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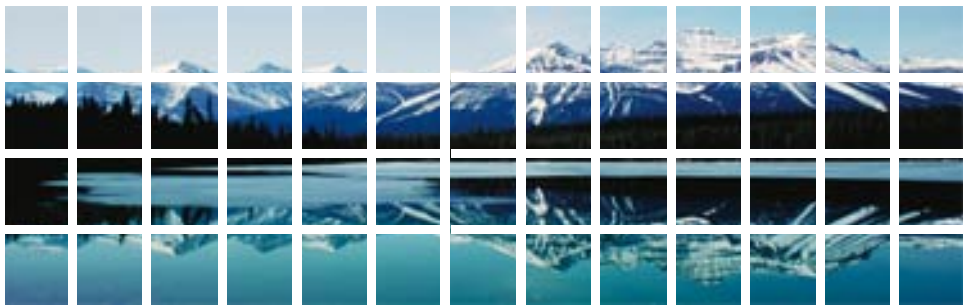

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Development of transition metal/ chalcogen based cathode catalysts for PEM fuel cells

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Ballard Power Systems
15th May 2007

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Overview

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Timeline

Project start: February 2004

Project ends: February 2007

Project 85% complete

Budget

Total funding: $1,975,175

DOE share: $1,580,139

Ballard share: $ 395,036

FY'06 funding: $ 520,139

Funding '07: $ 0

Barriers & Targets

A. Durability:-

Drive cycle lifetime of 5,000 hours

B. Cost: $8kW^{-1}

C. Electrode Performance:-

50Acm^{-3} @ 800mV (iR free)

Partners

- University of British Columbia
- Case Western Reserve University

Objectives

- To develop a non-precious metal cathode catalyst for PEM fuel cells which is as active and as durable as current PGM based catalysts at a significantly reduced cost.
  - Optimization of composition and structure
  - Manufacturing process development
  - Evaluation, optimization and demonstration in fuel cell stacks.

Approach

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- **Materials based on transition metals such as Cr, Fe, Co and two chalcogens (Se and S) are used to screen for stability and activity for oxygen reduction in dilute acid.**
- **The surface area of nano-disperse catalysts is difficult to measure, so sputtered thin films with a well-defined surface area are used for screening. Samples were characterized before and after electrochemical evaluation (EC) by EDX, SAM and XPS. After EC, XRD and Raman spectroscopy were also carried out.**
- **The down selected materials are then synthesized as supported catalysts for ex-situ evaluation as nano-dispersed materials. HRTEM, Raman Spectroscopy and XRD was used for characterization of the powders**
- **Finally, the best catalyst is optimized and evaluated in PEM fuel cells to demonstrate activity and durability to meet the technical targets.**

Technical Accomplishments

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- Addition of W and Ni to CoS_2 thin films has been completed.
- These films have been characterized and evaluated
- Supported, dispersed catalysts of $CoSe_2$, CoS_2 and $(CoNi)S_2$ have been made, characterized and evaluated.
- The go/ no-go decision in September 2006 was to extend the project until February 2007 where another go/ no-go decision would be made about whether to carry out fuel cell testing.

Elemental analysis of WS_2 and WS_2/CoS_2 thin films

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Thin film composition determined using SAM		
Target: sintered WS_2 powder and elemental S		
element (at %)	As prepared	After EC
S	60.13	39.53
C	37.00	57.77
O	0.43	0.88
W	2.44	1.88
S/W	24.64	21.84

Sputtered WS_2 thin film			Sputtered W-Co-S thin film		
E_{eq} (V vs. RHE)	0.73		E_{eq} (V vs. RHE)	0.73	
Elemental ratios	As prep.	After EC	Elemental ratios	As prep.	After EC
Bulk atomic ratio S/W from EDX	5.6	NA	Bulk atomic ratio Co/W from EDX	1.1	NA
Surface S/W atomic ratio from XPS	4.1	4.4	Surface S/M atomic ratio from XPS	0.7	7.2
			Surface Co/W atomic ratio from XPS	0.4	6.2

After EC, W dissolves from W-Co-S film

W-Co-S thin films

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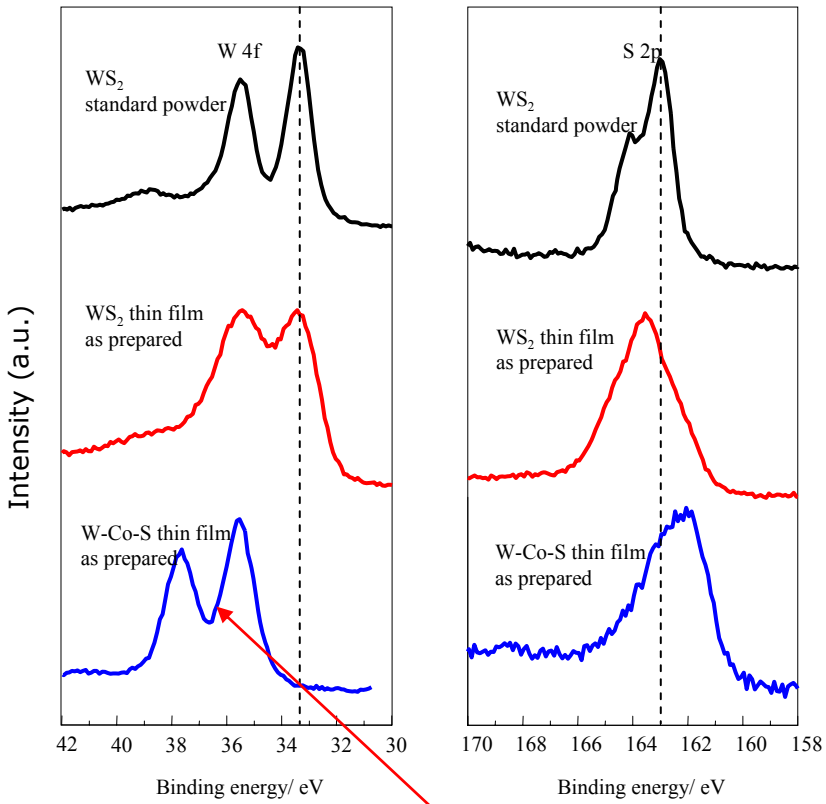
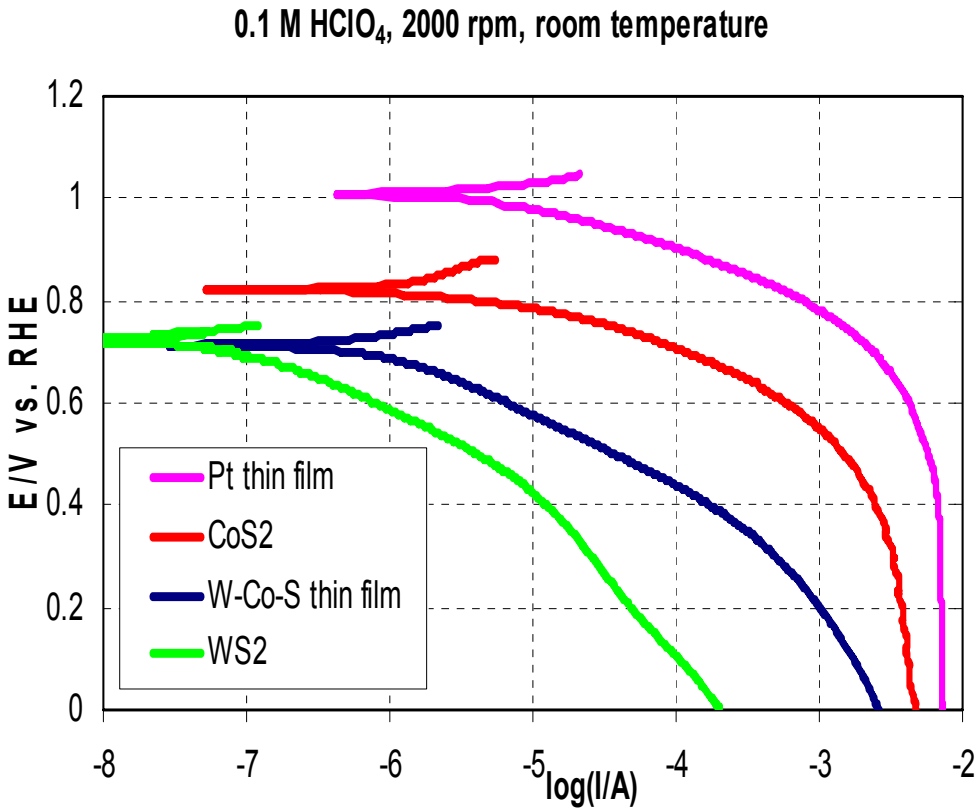


In W-Co-S film,
W present at WO_3



Addition of W lowers OCP

Addition of Ni to CoS_2 thin films

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Thin film compositions determined using XPS			
Magnetron sputtering	Target: sintered NiS_2 powder + elemental S	Target: sintered NiS_2, CoS_2 elemental S powders	Target: sintered NiS_2, CoS_2 and elemental powders
As prepared			
film	**NiS_2**	**$(Ni,Co)S_2$**	**(Ni,Co)S**
	primarily disulfide	primarily disulfide	primarily monosulfide
Sulfur/total metal	3.5	3.1	2.2
Ni/Co	NA	0.92	1.5
S_n^{2-} (%)	15.3	15.8	8.6
S_2^{2-} (%)	75.5	75.1	27.0
S^{2-} (%)	9.2	9.0	64.3
After electrochemical measurement			
Sulfur/total metal	4.3	3.8	2.3
Ni/Co	NA	0.7	0.8
S_n^{2-} (%)	14.1	15.6	6.9
S_2^{2-} (%)	77.1	73.8	24.4
S^{2-} (%)	8.7	10.5	68.6

ORR Tafel plots for $(Co,Ni)S_2$ thin films

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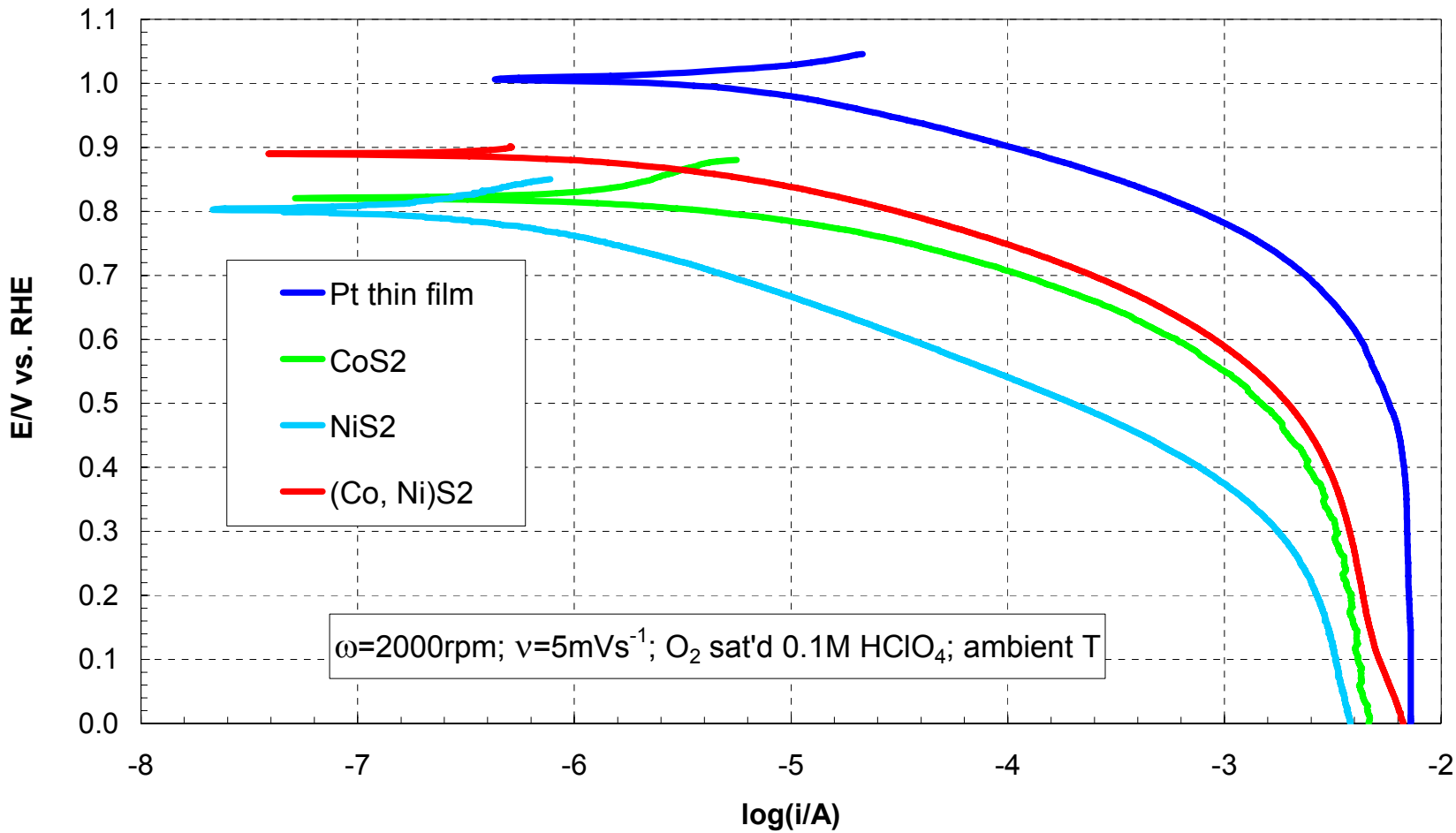
OCP of ternary thin film raised by 80mV



Valence band edge XPS spectra of Co-Ni-S thin films

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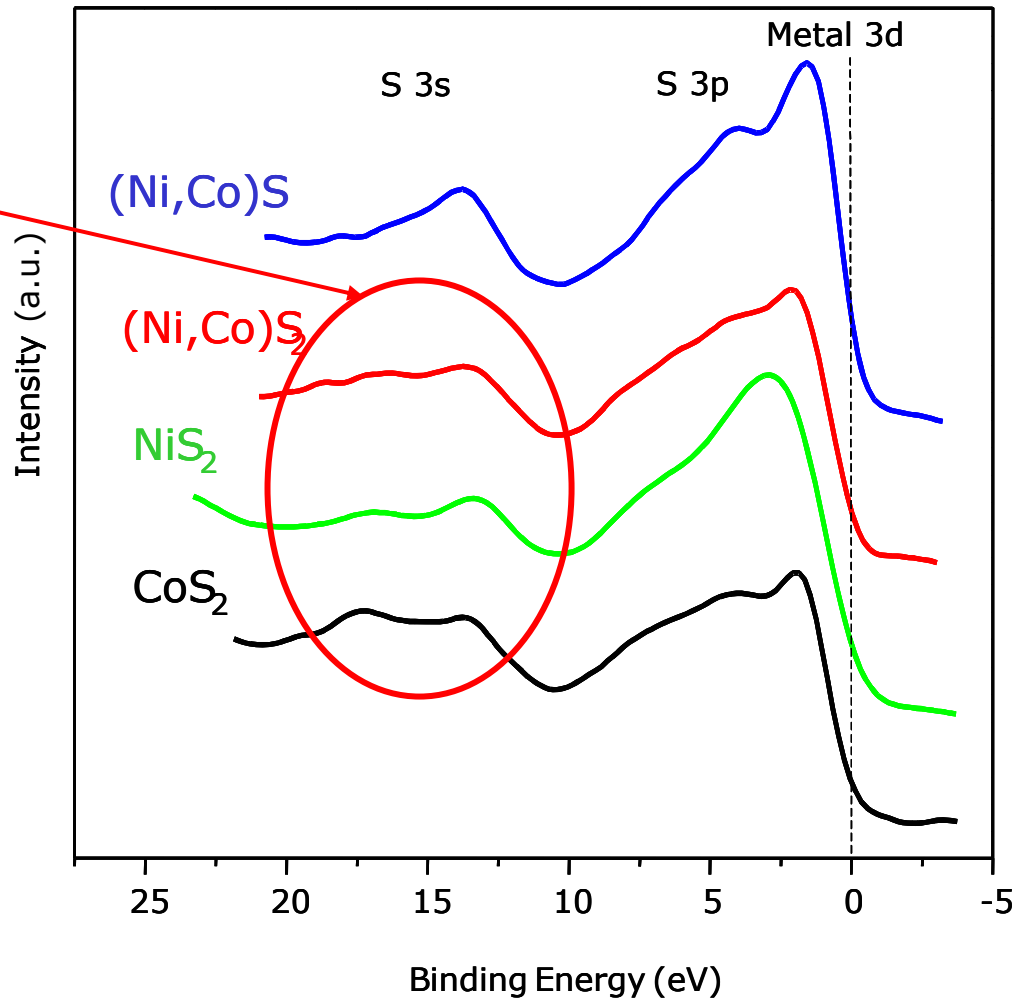
The splitting of the S3s indicative of S_2^{2-} pyrite structure is evident for CoS_2, NiS_2 and one of the Co-Ni-S films.



Raman analysis of Co-Ni-S_2 thin films

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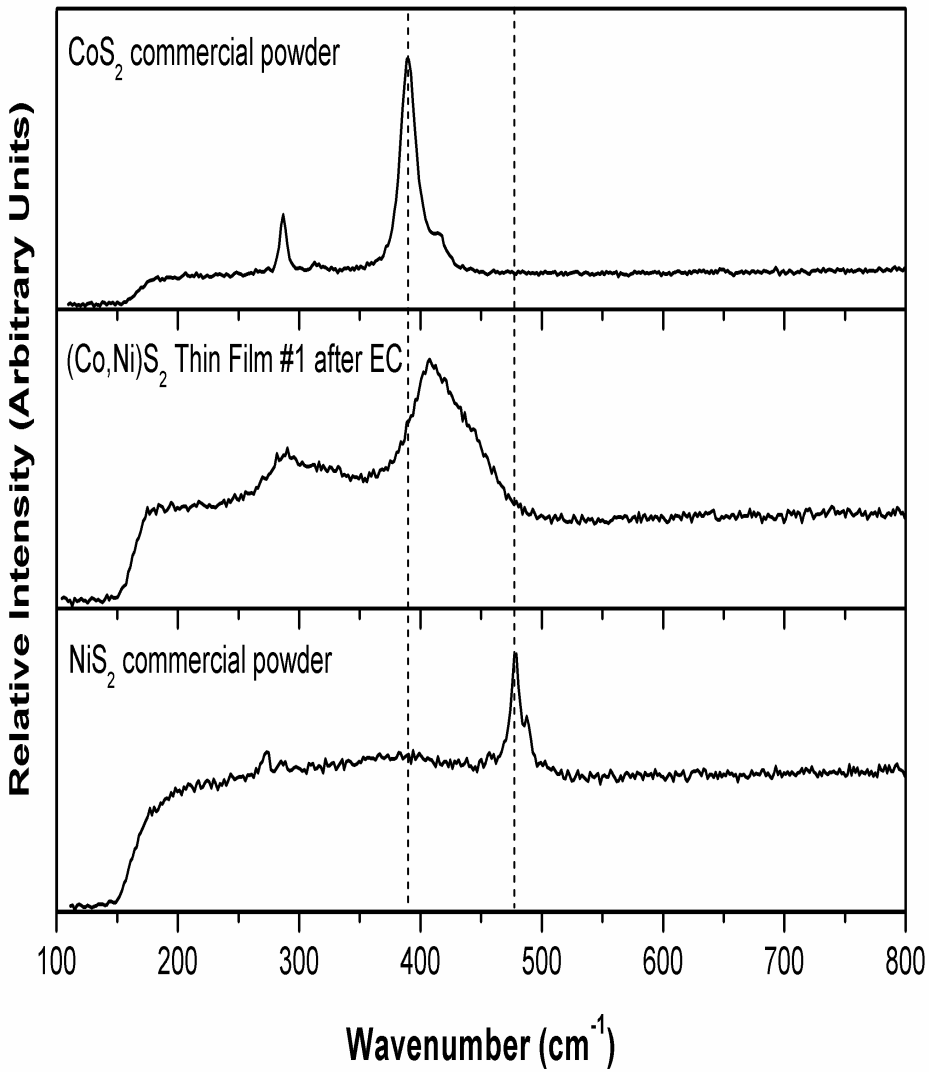

- For the Co-Ni-S_2 thin film, there is a broad Raman peak around 425cm^{-1} which is midway between the sharp peaks for the commercial powders.
- This indicates that this is not a two-phase system.
- May indicate a solid solution.

Carbon supported $CoSe_2$ powder catalyst

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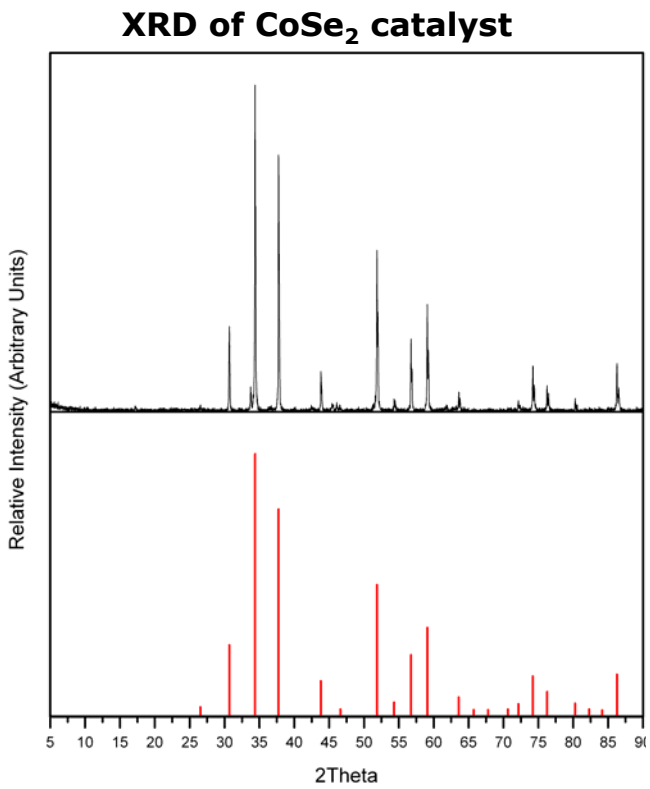

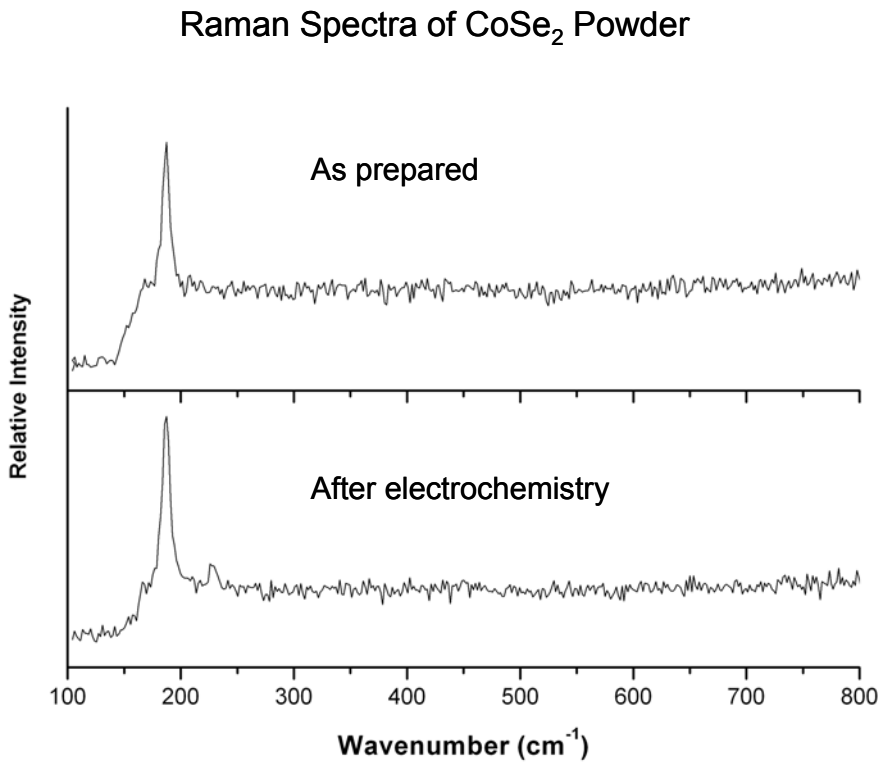

XRD pattern matches powder file

Raman spectrum after electrochemistry shows no change

Carbon supported $CoSe_2$ powder catalyst

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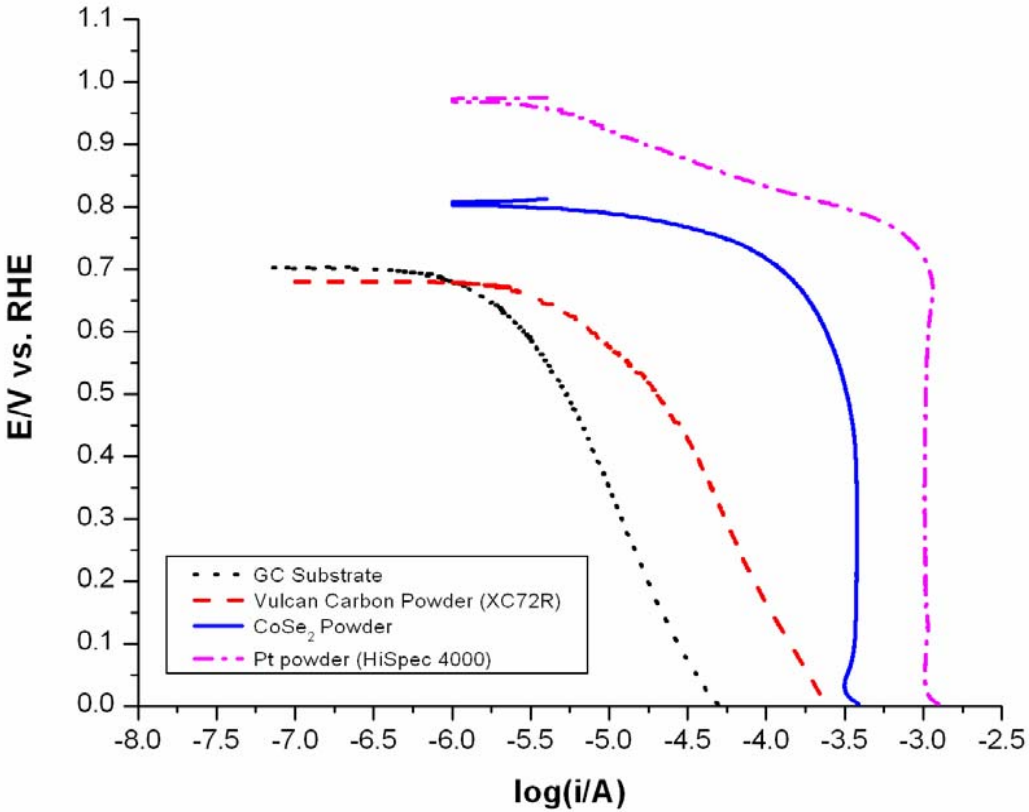
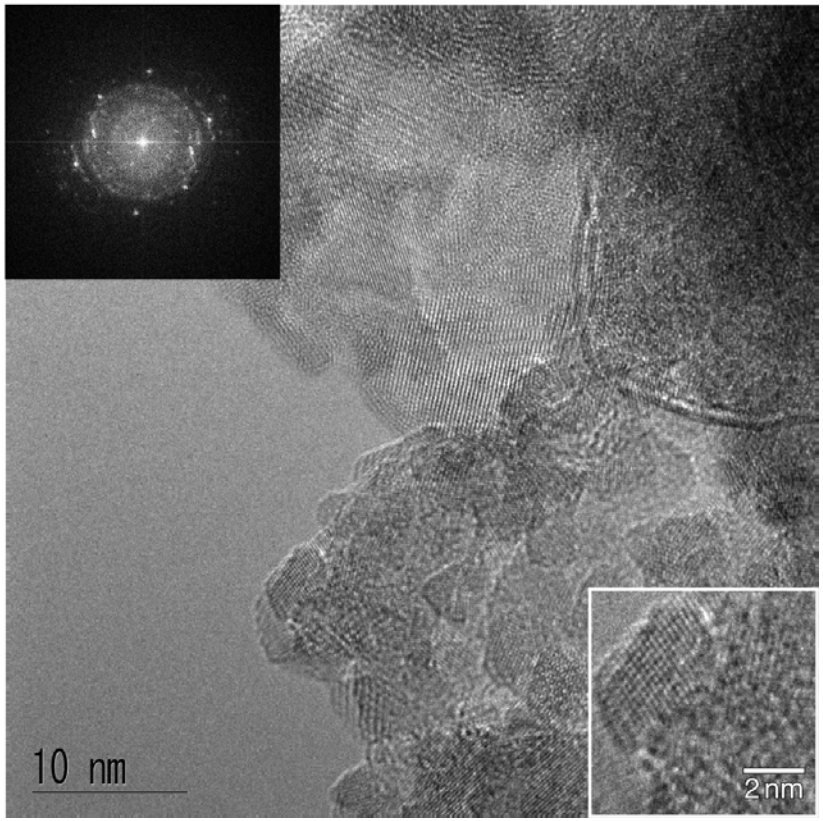


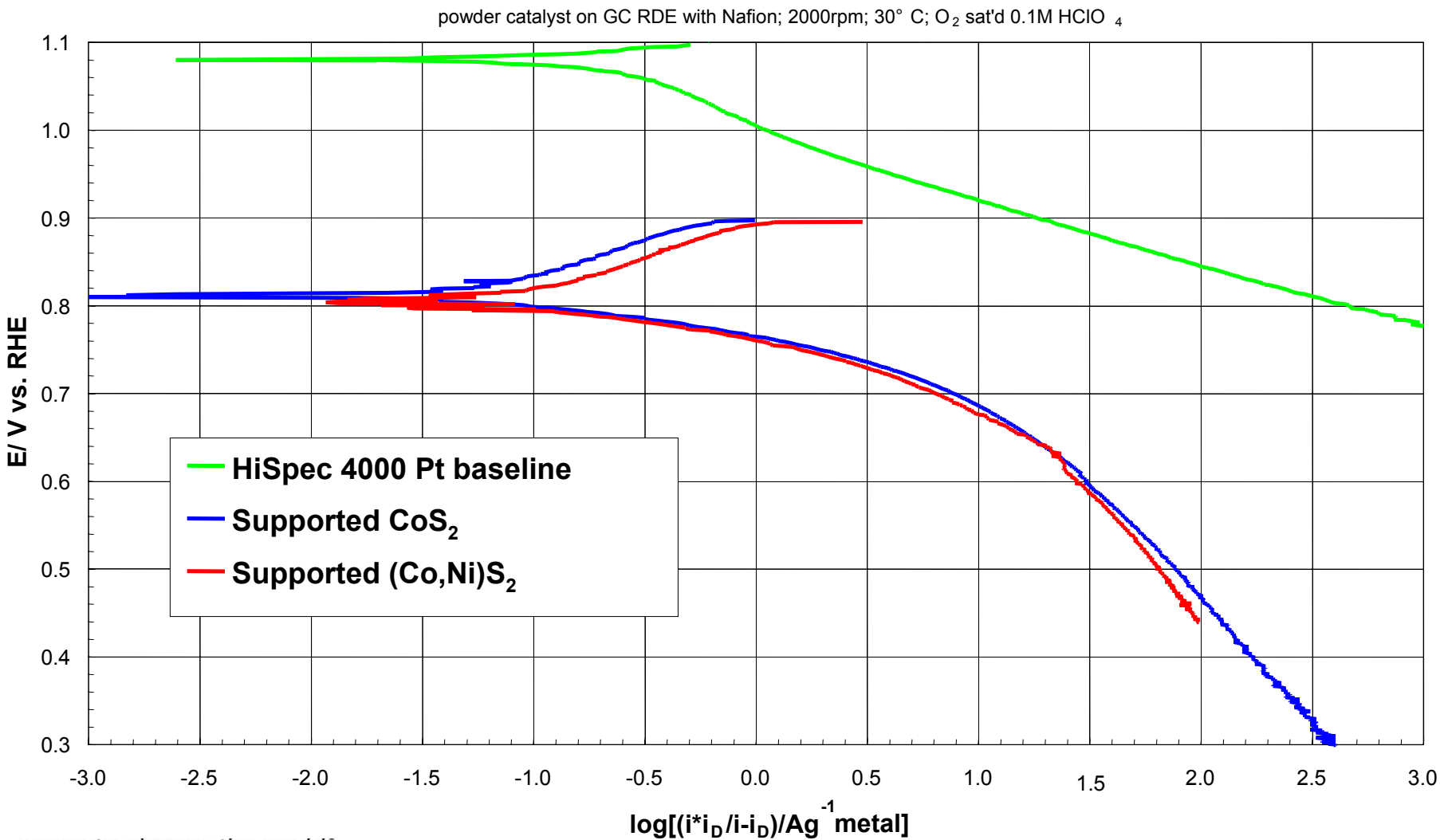
- Supported $CoSe_2$ catalyst performs well with an OCP of 0.8V vs. RHE.
- Active surface area much lower than Pt catalyst.
- Smaller limiting current indicates n<4.

HRTEM of supported CoS_2 powder catalyst

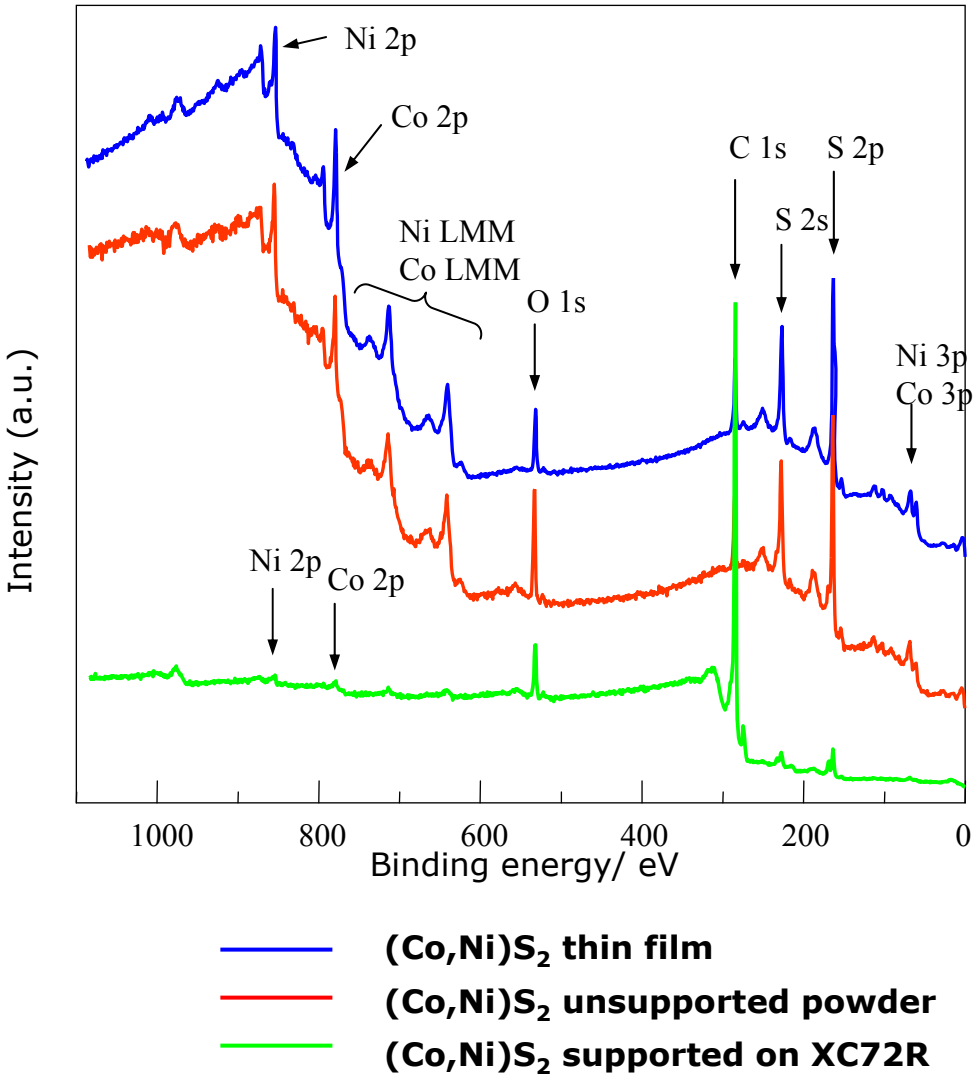


- Micrograph shows nanocrystalline CoS_2 particles on globular XC72R support.
- Insert shows single particle ~5nm in size as single crystal.
- Diffraction pattern of the crystals confirm structure as pyrite.

Tafel plots from supported disulfide catalysts

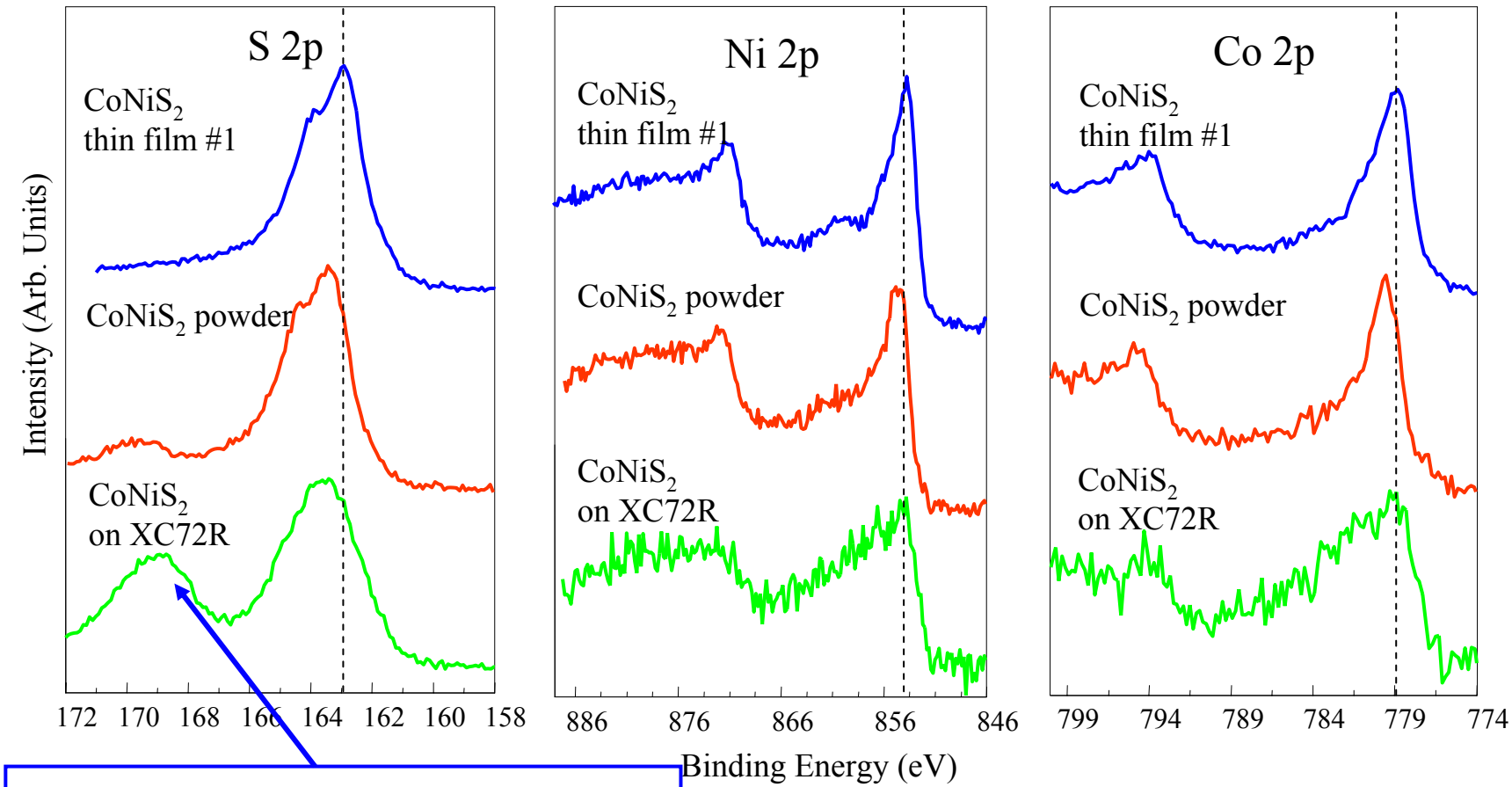


$(Co,Ni)S_2$ powder catalyst characterization



$CoNiS_2$ synthesized powders		
Sample	**powder**	**supported**
E_{eq} (V vs. RHE)	0.81	0.80
Bulk atomic ratio Co/Ni from EDX	0.8	1.0
Surface S/M atomic ratio from XPS (as prepared)	4.3	4.7
Surface Co/Ni atomic ratio from XPS (as prepared)	0.9	1.0

Narrow scan XPS spectra of supported Co-Ni-S_2 powder catalyst



S2p peak at 169eV indicates some sulfate in powders

XRD analysis of $CoNiS_2$ powder catalysts

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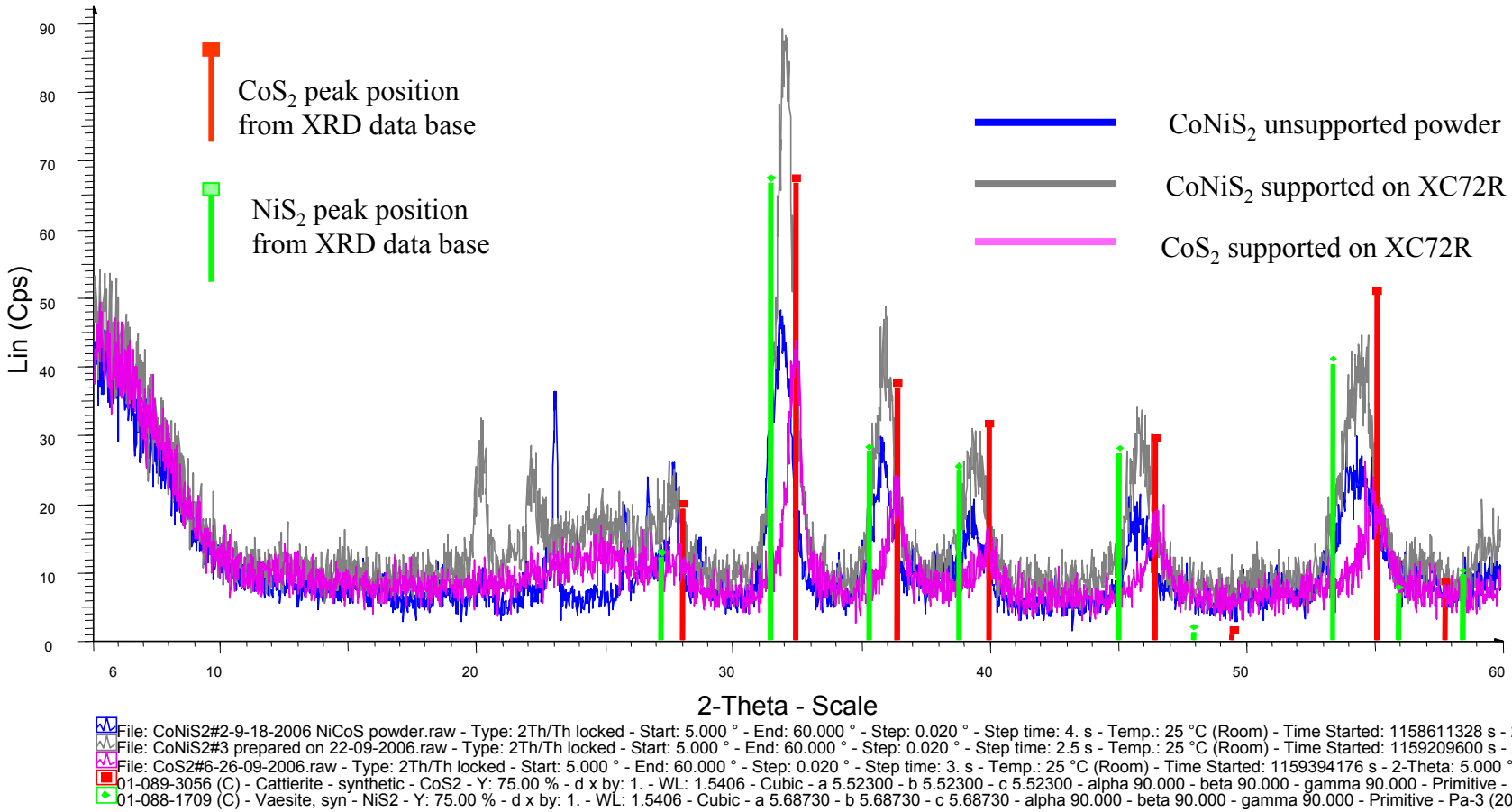

Effect of cycling powder catalysts

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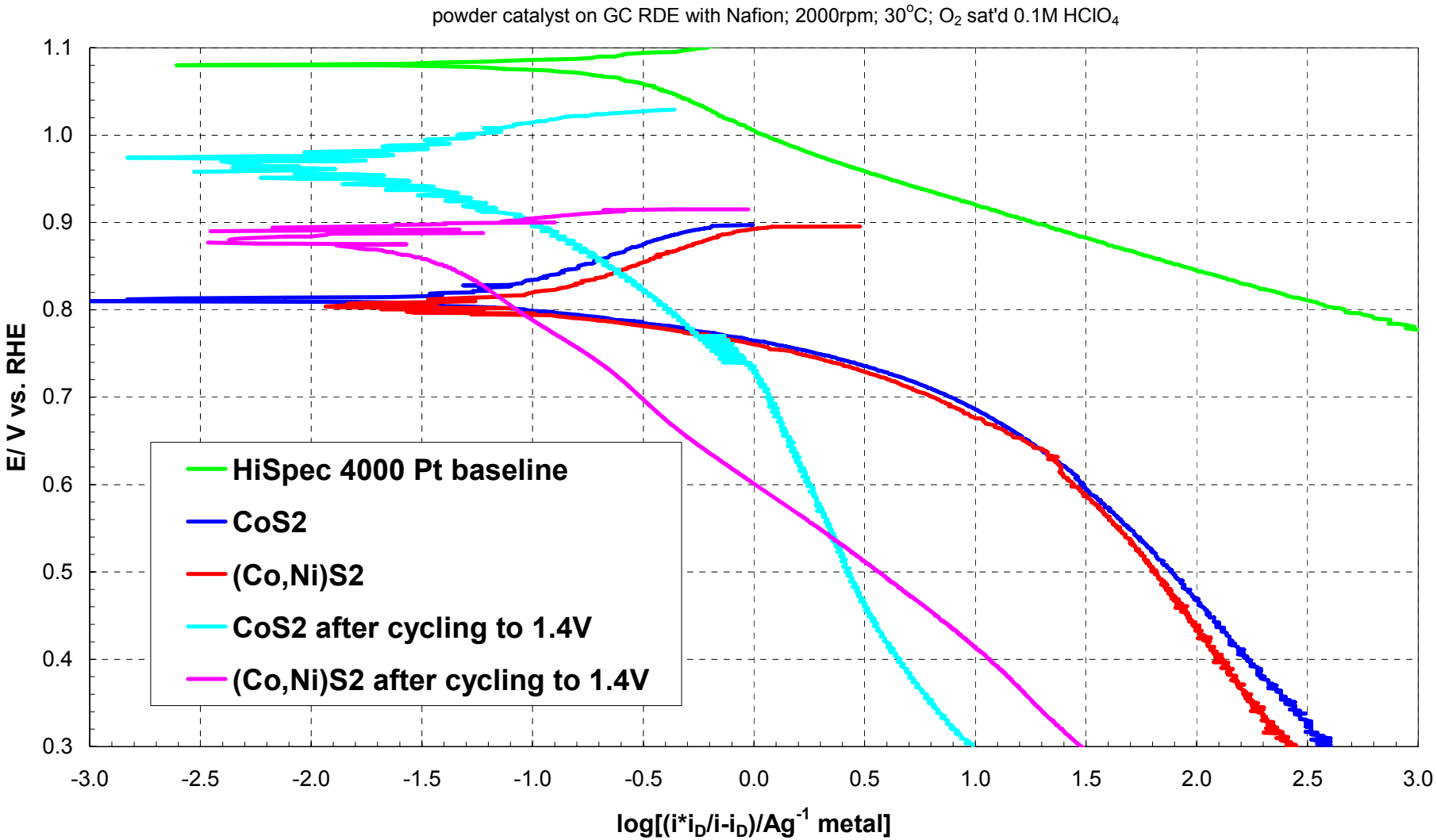

Summary

- The addition of W and Ni to CoS_2 thin films has been carried out successfully.
- The addition of W did not raise the OCP but the addition of Ni to form a solid solution with the CoS_2 pyrite did raise the OCP by 80mV to 0.89V vs. RHE.
- Supported catalysts have been made with CoS_2 and $(Co,Ni)S_2$. Both these had an OCP of about 0.81V vs. RHE.
- Cycling these powders to 1.4V raised the OCP significantly but with a loss in current.
- Surface analysis indicates the presence of polysulfide species on the sputtered thin films.
- It is possible that these are responsible for the difference between the thin films and the powders.

Future work

- In February 2007 it was decided that, given the inability to replicate the higher OCP in powder catalysts, the project would not be extended to carry out fuel cell testing.
- No further work is planned in this project.