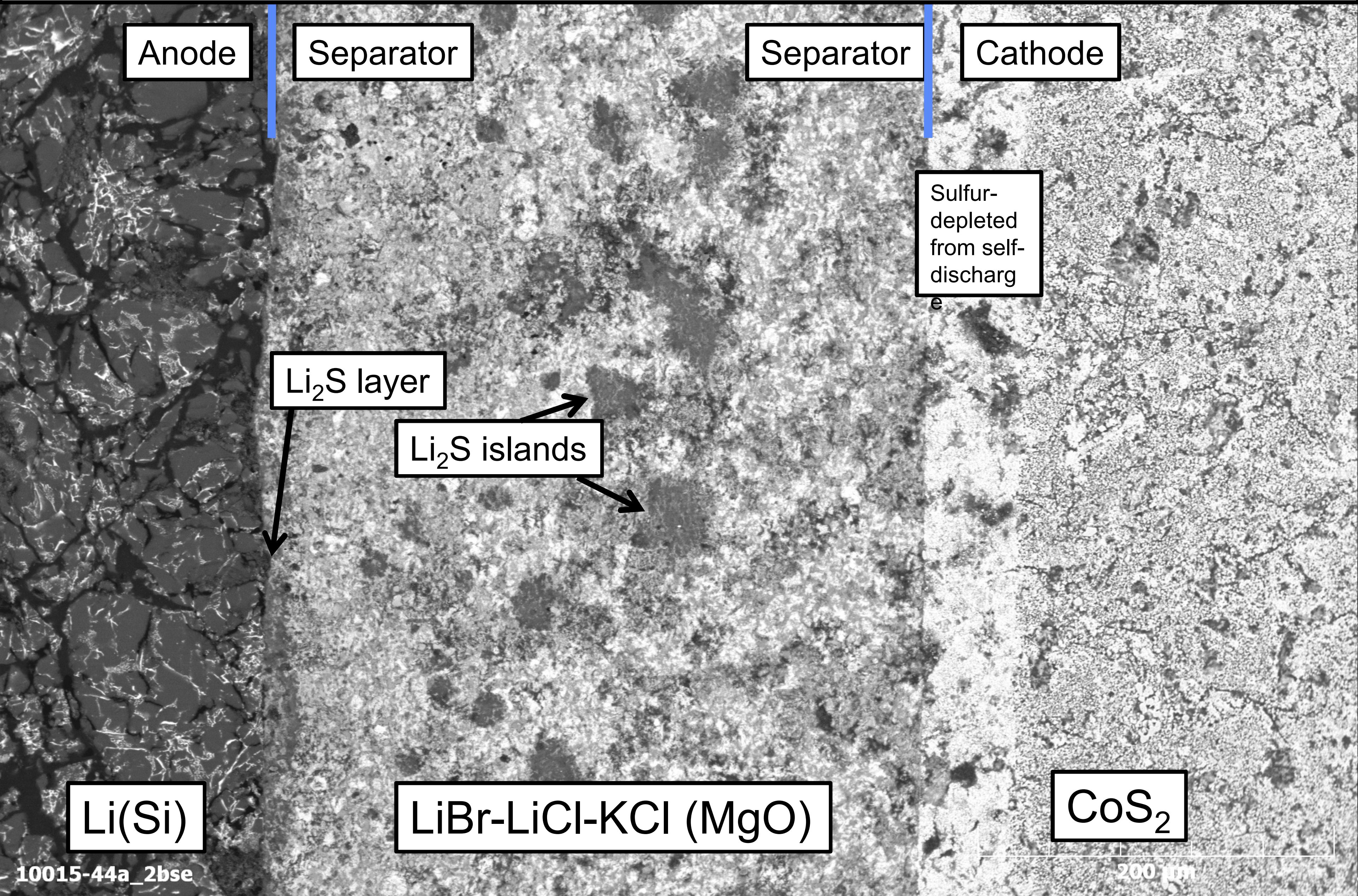
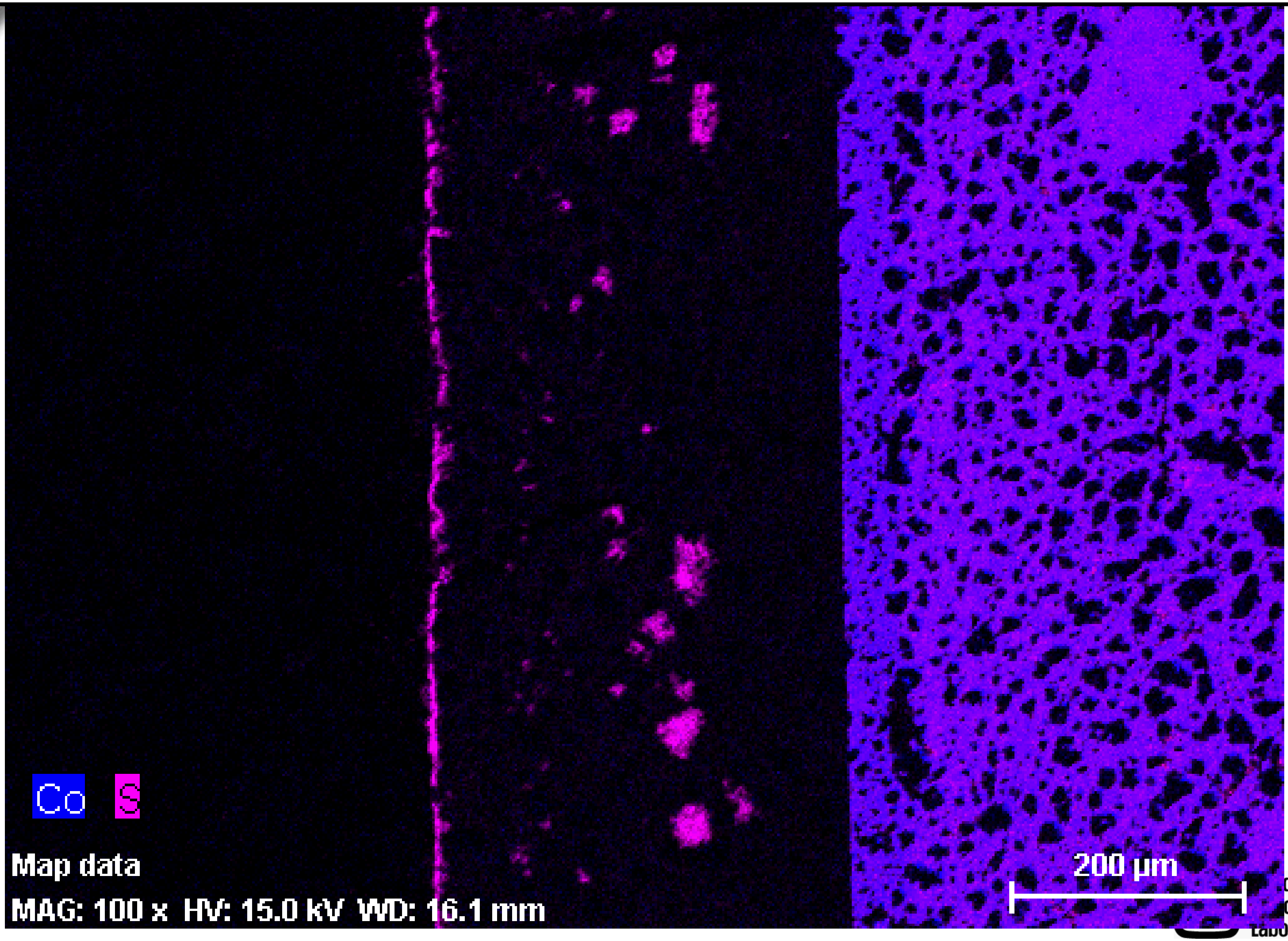
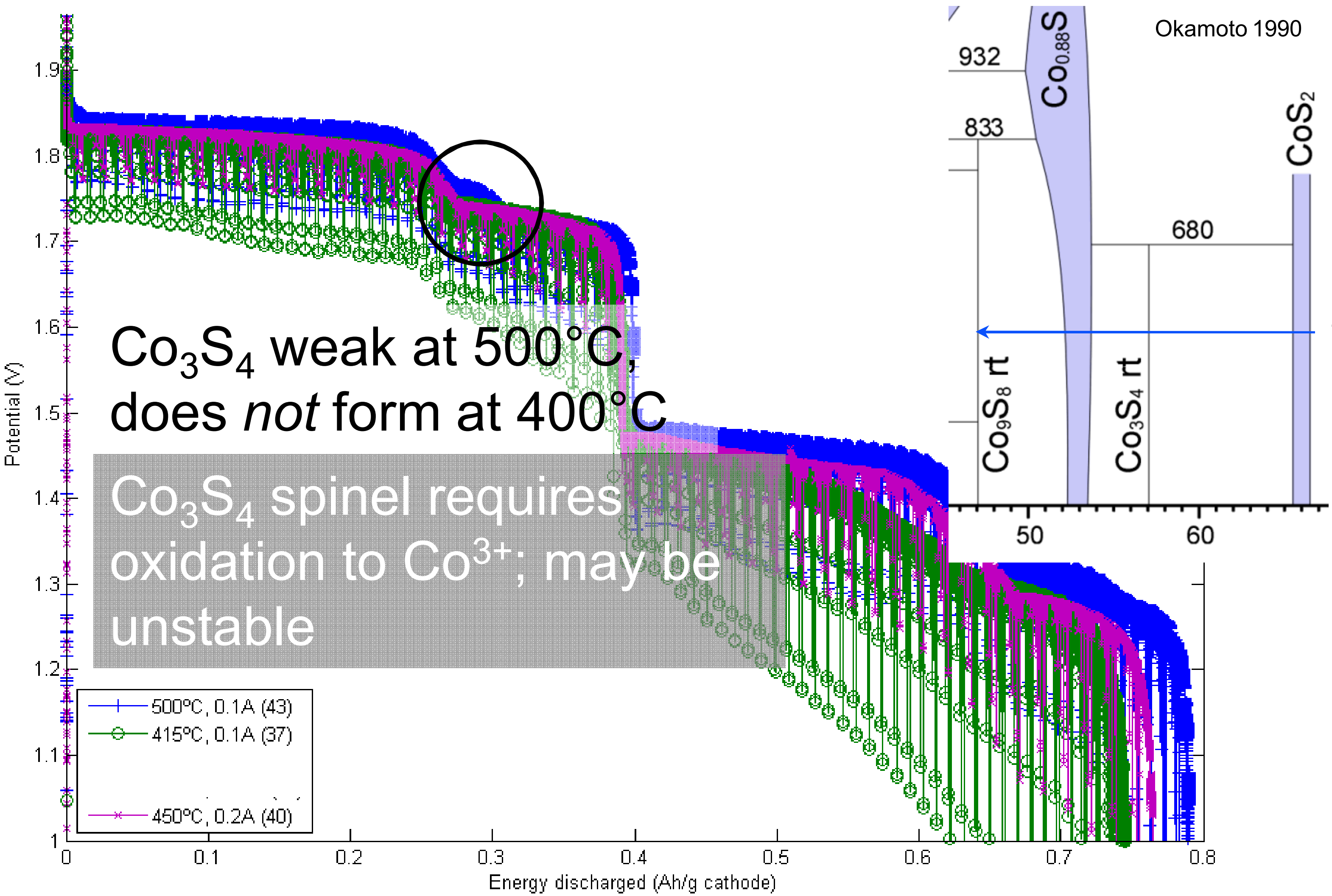
Single-cell quenched at approx. end of service life: BSE (Z-contrast) image



Single-cell quenched at approx. end of service life:
EDS (x-ray element map) showing Co and S distribution



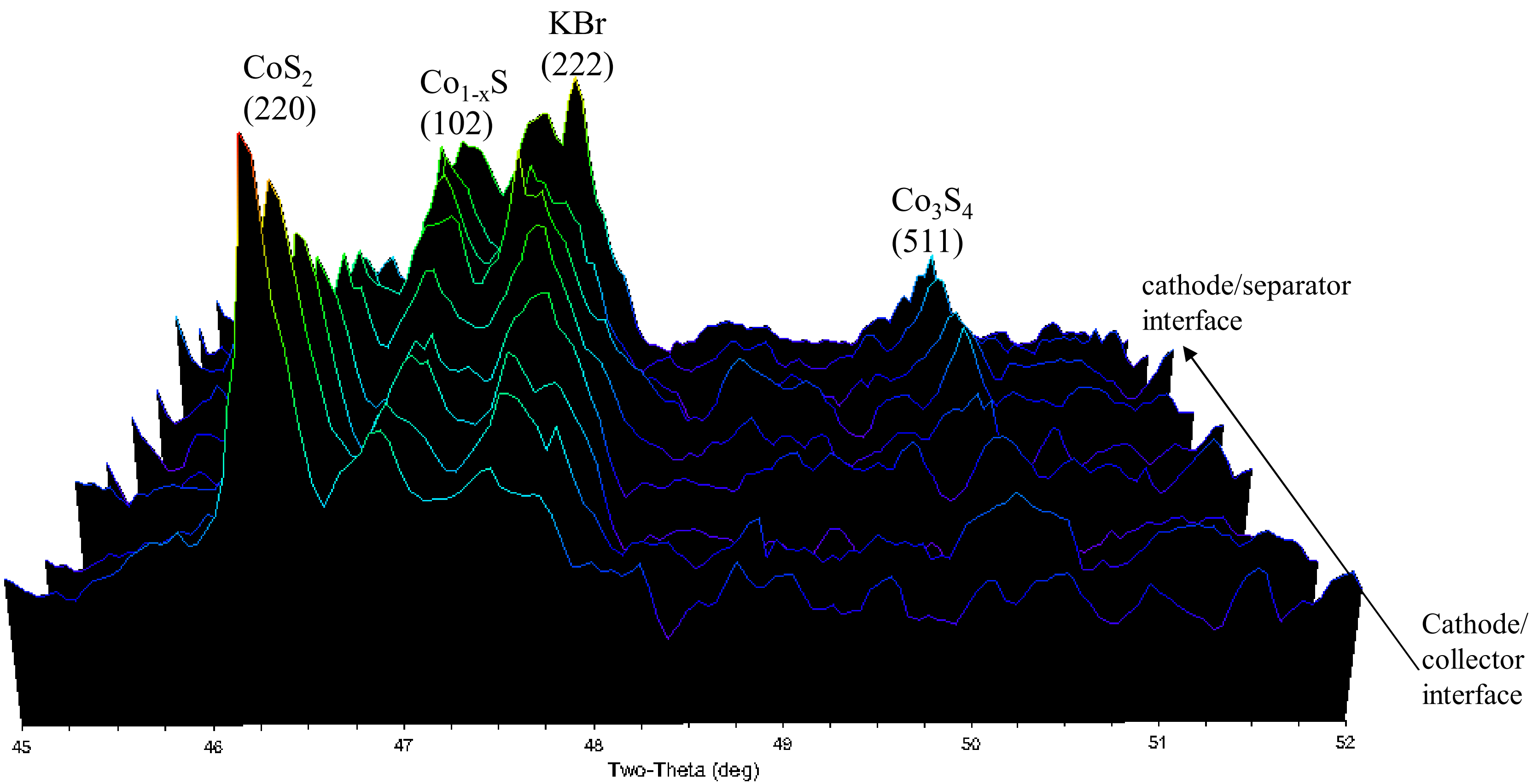
Co_3S_4 is not present at all T



Co_3S_4 weak at 500°C, does *not* form at 400°C

Co_3S_4 spinel requires oxidation to Co^{3+}; may be unstable

Spatially-resolved XRD of cathode shows gradient of Co-S phases with position



$Co_{1-x}S$ and Co_3S_4 are coincident in cathode: indication of spontaneous decomposition of Co_3S_4?

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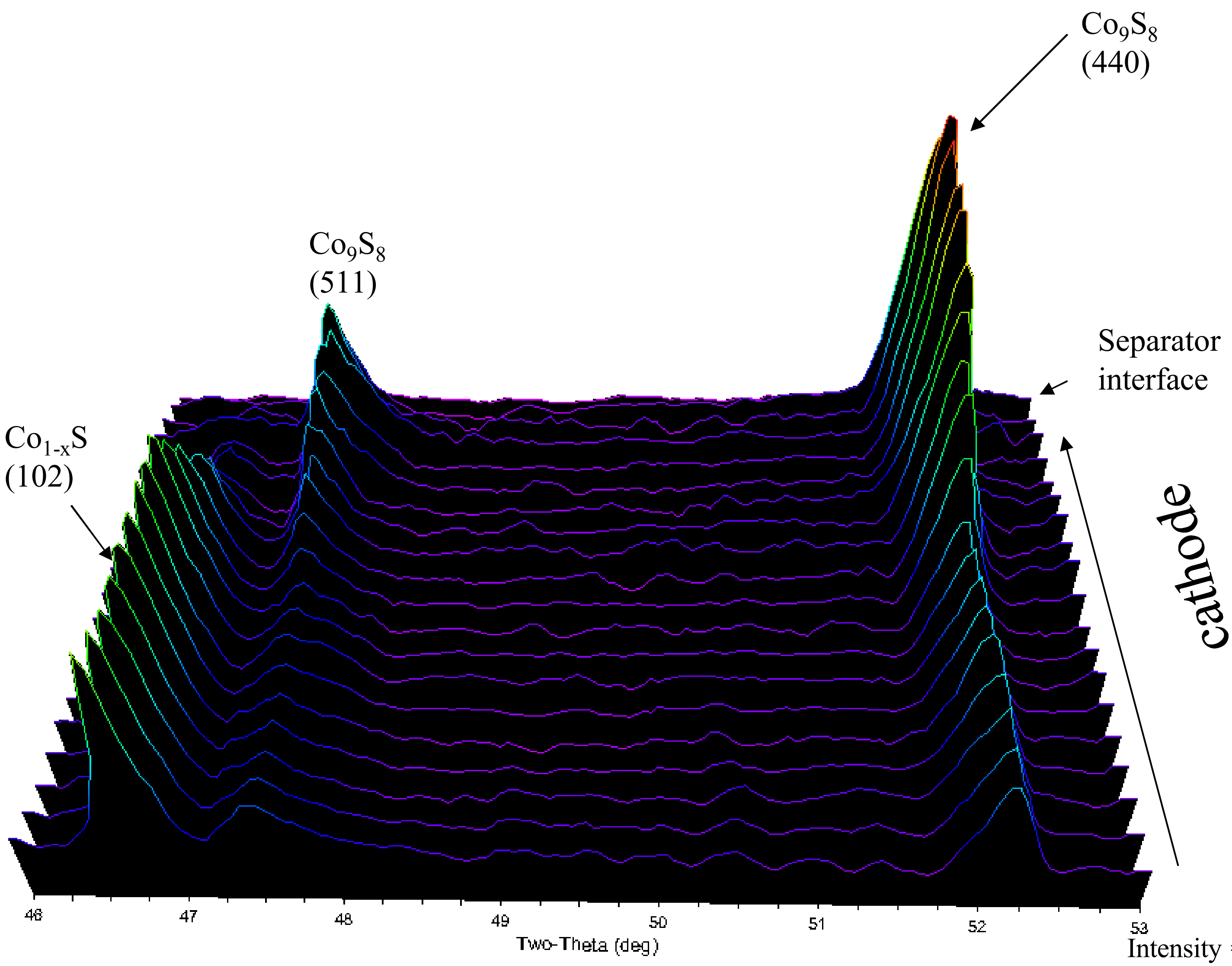
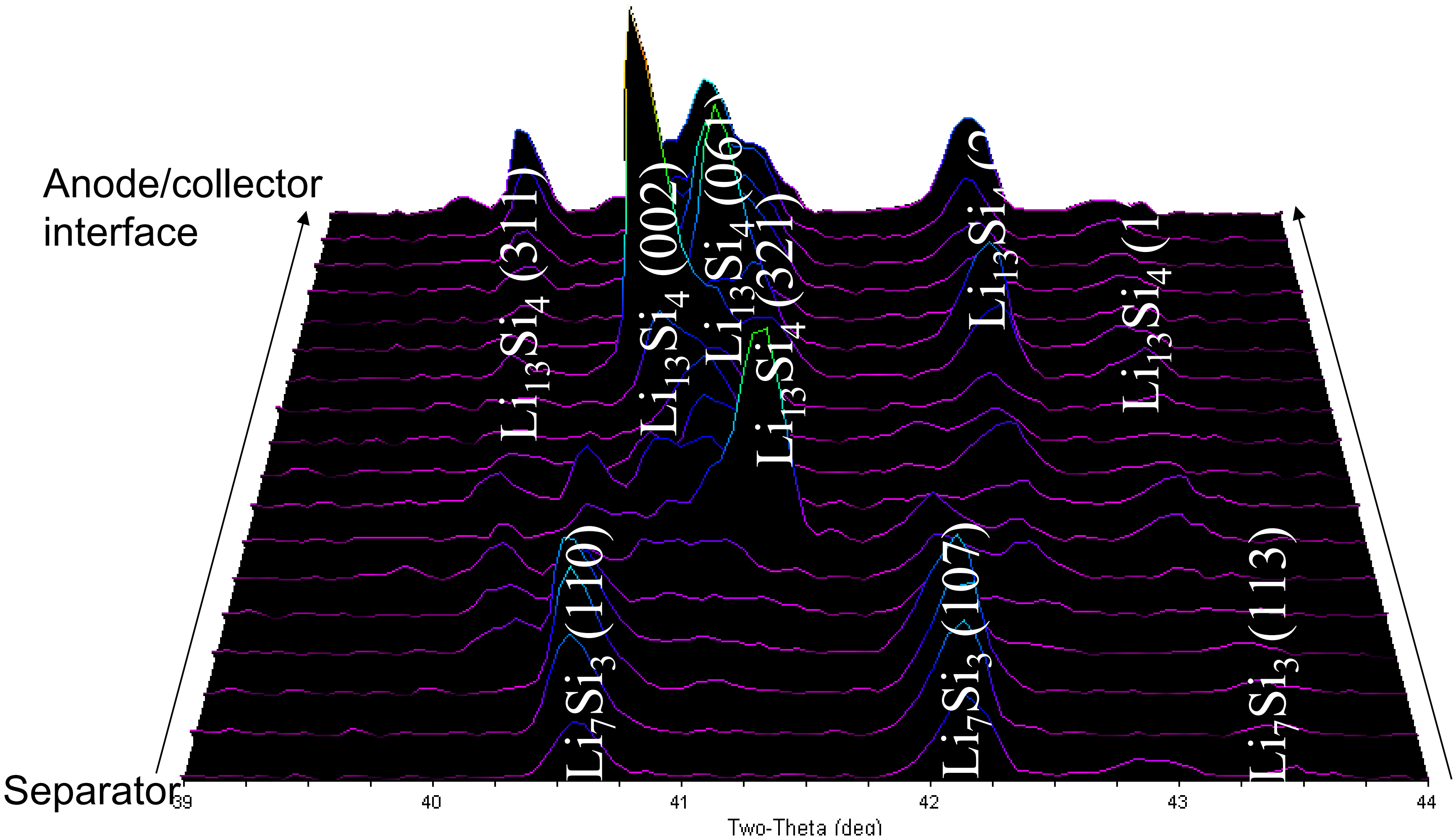
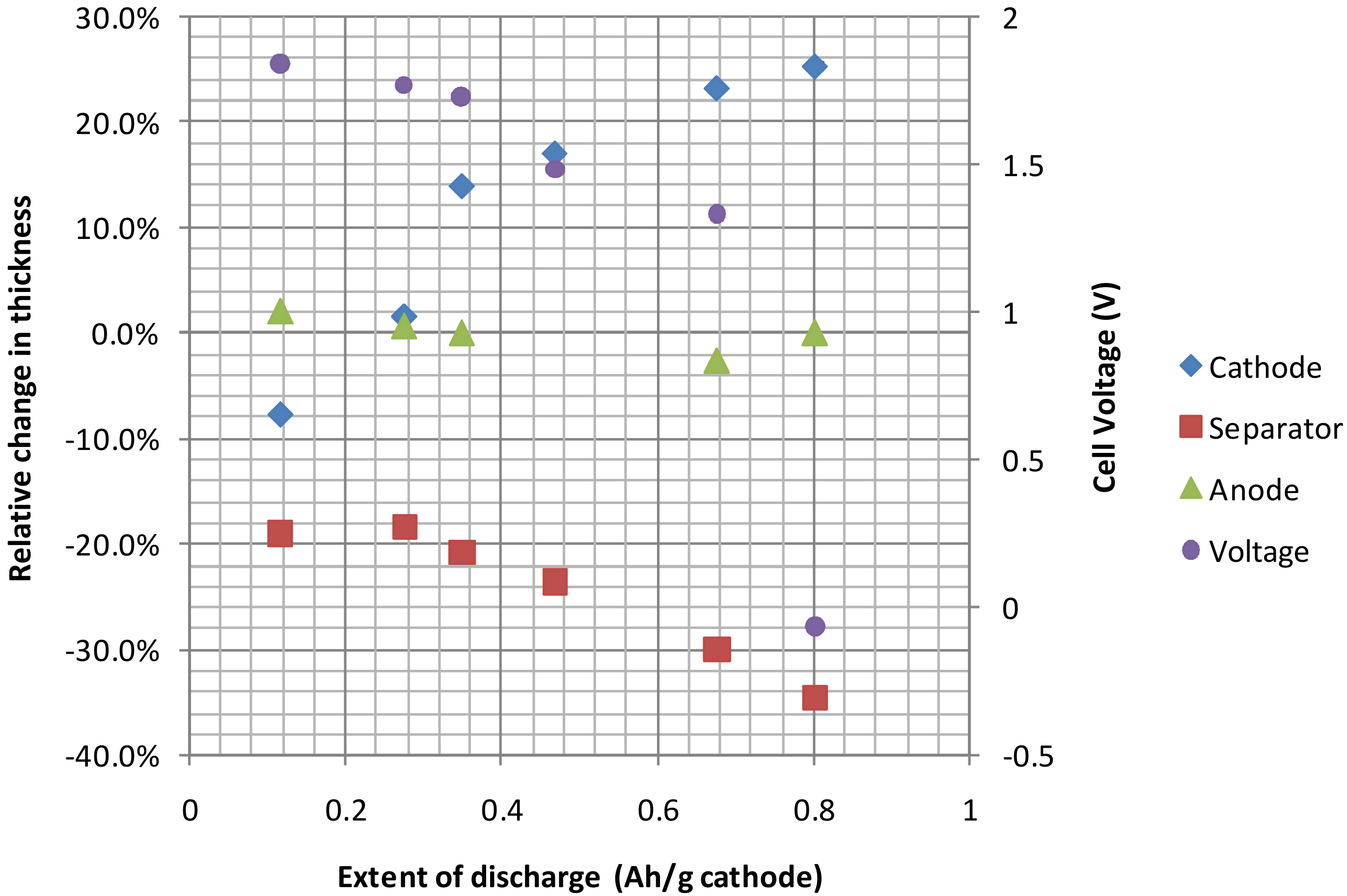
Concentration gradients become more pronounced as discharge continues



Anode XRD shows gradient of lithium-silicon phases with position



Cell thickness changes during discharge, CoS_2 / KCl-KBr-LiCl / $Li_{13}Si_4$ system



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Summary

- DOE was used to create an empirical model of voltage and polarization as a function of T, P, and current density
- Metallurgical evaluation techniques adapted for moisture-sensitive components provide insight into chemistry
  - Co_3S_4 spinel decomposes during first transition and does not form as expected at low temperature
  - Li_2S self-discharge is apparent CoS_2
    - Electrolyte dependent behavior
    - Mechanism unclear
  - Concentration gradients exist in all components during discharge, even at low rates

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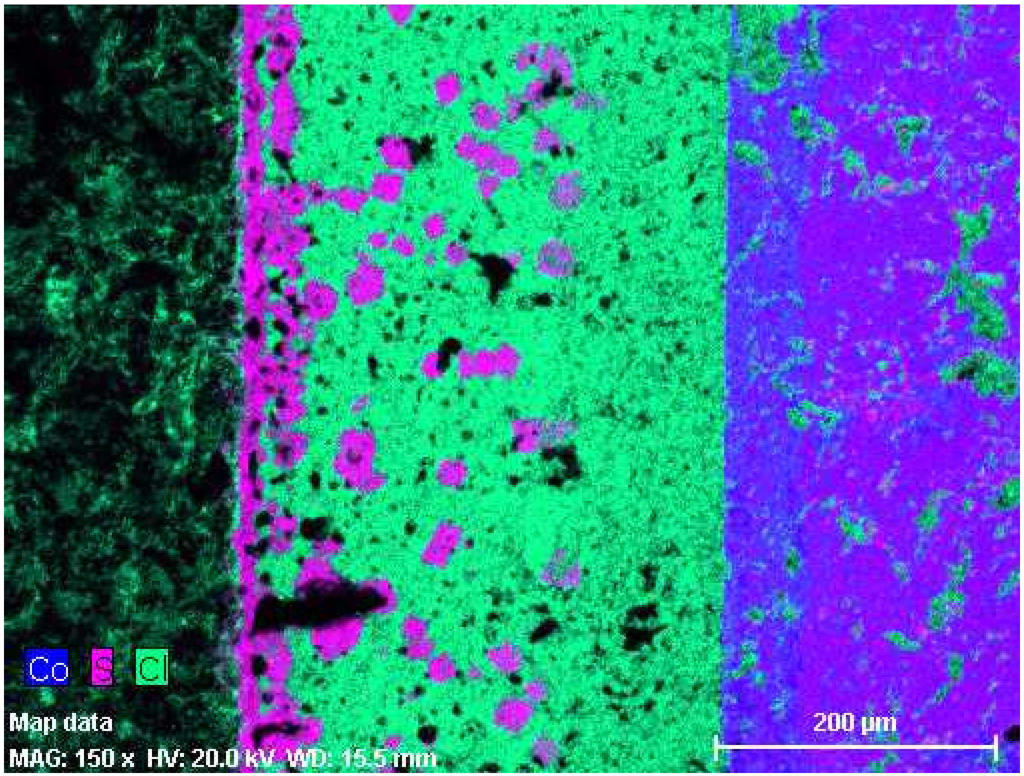
Extra slides

Chemical gradients also likely in separator



Li$_2$S phases may track Li gradient

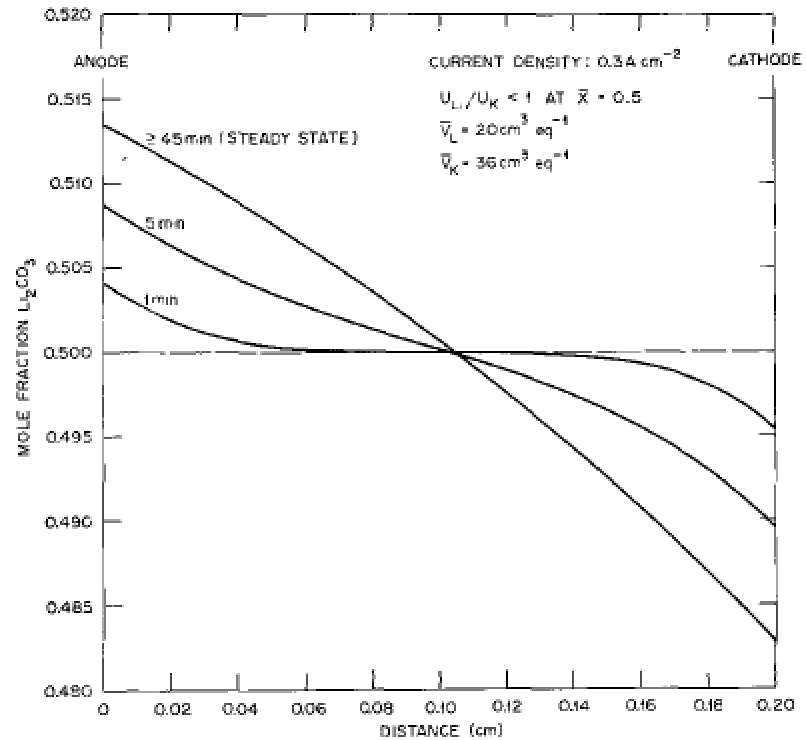


Fig. 6. Development with time of composition profiles in 0.5 mole fraction Li_2CO_3-K_2CO_3 if $u_L < u_K$. $D = 1 \times 10^{-5}$ cm^2 sec^{-1}, $\overline{V_L} = 20$ cm^3 equiv.$^{-1}$, $\overline{V_K} = 36$ cm^3 equiv.$^{-1}$, $t_L^C = 2.82X_L^2 - 1.82X_L^3$, $I = 0.3$ A cm^{-2}. Effect of activity coefficient correction, mobility ratio (r) and diffusion coefficient (D).

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Voids in anode filled with electrolyte as Li loss occurs without volume change

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