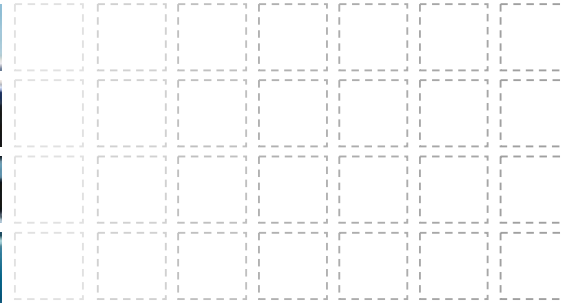
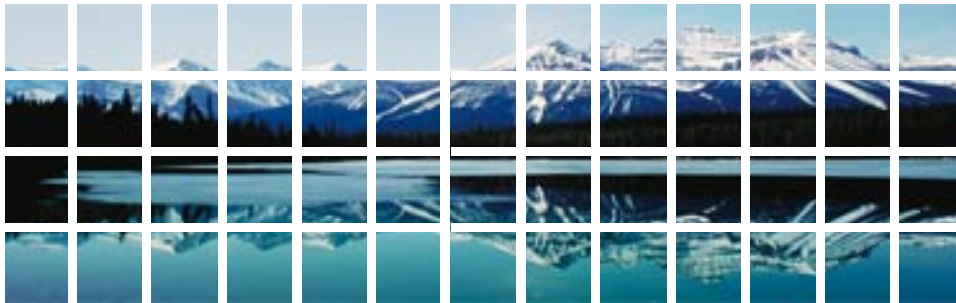


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Ballard Power Systems



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

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Ballard Power Systems

16th May 2006

FC11

Timeline

Project start: February 2004
Project ends: December 2006
Project 70% complete

Budget

Total funding: \$1,975,175
DOE share: \$1,580,139
Ballard share: \$ 395,036
FY'05 funding: \$ 438,781
Funding FY'06:\$ 520,139

Barriers & Targets

A. Durability:-

Drive cycle lifetime of 5,000 hours

B. Cost:-

\$8/kW

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 cells and stacks
- Note that this objective does not reflect the recent changes to technical targets as stated in the previous slide.

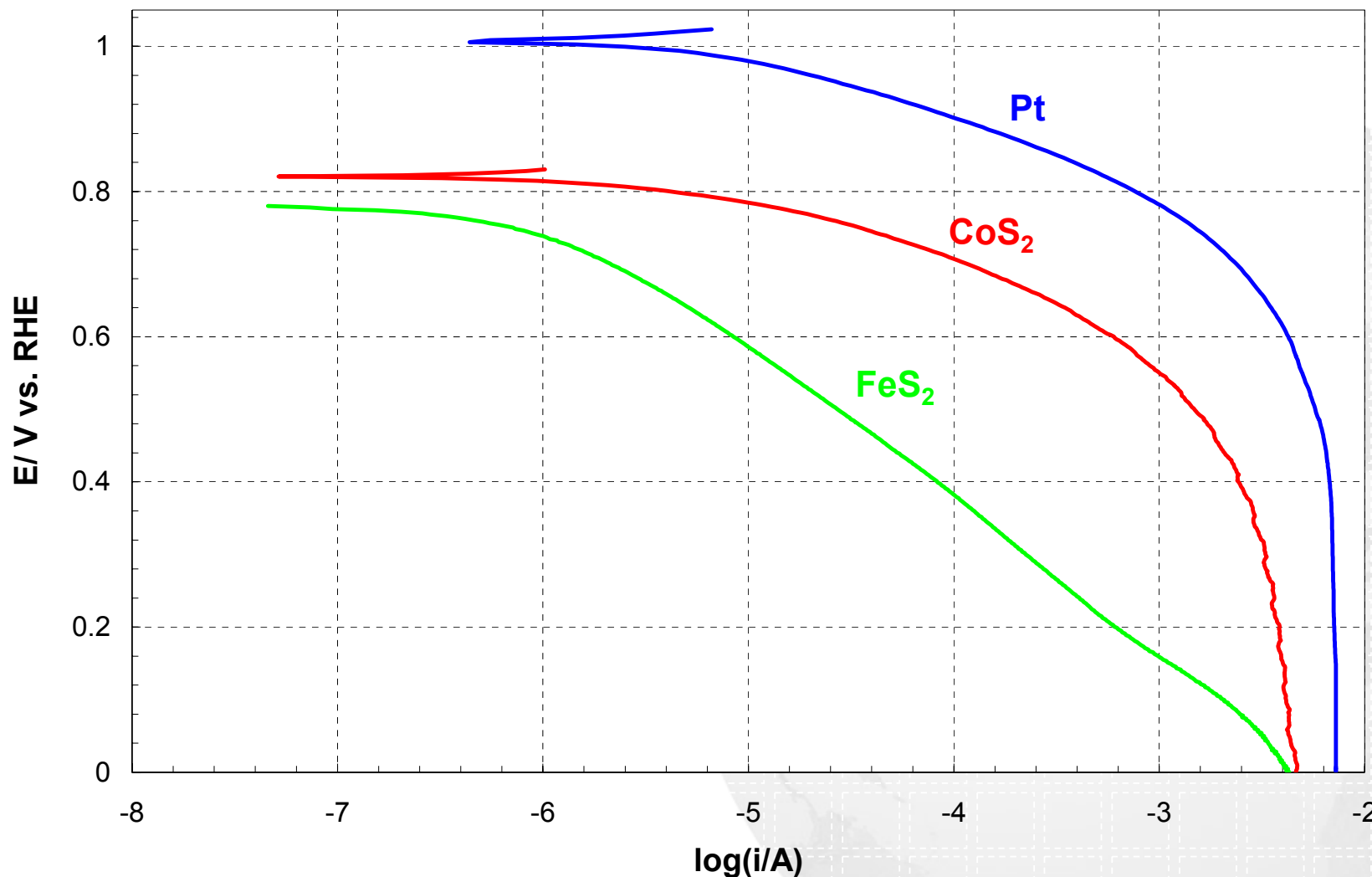
- Materials based on transition metals such as Cr, Fe, Co and two chalcogens Se and S are used to screen for stability and activity for oxygen reduction in sulfuric acid.
- The surface area of nano-disperse catalysts is difficult to measure, so sputtered thin films with a defined surface area were used for characterization and comparison using EDX, XRD, SAM, XPS, SEM, TEM etc.
- The down-selected materials are then synthesized as supported catalyst for ex-situ evaluation as nano-dispersed materials.
- Finally, the best catalyst is optimized and evaluated in PEM fuel cells and short stacks to demonstrate activity and durability to meet the technical targets.

Technical Accomplishments

- Since the last review in 2005 the metal-sulfur system has been studied. It has been found that the disulfide pyrite structure is stable and active. Monosulfides are not stable.
- The most active pyrite is CoS_2 but the highest OCP was 0.83V vs. RHE.
- Ex-situ XPS analysis of the thin films indicate that the S-rich surface interacts with the underlying metal to enhance activity.
- Powder supported FeS_2 and CoSe_2 catalysts have been fabricated. CoS_2 is in process.

Tafel plots of ORR on pyrite thin films

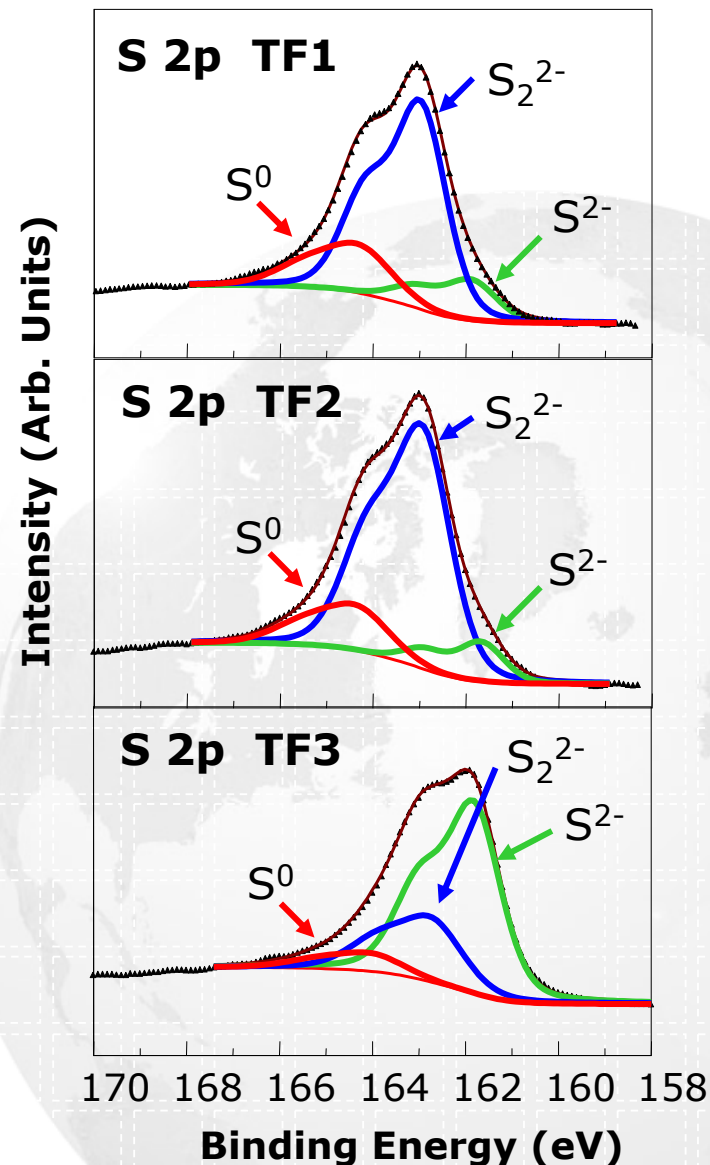
O_2 sat'd 0.1M HClO_4 ; ambient T; $\omega = 2000\text{rpm}$; $\nu = 5\text{mVs}^{-1}$



XPS spectra of S 2p from Co-S thin films measured after EC analysis

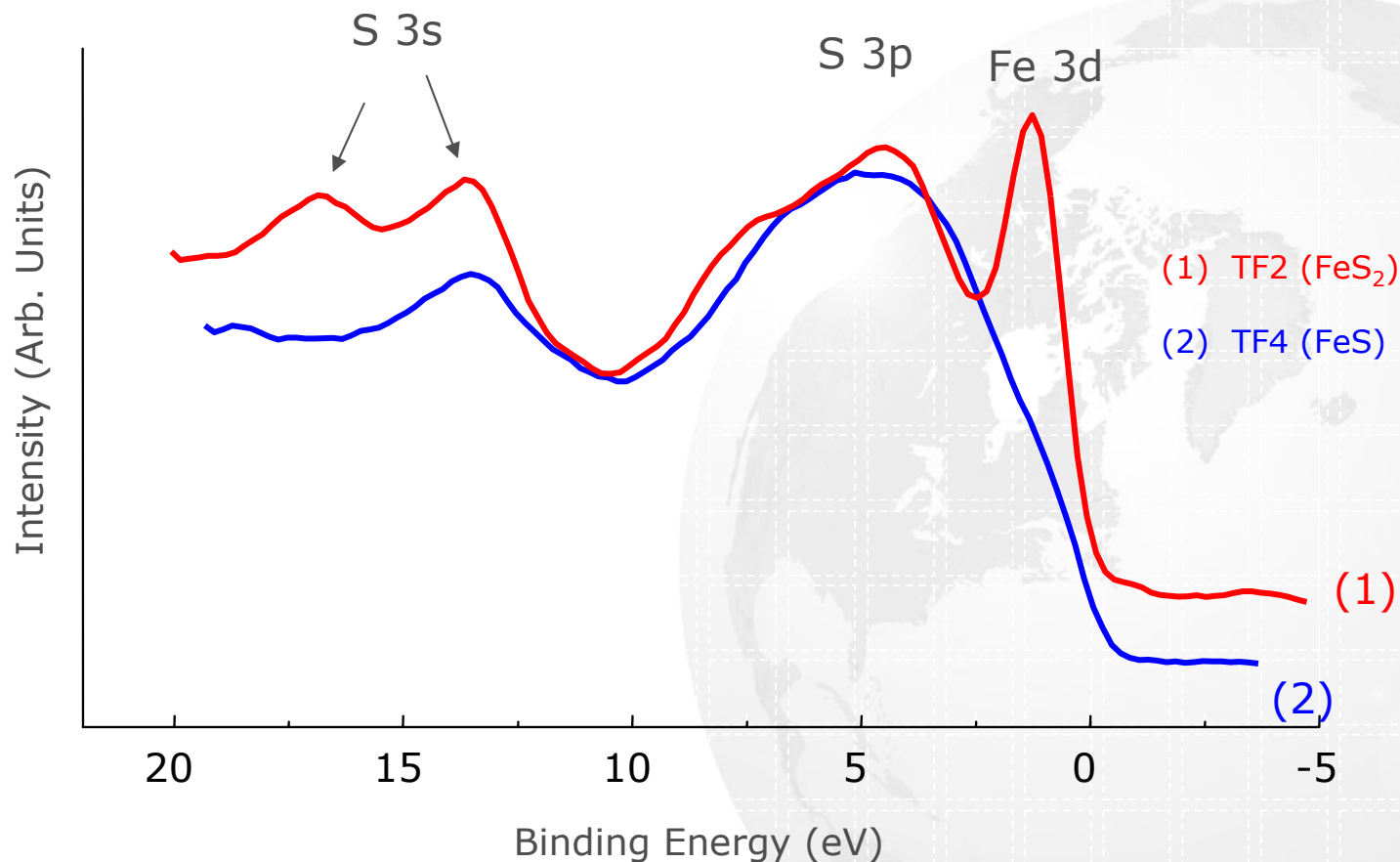
Different S species present at the surface of thin films (after EC analysis)

S oxidation state (%)	TF1	TF2	TF3
S_2^{2-}	67.6	74.0	25.5
S^{2-}	13.4	10.5	67.1
S^0	19.0	15.5	7.4



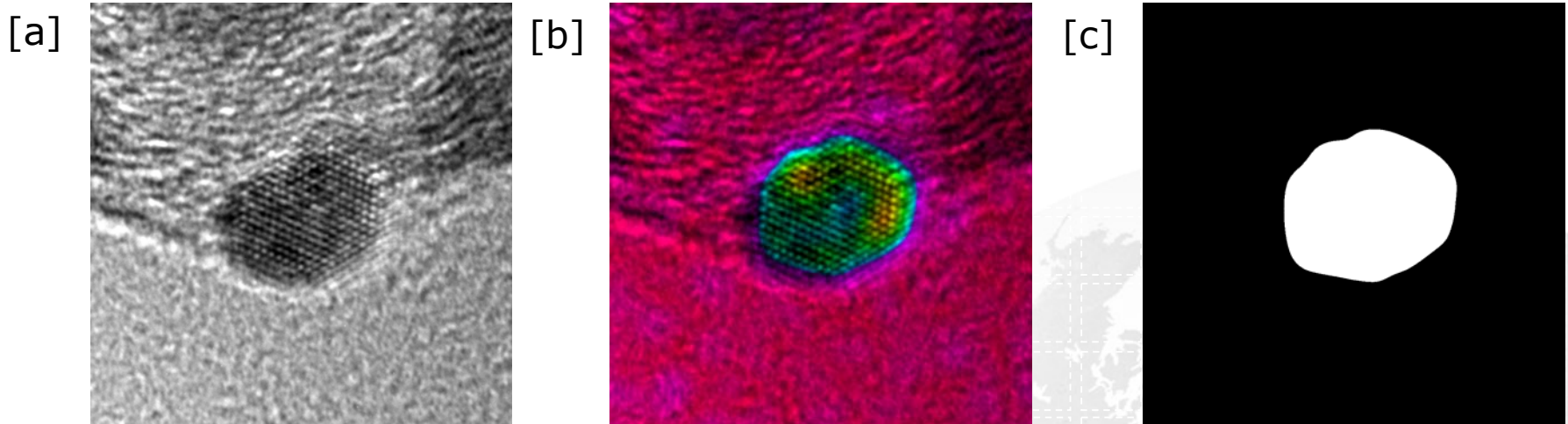
XPS S 3s and valence region for two thin films in as prepared from

In FeS_2 pyrite thin films, S 3s shows a doublet, while only one peak is present in FeS. In addition, Fe 3d states are not observed in XPS spectrum of TF4 (FeS).



- A methodology has been developed to use HRTEM image analysis to determine the particle size distribution of supported catalysts. This gives greater accuracy of surface area measurements than XRD particle size determination because it accounts for:-
 - asymmetric size distribution
 - non-spherical particles
- This is now being applied to FeS_2 and CoSe_2 supported catalyst samples.

Image analysis for particle size measurement



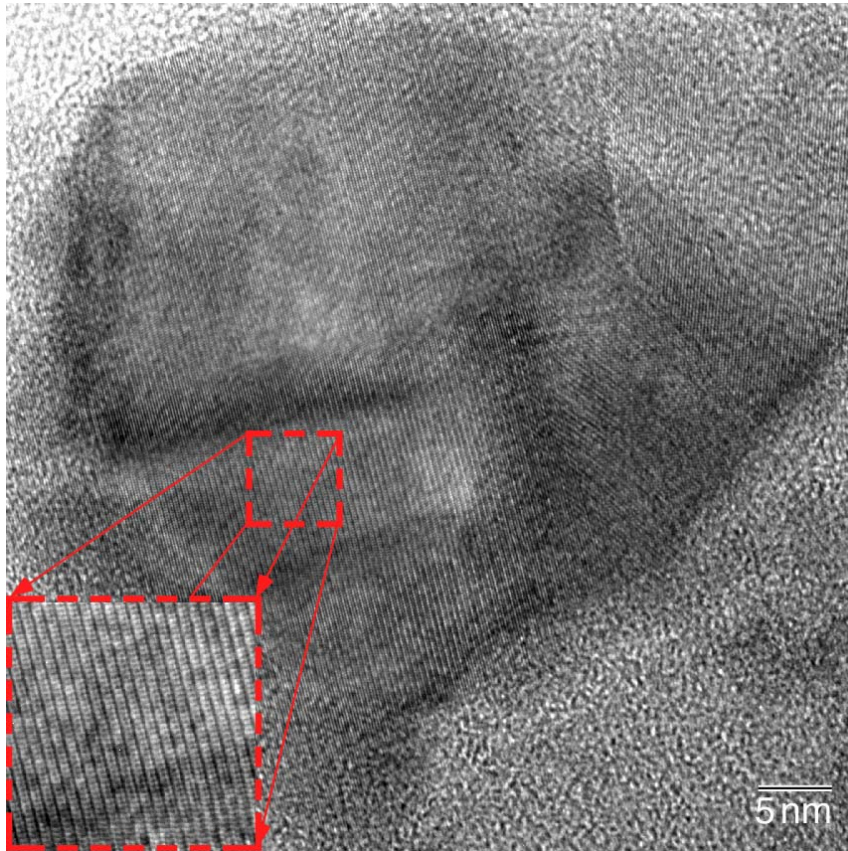
[a] HRTEM image of Pt particle. Viewed in $\langle 110 \rangle$ direction.

[b] Application of SFCI (selected Fourier component imaging).

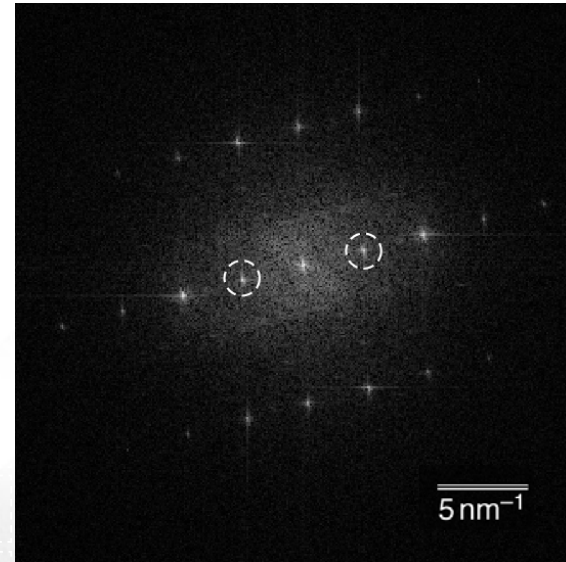
[c] Application of threshold criterion to SFCI image.

- This analysis is necessary to allow accurate particle size measurement
- Then particle size distribution can be determined

HRTEM of single FeS₂ particle on carbon



FeS₂ supported on carbon
produced large particles.



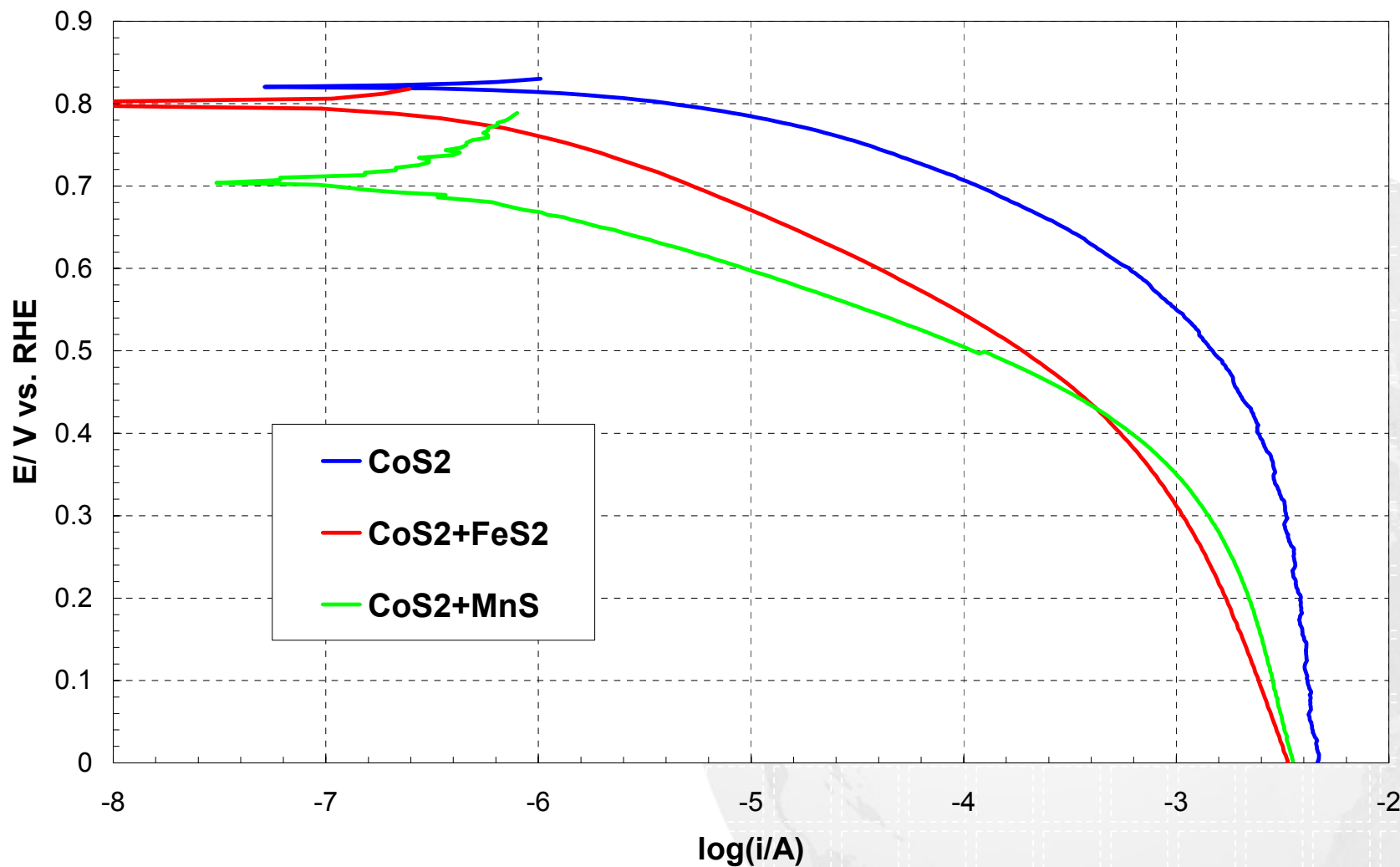
Fast Fourier transform of
the HRTEM image allows
crystal structure to be
determined.

Phase confirmed as pyrite.

Project redirected in September 2005

- It was determined that the low OCP made it premature to build stacks in the last phase of the project. The project was redirected to specifically address the issue of the OCP in the final year.
- Focussed on raising OCP by adding additional elements (ternary systems).
- Go/ no-go decision point in September '06 for single cell testing and demonstration.
- The addition of Se, Fe or Mn to CoS_2 did not increase the OCP. Currently studying addition of Ni and W.

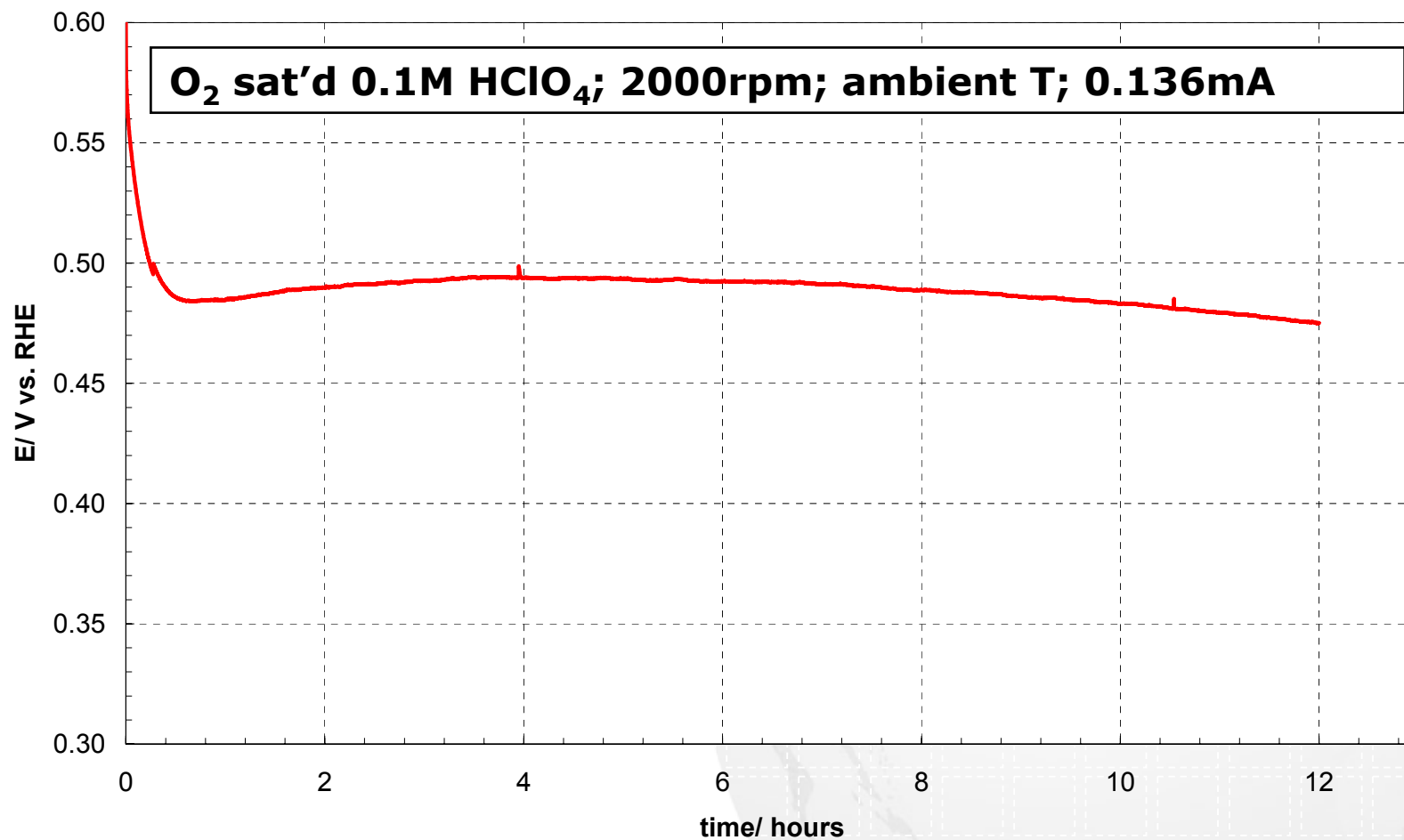
Tafel summary of ternary systems to date **BALLARD®**



Initial durability studies on thin films.

- Stability of CoS_2 thin films was studied during ORR galvanostatically at 0.136mA (potential initially between 0.6V and 0.5V).
- After initial drop the potential is stable over for ~ 6 hours and then begins to decrease.
- Powder, supported CoSe_2 and CoS_2 will be assessed for durability.

Stability of CoS₂ thin film during ORR



Future Work

- Thin film studies of the Co-Ni-S₂ and Co-W-S₂ systems are underway.
- Powder, supported CoS₂ material will be prepared and evaluated electrochemically using surface area measurements made by HRTEM.
- Go/ No-go decision on fuel cell testing planned in September 2006.

- Cobalt-sulfur films with a sulfur-rich surface containing a predominantly CoS_2 (pyrite) component shows the highest activity for ORR of the metal-chalcogen films studied. The OCP was 0.83V.
- Catalyst surface is S-rich and the valence band spectra suggest that the underlying metal couples electronically with the sulfur. Nevertheless, mechanistic studies are outside the scope of the project.
- The study of ternary systems is underway to raise the OCP. Metals have been added to CoS_2 (Fe, Mn). Ni and W are being tested.
- Powder, supported CoSe , FeS_2 and CoSe_2 have been fabricated. Supported CoS_2 in progress.

Response to last year's reviewers



- Lack of durability studies:-
 - The original plan was to delay durability studies until fuel cell testing. Ex-situ durability studies on the sputtered thin films is now being carried out as, following the redirect, the fuel cell testing has been postponed.
- Methodology needed to measure surface area of chalcogenide catalysts:-
 - This is the basis of the work being carried out at CWRU. A HRTEM methodology has been developed using Pt catalysts and this is now being applied to powder chalcogenide catalysts.
- Rôle of university partners in collaboration not clear:-
 - 90% of this work has been carried out at UBC and CWRU. The powder catalyst synthesis and evaluation is carried out at Ballard. The fuel cell testing will be at Ballard.

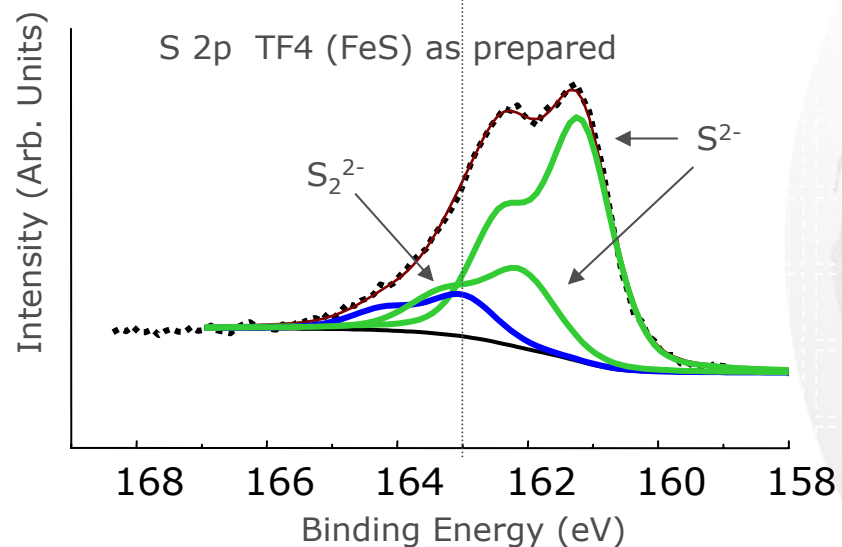
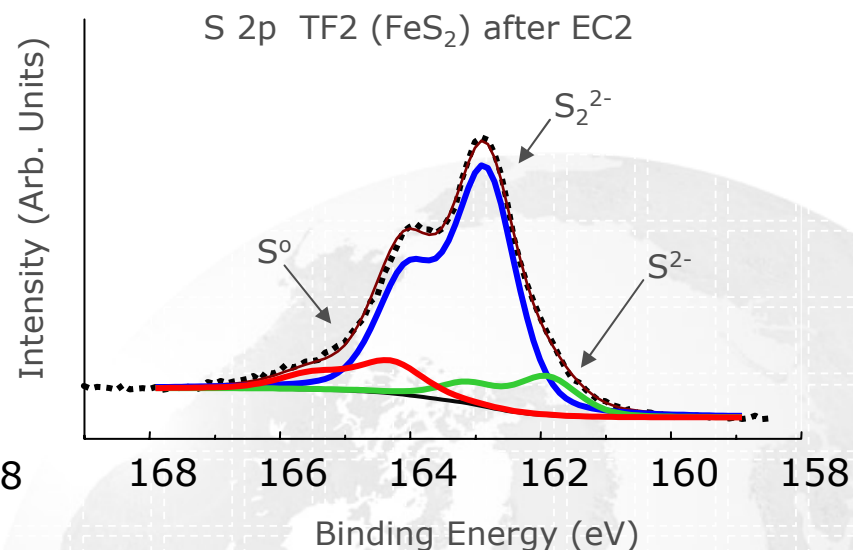
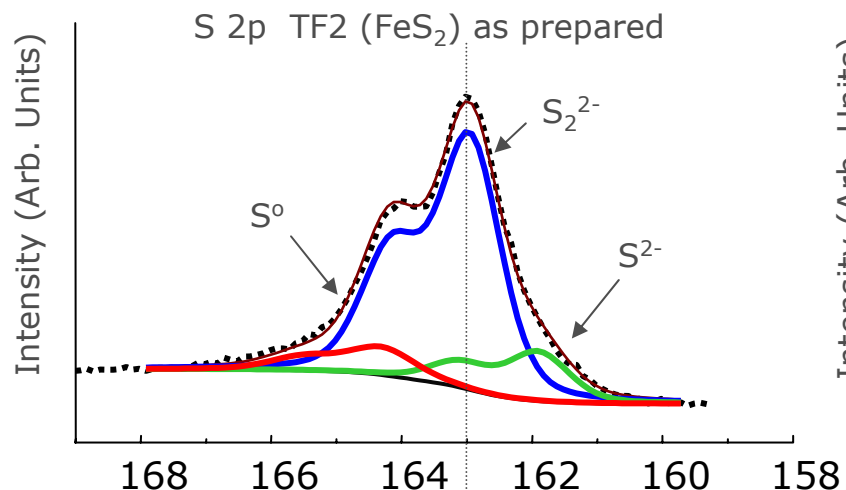
1. M. Teo, P.C. Wong, L.Zhu, D. Susac, S.A. Campbell, K.A.R. Mitchell, R.R. Parsons, D. Bizzotto; *"Characterization of a Co-Se thin film by scanning Auger microscopy and Raman spectroscopy"*, Applied Surface Science, in press.
2. Kui Du and Frank Ernst; *"Quantitative assessment of nanoparticle size distributions from HRTEM images"*; submitted to Zeitschrift für Metallkunde, December 2005
3. D. Susac, A. Sode, L.Zhu, P.C. Wong, M. Teo, D. Bizzotto, K.A.R. Mitchell, R.R. Parsons, S.A. Campbell; *"A methodology for investigating new non-precious metal catalysts for PEM fuel cells"*; Journal of Physical Chemistry B, in press.
4. Three more papers are in preparation.

Critical Assumptions & Issues

- Currently, OCP is too low for viability in transportation fuel cells. The redirect of the project in September '05 expanded the scope to include ternary systems to raise the OCP. The addition of noble metals has been demonstrated to achieve this but this falls outside the scope of the project.
- It has been assumed that the thin film structures and compositions may be replicated as nano-dispersed, supported catalysts. This has been demonstrated for CoSe, FeS₂ and CoSe₂. It may be possible to sputter materials onto powder supports to achieve the same end. This falls outside the scope of the project.

Appendix

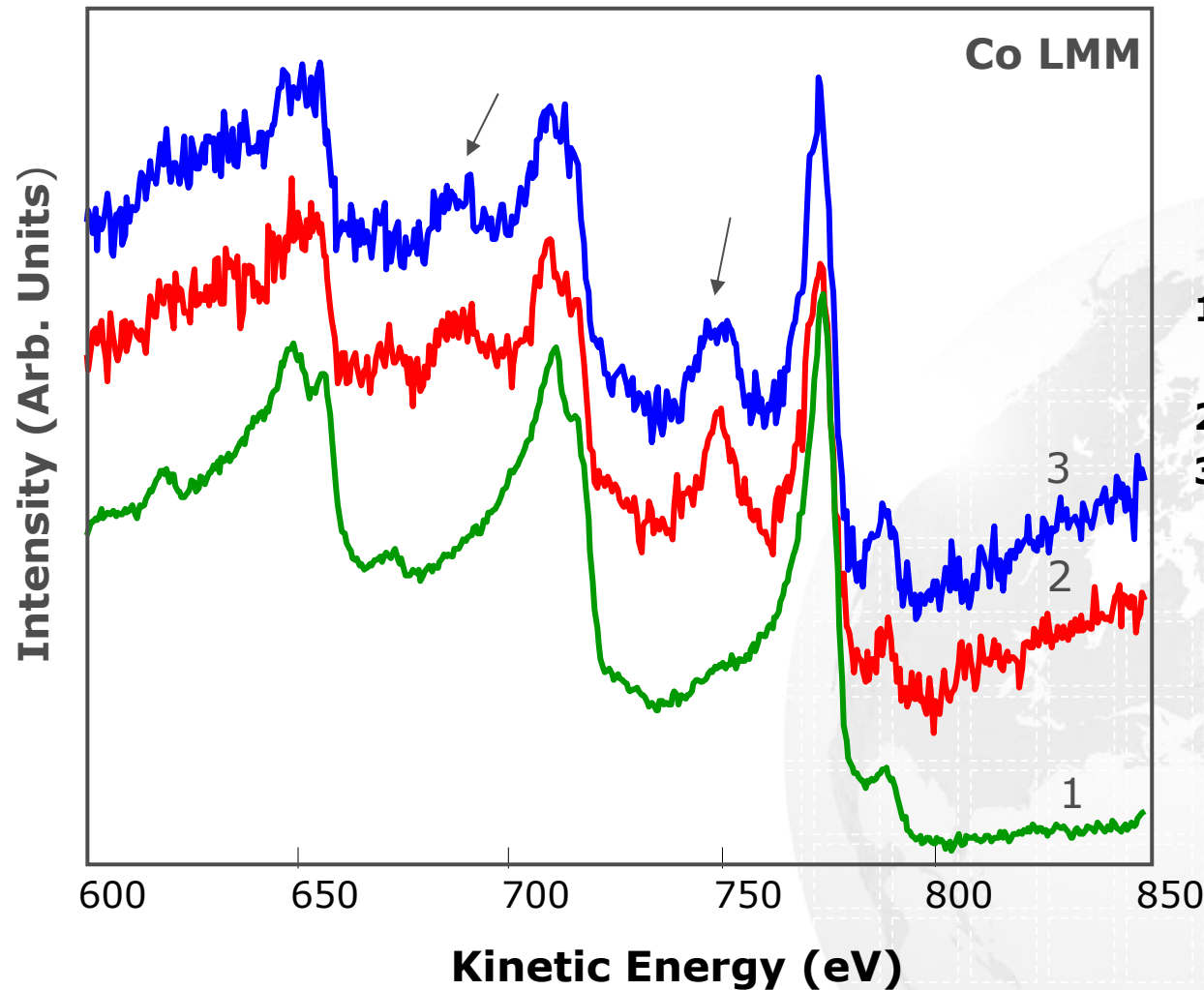
XPS S2p spectra for TF2 (FeS₂) in as prepared state and after EC2 and for TF4 (FeS) as prepared



In sputtered pyrite thin films (as prepared state and after EC2), major component is S_2^{2-} . Small contribution from elemental S and mono-sulfide phases is present.

S 2p from TF4 in as prepared state however shows that major components are related to mono-sulfide species with little contribution from FeS₂.

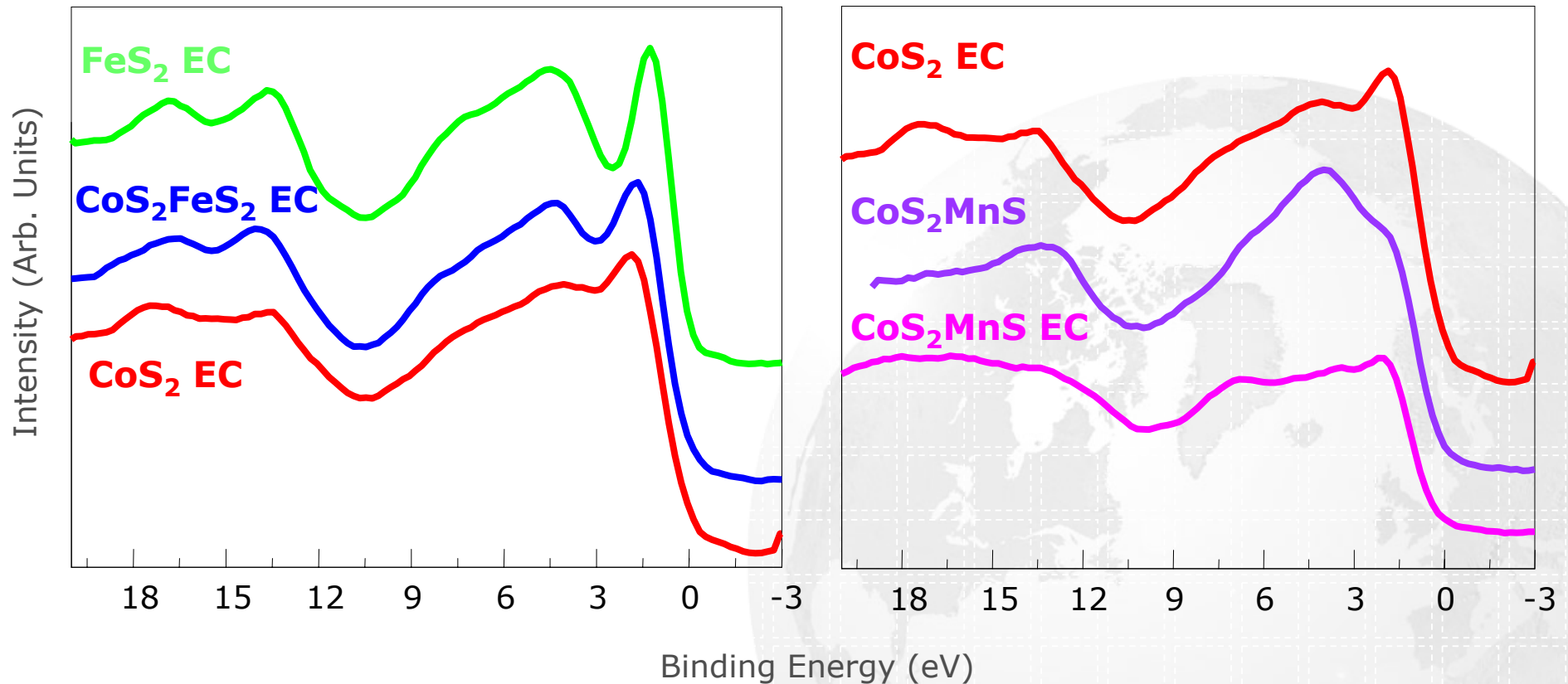
High resolution Co LMM Auger spectra for Co-S TF1



1. Co metal
(Co thin film standard)
2. TF1 (as prepared)
3. TF1 after EC

Additional Auger transitions present in spectra 1 and 2 (marked by arrows) are due to metal chalcogen bond.

XPS spectra of the valence region for Co-Fe and Co-Mn sulfide thin films



Mixture of CoS₂ and FeS₂ is stable after EC

Mn is monosulfide and dissolves during EC leaving CoS₂

Impact of S on CoSe ORR activity

