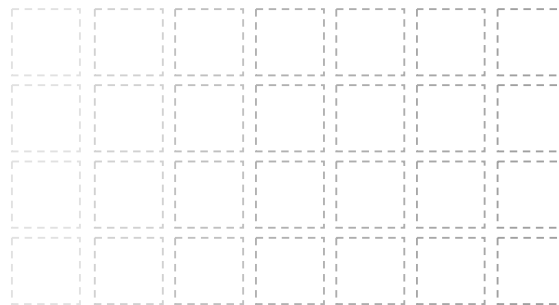
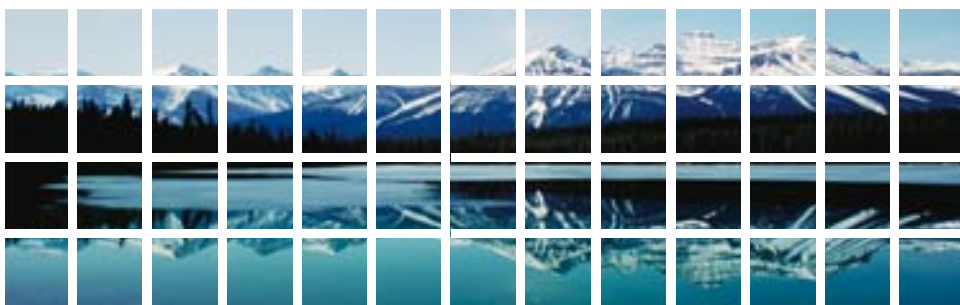


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 Ballard Power Systems



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

Stephen Campbell
Ballard Power Systems
23rd-26th May 2005

FC13

Timeline

Project start: February 2004
Project ends: December 2006
Project 30% complete

Budget

Total funding: \$1,975,175
DOE share: \$1,580,139
Ballard share: \$ 395,036
FY'04 funding: \$ 457,383
Funding FY'05:\$ 600,000

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.

Approach

- A matrix involving three transition metals (Cr, Fe, Co) and two chalcogens (Se, S) is used to screen for stability and activity for oxygen reduction in sulfuric acid.
- Because the surface area of nano-disperse catalysts is difficult to measure, sputtered thin films with a defined surface area were used for comparison and structural characterization using EDX, XRD, SAM, XPS, SEM, TEM etc.
- The downselected 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

- Co, Cr and Fe have been evaluated with Se as thin films.
- Indications from surface analysis (SAM, XPS) for Co-Se and Fe-Se thin films are that excess metal dissolves leaving a stable selenide with Se rich outer surface.
- These surfaces are stable in acid at room temperature and, especially for the Co-Se system, are active for ORR.
- Fe-Se films do not adhere to GC well due to internal stresses. A thin Ta underlayer greatly improves adhesion.
- Cr-Se films contain oxygen (in the bulk as well as surface). Oxygen is incorporated from the sputter chamber's high vacuum atmosphere. Oxygen can be reduced by lowering the chamber pressure, but this does not improve activity of the Cr-Se films.
- Co-Se thin films have higher open circuit potentials compared to those of the Fe-Se and Cr(O,Se) systems.

The Co-Se system

- Used Co-Se system to develop methodology.
- Developed in-house sputter target to deposit wide range of Co:Se ratios.
- Scanning Auger spectroscopy and XRD indicate that, after electrochemical evaluation, surface is always Se rich and excess Co dissolved leaving a stable Co-Se compound.
- ORR activity of thin film is lower than Pt and OCV is $<0.8V$ vs. RHE.
- Comparison with carbon supported, dispersed catalyst shows similar structure and composition. Activity of dispersed catalyst is higher than thin film but OCV is similar.

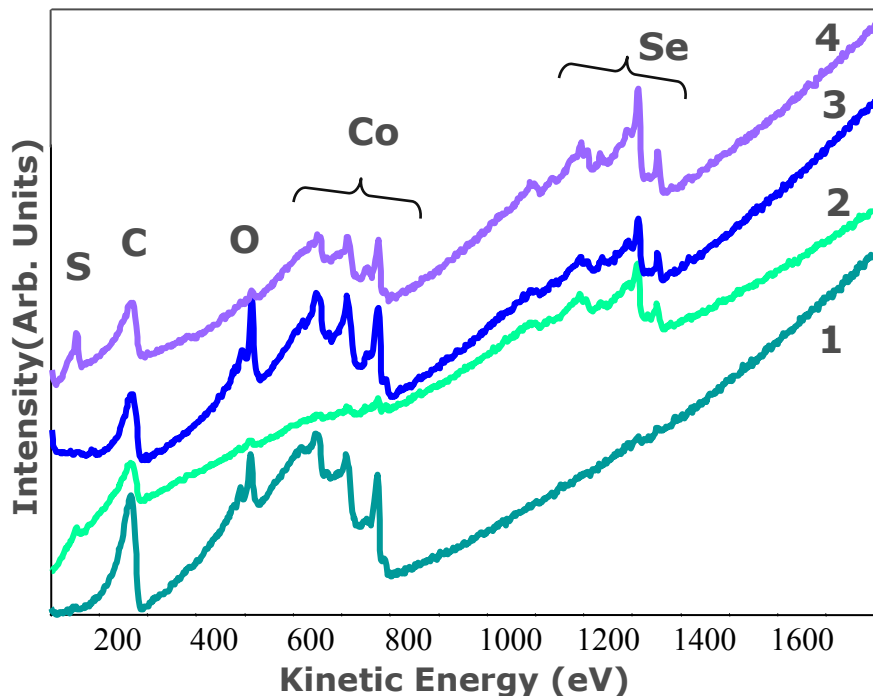
Co-Se catalyst compositions

catalyst	Bulk composition from EDX (at %)		
	Co	Se	Se/Co
1	72.47	27.53	0.38
2	51.58	48.42	0.94
3	44.86	55.14	1.23
4	27.61	72.39	2.62
Powder Co-Se catalyst	84.44	15.56	0.18

catalyst	Composition from scanning Auger microscopy (SAM) (at %)					
	S	C	O	Co	Se	Se/Co
1 (as prepared)	ND	88.97	3.33	5.14	2.55	0.42
1 (after EC)	13.07	69.79	1.39	1.92	13.83	12.64
2 (as prepared)	ND	71.40	2.73	6.79	19.07	3.94
2 (after EC)	12.74	66.94	ND	3.25	17.07	5.91
3 (as prepared)	ND	71.23	6.49	7.98	14.30	2.21
3 (after EC)	16.01	57.32	0.66	4.85	21.16	5.13
4 (as prepared)	ND	82.75	3.84	5.63	7.77	1.72
4 (after EC)	10.10	59.54	ND	5.32	25.05	5.85

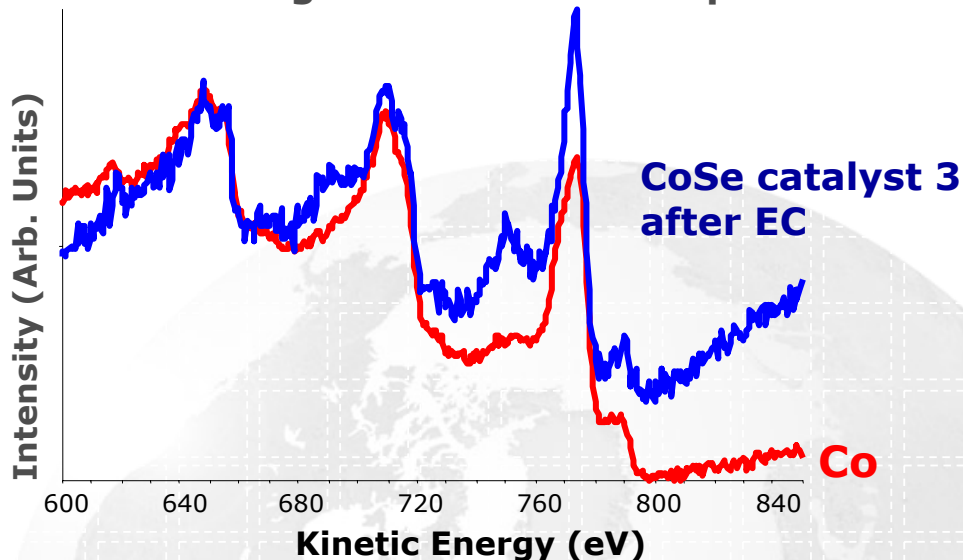
Co-Se Scanning Auger and XPS spectra

SAM low resolution spectra

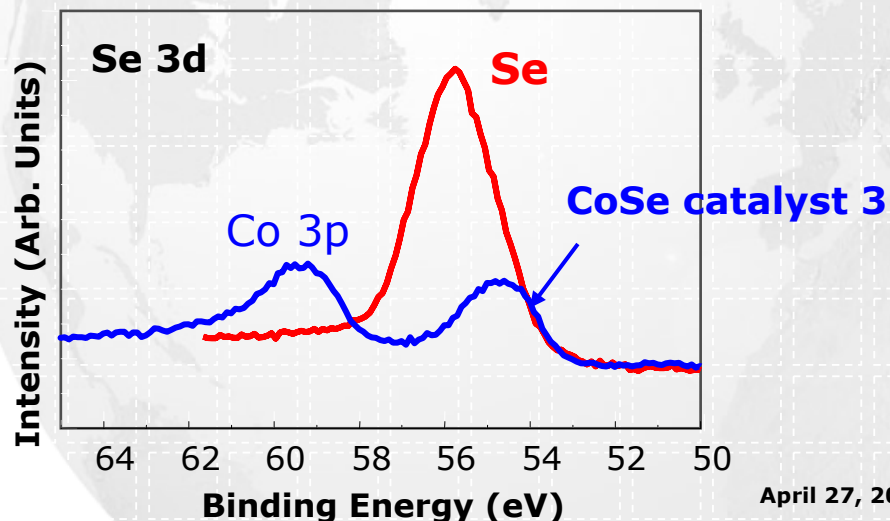


- 1 CoSe catalyst 1 as prepared
- 2 CoSe catalyst 1 after EC
- 3 CoSe catalyst 3 as prepared
- 4 CoSe catalyst 3 after EC

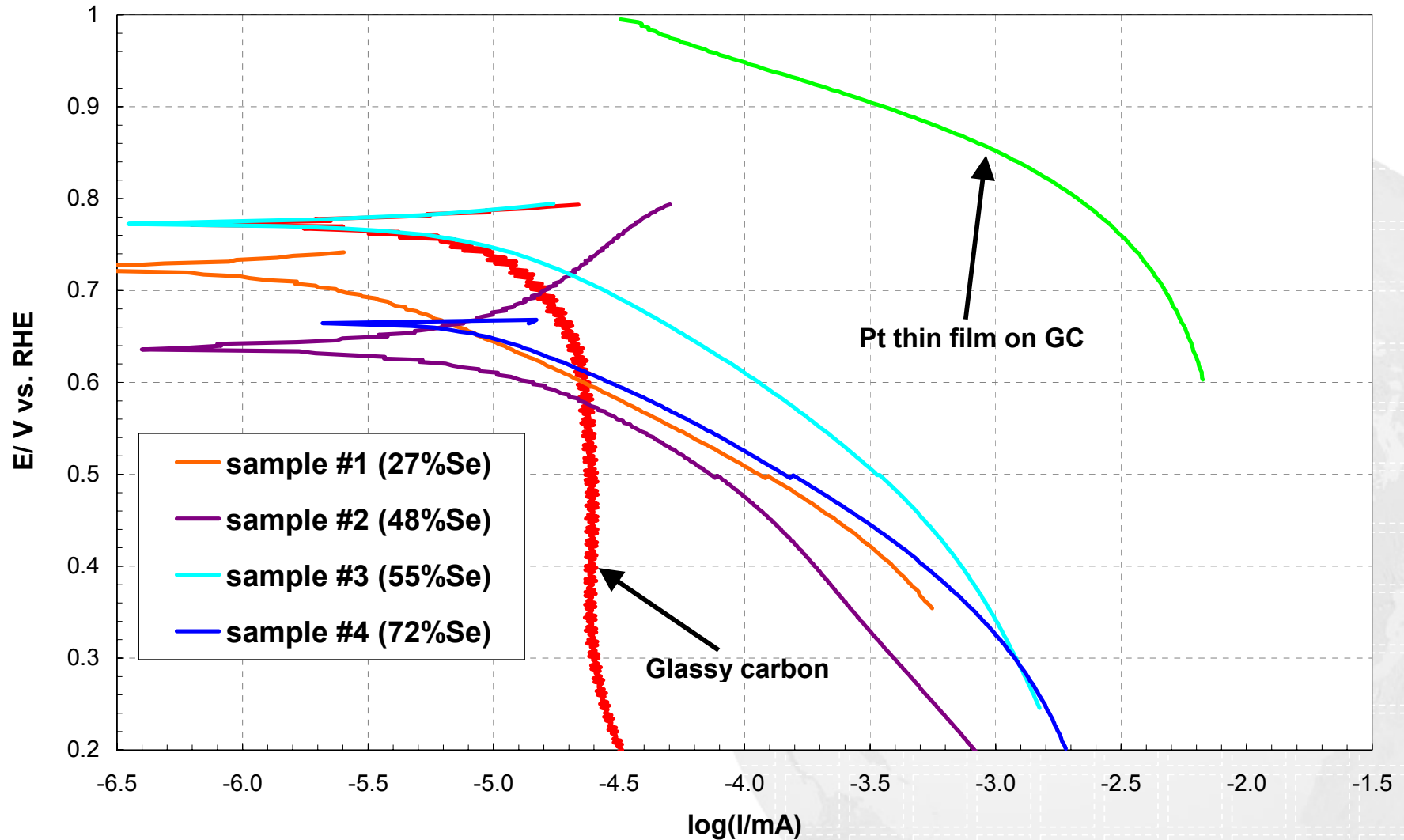
Co LMM high resolution SAM spectra



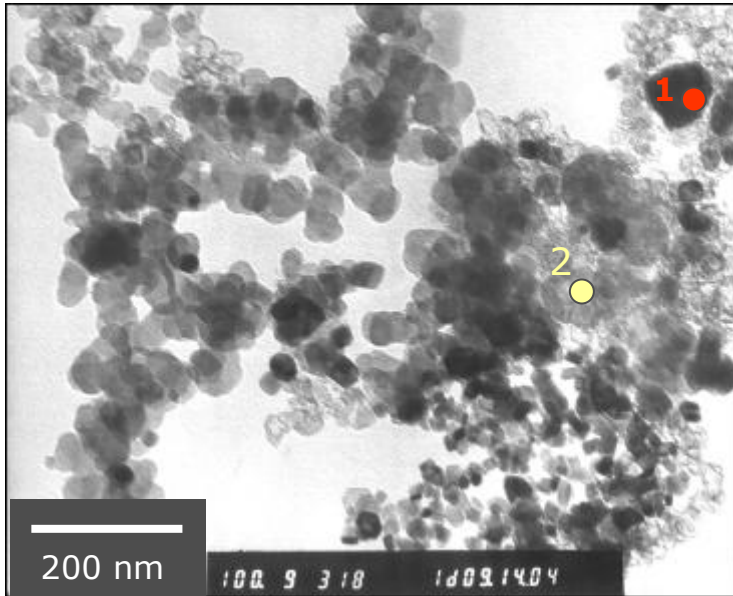
XPS Se 3d high resolution spectra



Comparison of Co-Se catalysts to glassy carbon and Pt thin film (cathodic scan)

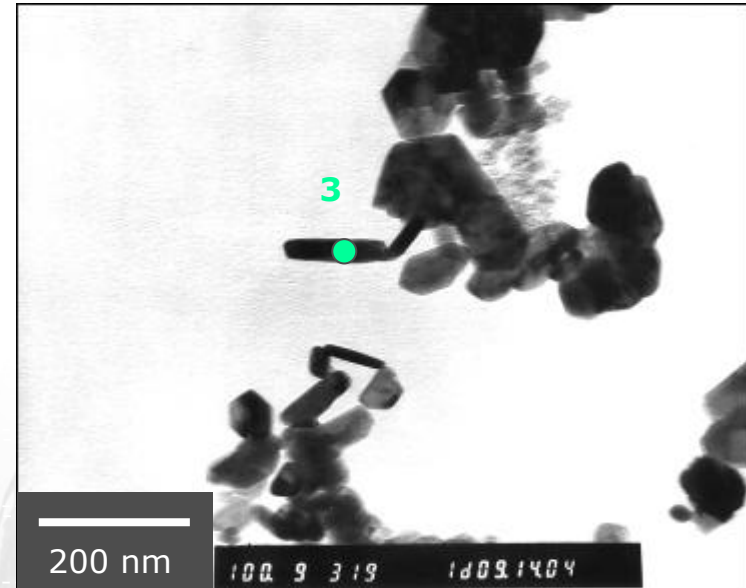


TEM images of Co-Se carbon supported powder catalyst



Region 1:

Co: 42.49 at %
Se: 57.51 at %
Se/Co = 1.35



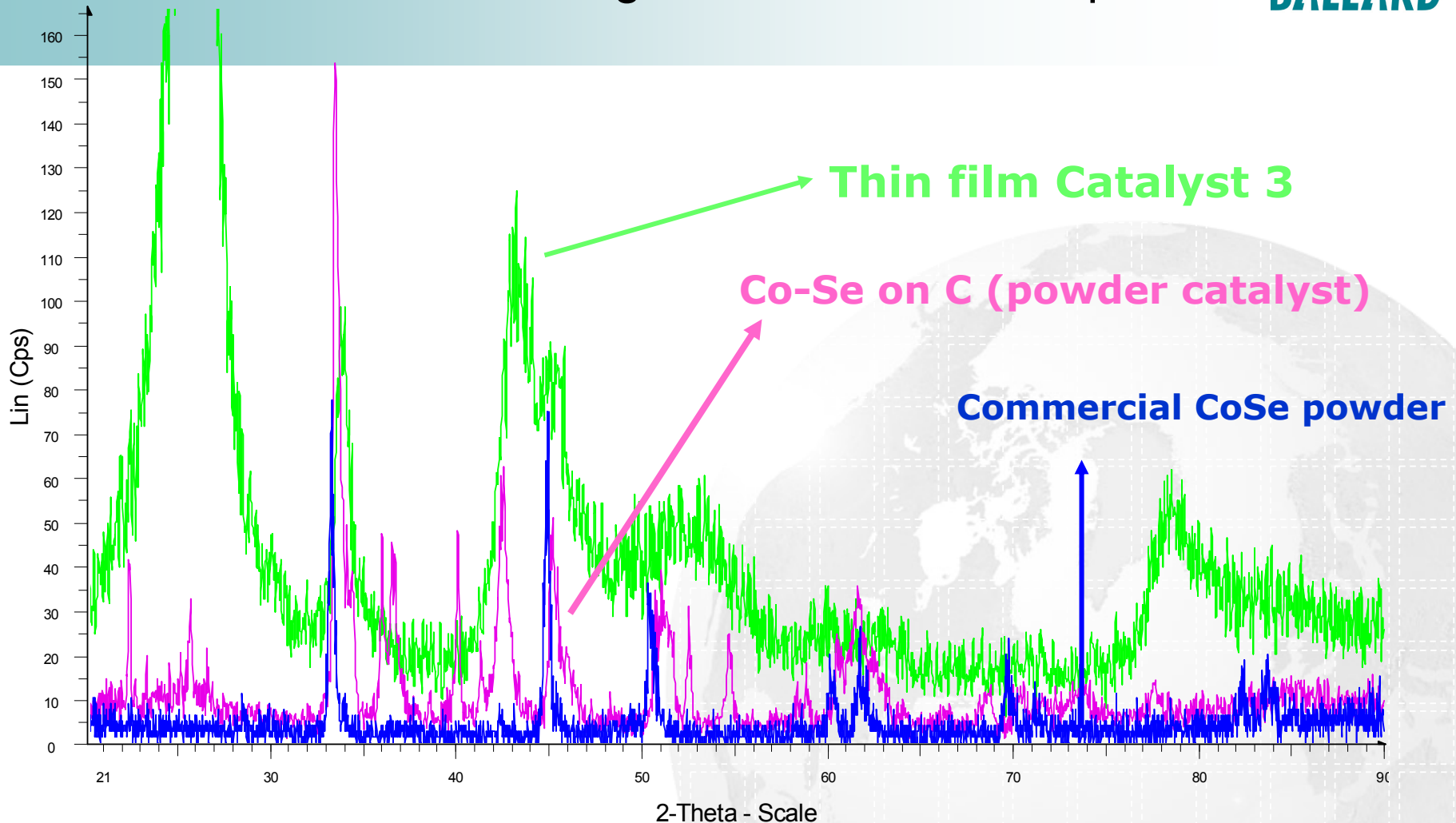
Region 2:

Co, C, O
Se (trace amount)

Region 3:

Co, C, O
No selenium

The differences among the three CoSe compounds **BALLARD®**

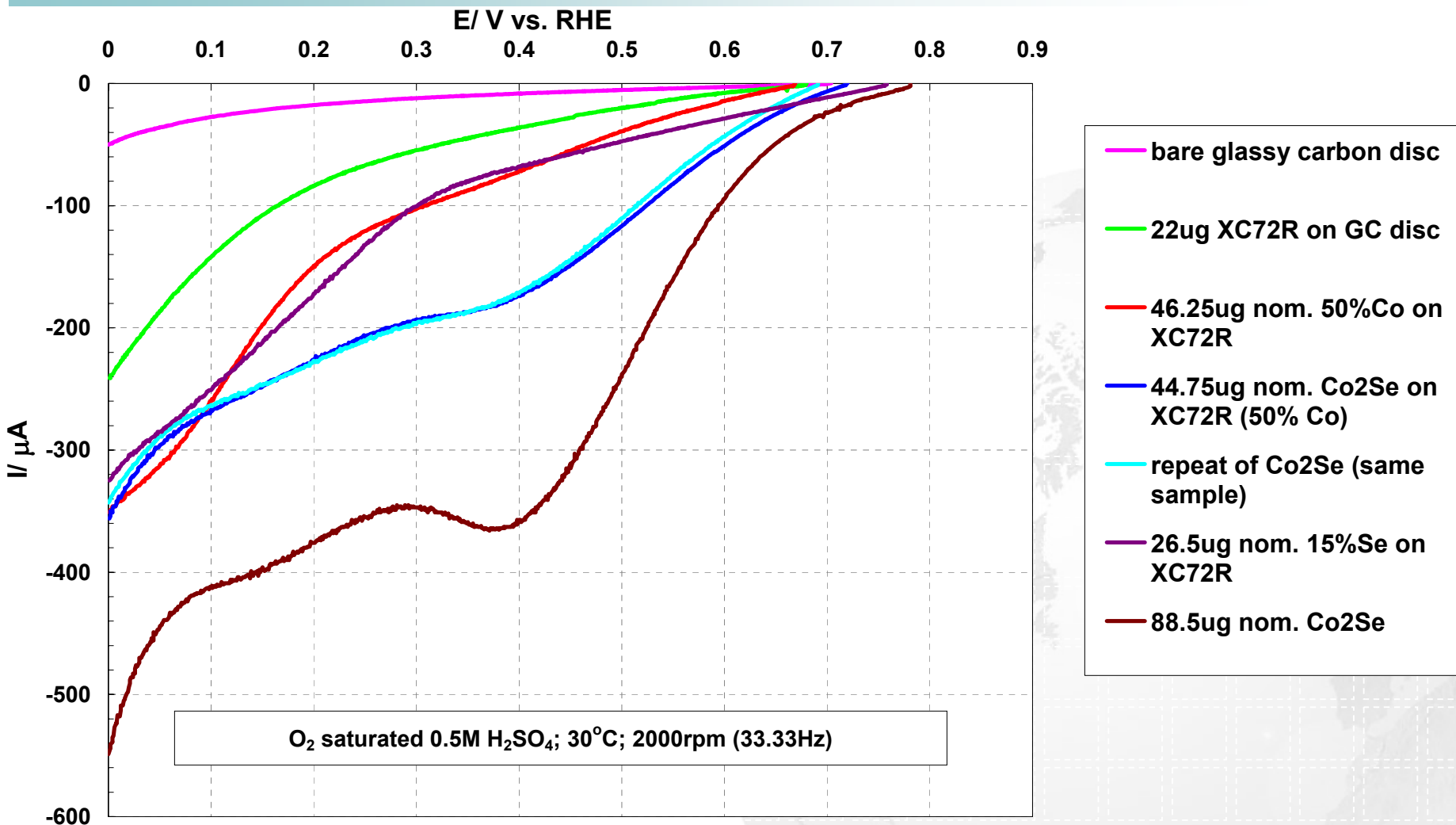


Co_Se commercial product from John Mathey - File: CoSe commercial one from John-Mathey.raw - Type: 2Th/Th locked - Start: 5.00 ° - End: 90.00 ° - Step: 0.02 ° - Step time: 0.8 s - Temp.: 25 °C (Room) - Operations: Import

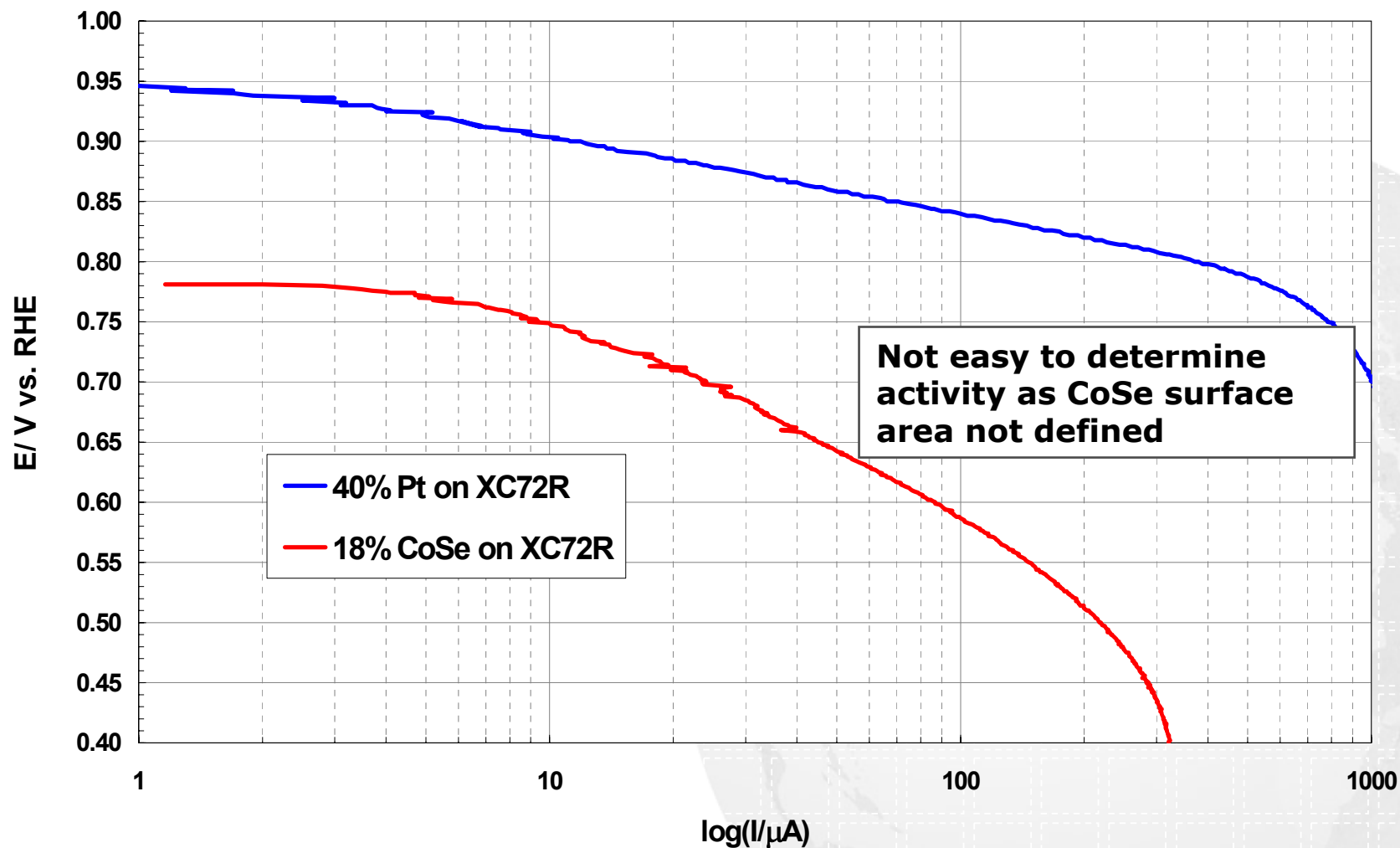
File: Co45Se55-5.raw - Type: 2Th/Th locked - Start: 20.00 ° - End: 90.00 ° - Step: 0.01 ° - Step time: 0.3 s - Temp.: 25 °C (Room) - Time Started: 1097705856 s - 2-Theta: 20.00 ° - Theta: 10.00 ° - Chi: 0. - Operations: Fourier 20.000 x 1 | Import

File: Stephen powder1.raw - Type: 2Th/Th locked - Start: 5.00 ° - End: 90.00 ° - Step: 0.02 ° - Step time: 0.8 s - Temp.: 25 °C (Room) - Time Started: 1099073536 s - 2-Theta: 5.00 ° - Theta: 2.50 ° - Chi: 0. - Operations: Fourier 20.000 x 1 | Import

ORR activity of carbon supported Co-Se based catalysts



Comparison of carbon supported CoSe catalyst with supported Pt baseline



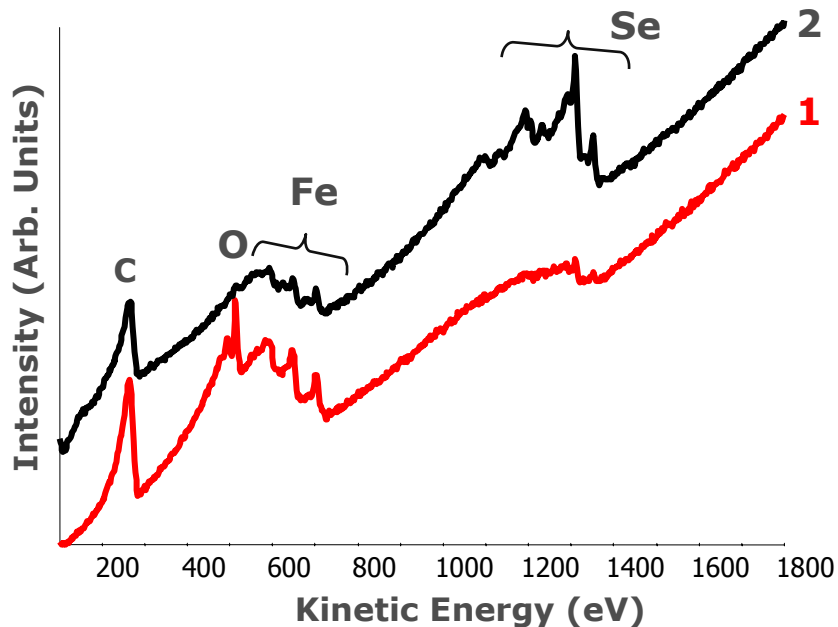
- Fe-Se thin films with low Se content (i.e. <40 atomic% in the bulk) dissolve upon acid exposure.
- Films with higher Se content do not adhere well to the GC surface. Films peel off after electrochemical analysis exposing the GC surface with trace amounts of Se.
- The adhesion problem is overcome for films with medium Se content, by sputtering a thin film of Ta onto GC surface prior to deposition of Fe-Se. However, this procedure does not help with the adhesion of Fe-Se films with high Se content (i.e. > 70 atomic %). These films show internal stress even before electrochemical testing.
- Stable Fe-Se/ Ta thin films have a Se-rich surface (SAM Se/Fe atomic ratio: 3-9) after electrochemical test. Open circuit potentials are lower than the Co-Se system (0.59V vs. RHE).

Fe-Se/Ta Scanning Auger spectra

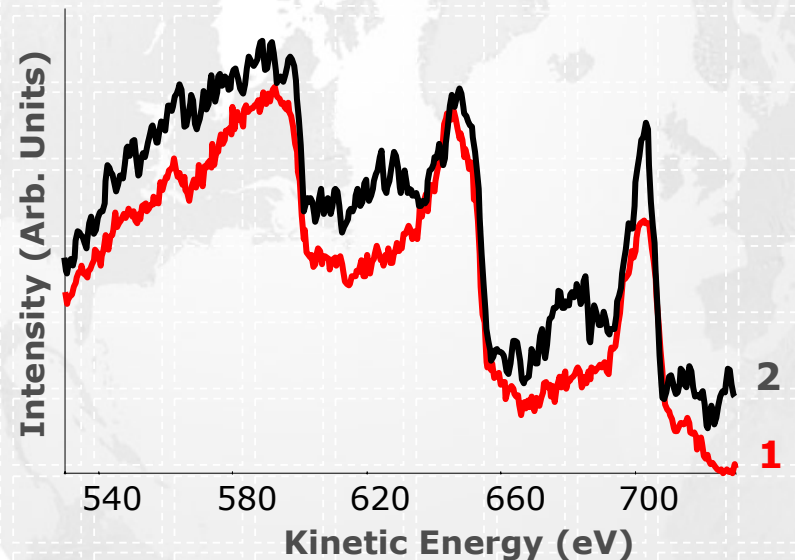
Fe-Se thin films with Ta underlayer	Bulk Se/Fe atomic ratio (from EDX)	Surface Se/Fe atomic ratio (from SAM)	Surface Se/Fe atomic ratio after EC (from SAM)
TF 1	0.90	Fe rich film	2.97
TF 2	1.97	0.68	9.07

SAM spectra for Fe-Se/Ta

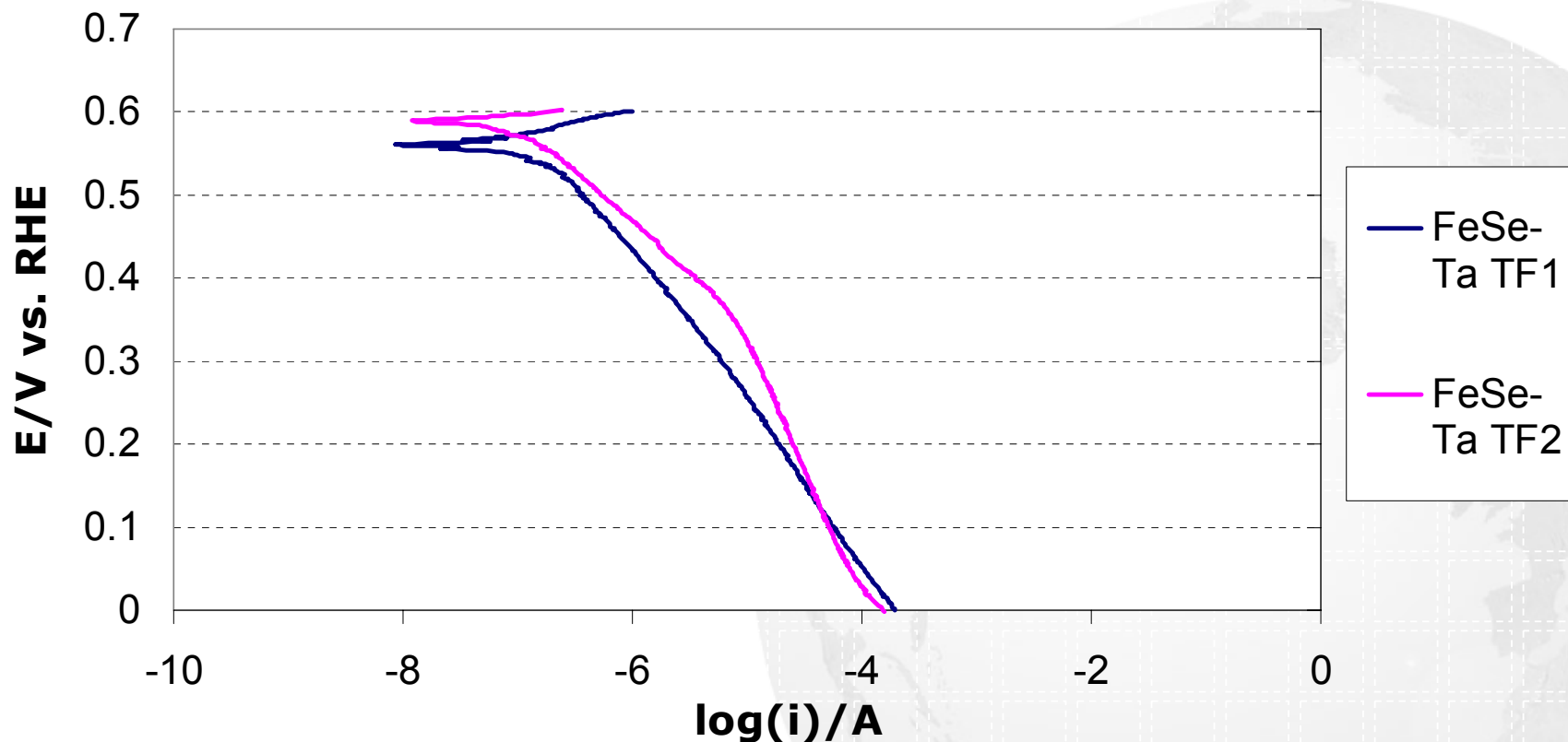
TF 2: (1) before and (2) after EC



SAM Fe LMM high resolution spectra for Fe-Se/Ta TF 2: (1) before and (2) after EC



Polarization curves of FeSe - Ta thin films

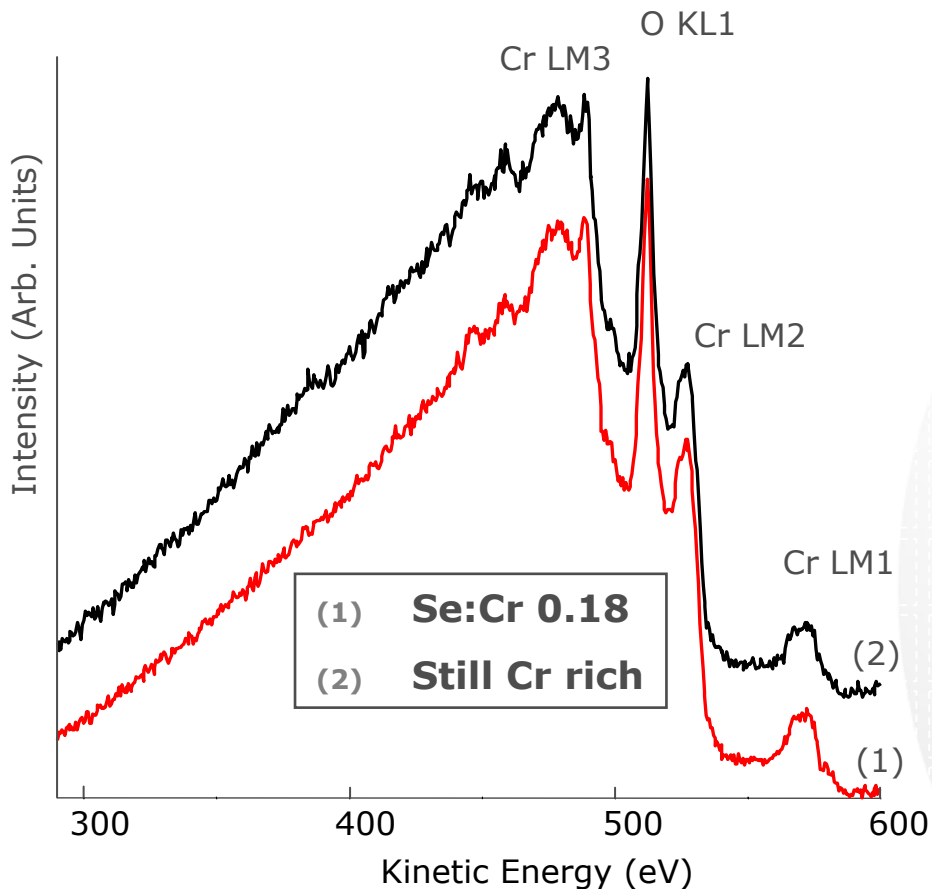


Cr-Se system

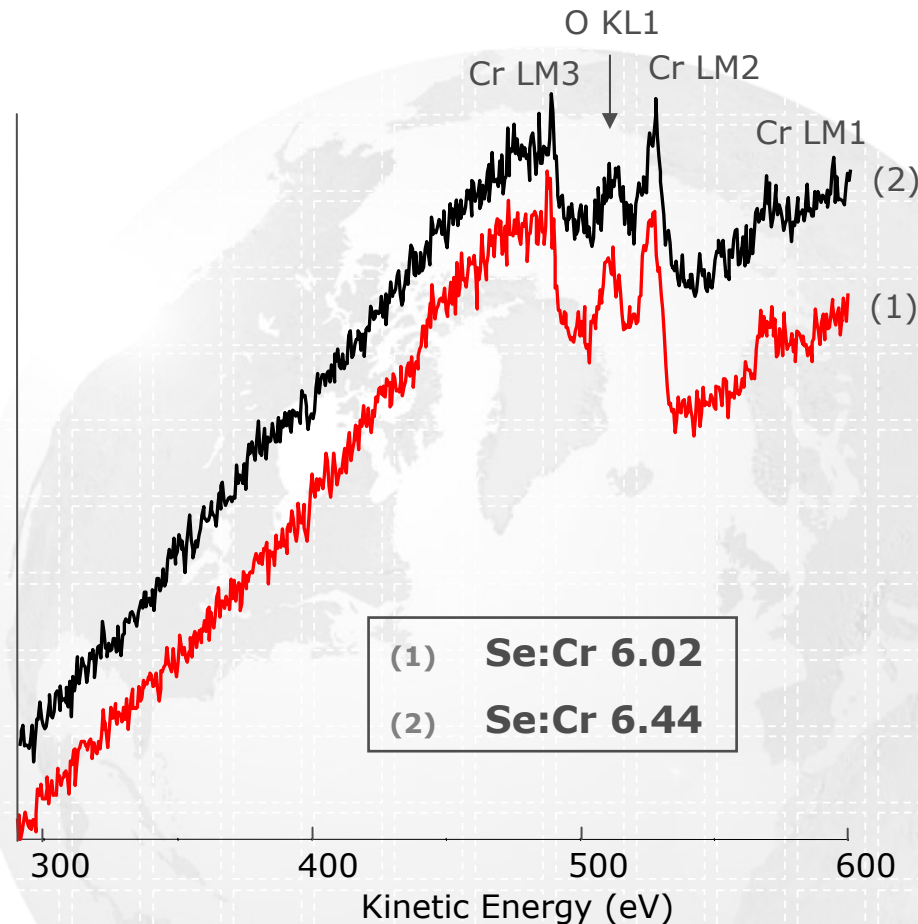
- Cr-Se thin films containing oxygen were obtained by sputtering method under high vacuum conditions.
- The oxygen content can be reduced to ~ 3 atomic % by lowering the background pressure of the chamber, but not completely eliminated.
- Open circuit potentials for Cr-(O,Se) thin films were significantly lower compared to both Fe-Se and Co-Se systems.

High resolution Cr LMM Scanning Auger spectra

Cr-(O,Se) TF1 before (1)
and after (2) EC2

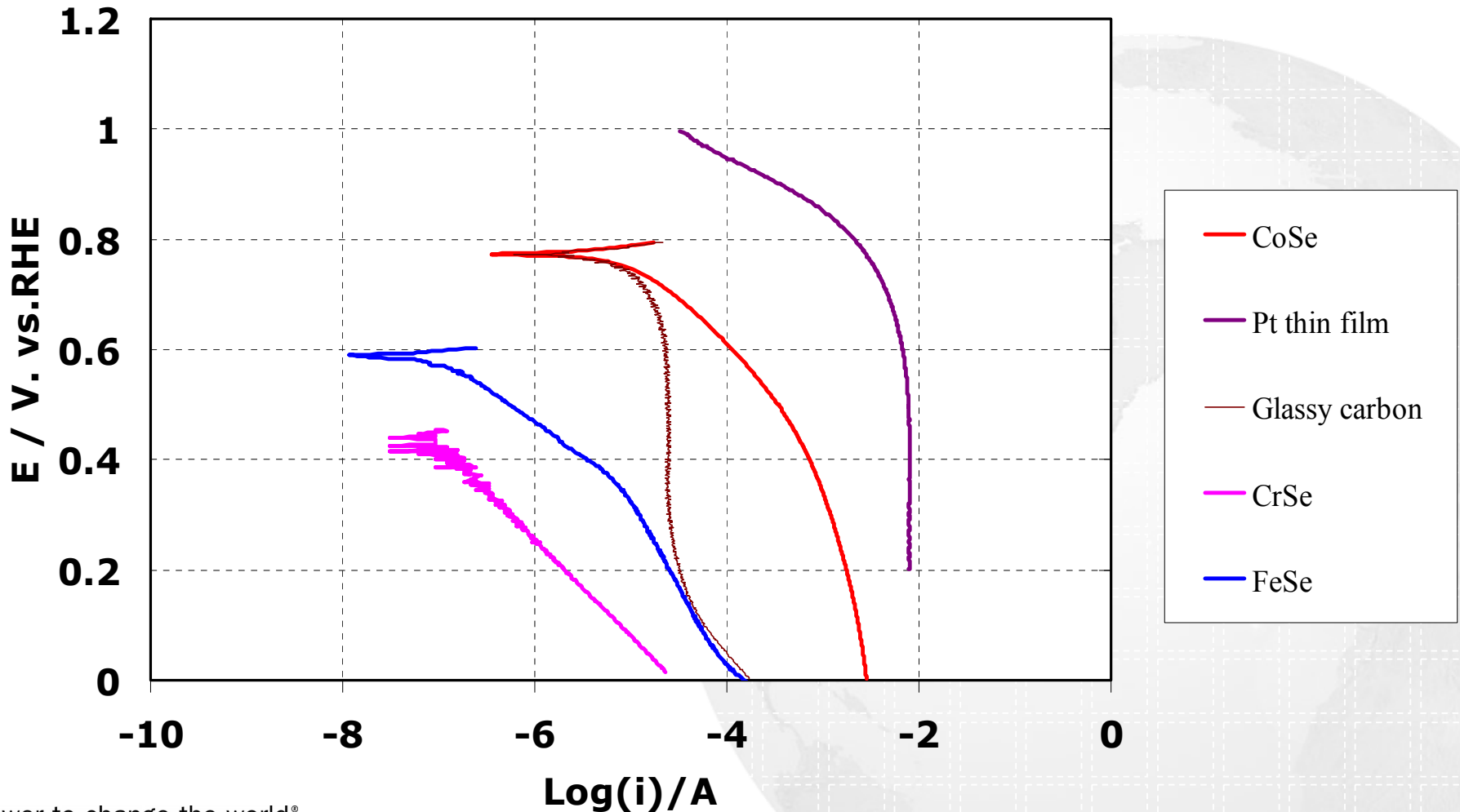


Cr-(O,Se) TF2 before (1)
and after (2) EC2



Comparison of polarization curves from Pt thin film, glassy carbon, Co-Se, Fe-Se/Ta and Cr-(O,Se) thin films **BALLARD®**

Polarization curves



- Studies on Co-Se, Fe-Se and Cr-Se thin films have been completed.
- Co-Se thin films have Se rich surfaces after electrochemical characterization. These are stable and active for ORR.
- Fe-Se thin films are less stable and do not adhere well without introducing a Ta underlayer. Potentials are lower compared to Co-Se system as well as activity.
- Cr-Se thin films contain oxygen. They have lower potentials compared to both Fe-se and Co-se systems and lower activity.

Response to reviewers' comments

- “Need to confirm that the “model” catalyst is truly representative of actual catalyst.”
 - Have evaluated carbon supported CoSe catalyst and found similar composition, structure and activity.
- “Lack of effort focussing on catalyst durability/ stability, especially prior to stack performance & assessment testing.”
 - Plan to test durability at elevated temperature in thin films and ex-situ with powders prior to fuel cell testing.
- “Incorporate Go/ No-go decision into work plan!”
 - Go/ No-go decision will be made prior to stack testing.

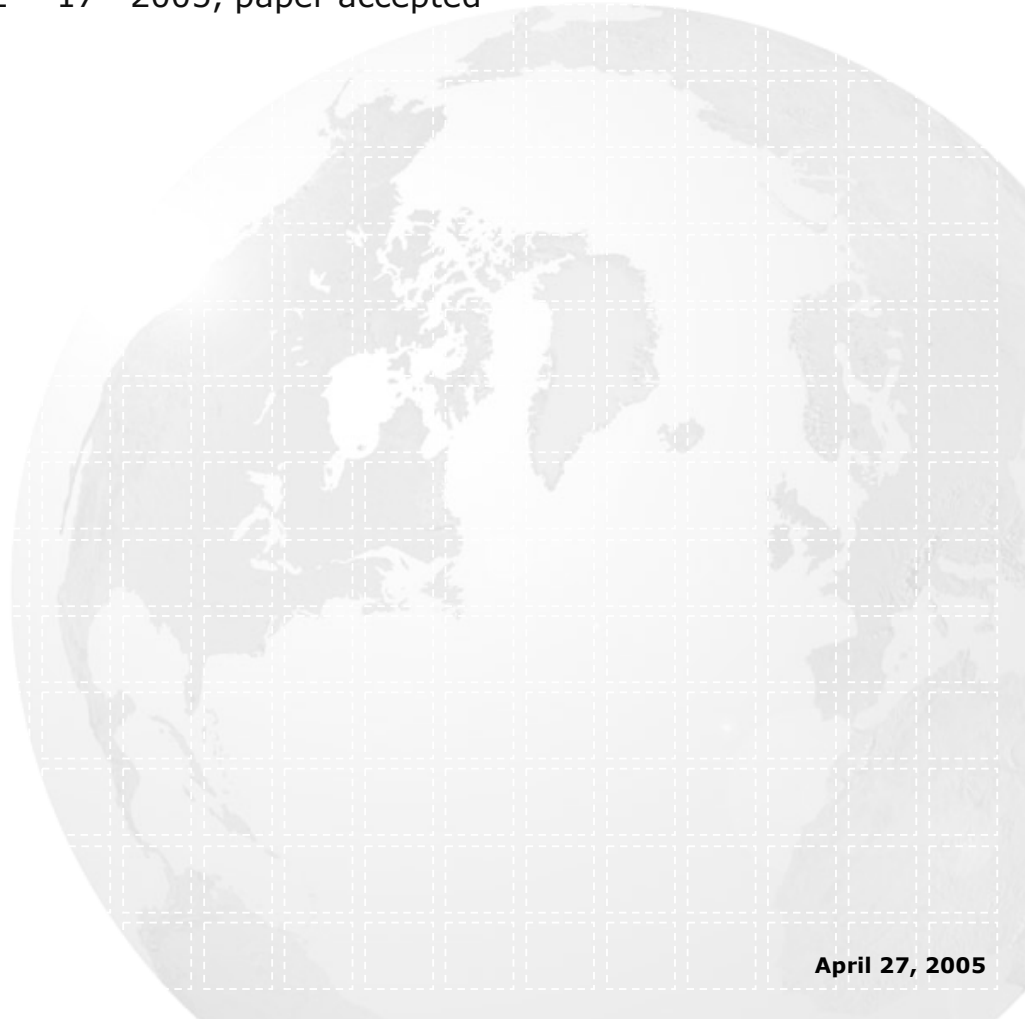
Future Work

- Remainder of 2005
 - Complete evaluation of sulfide based thin films.
 - Develop solution chemistry for deposition of nano-dispersed catalysts.
 - Evaluate chosen candidate at elevated temperature.
- End of 2005 milestone
 - Deliver preferred candidate in sufficient quantities to start fuel cell evaluation.
 - Go/ No-go decision prior to fuel cell testing.
- 2006
 - Optimize catalyst layer structure/ catalyst loading for performance and durability in single cells.
 - Short stack build and evaluation.

Publications and Presentations



1. S.A. Campbell; 2005 PCAMM conference paper, Vancouver BC, December 4th 2004
2. S.A. Campbell, D. Susac, P.Wong, L. Zhu, A. Sode, M. Teo, D. Bizzotto, K. Mitchell, R. Parsons; PBFC2 conference paper, Las Vegas, June 12th- 17th 2005, paper accepted
3. Paper in JACS planned for 2005



Hydrogen Safety

The most significant hydrogen hazard associated with this project is:-

the ignition of an external hydrogen leak in a fuel cell or short stack during the final phase of the project.



Hydrogen Safety

Our approach to deal with this hazard is:-

- **The Ballard fuel cell R&D facility is designed to manage the flammable and explosive aspects of hydrogen. The facility is a 28' tall, high-bay building.**
- **During non-leak operations 6 exhaust fan systems draw between 80,000 to 160,000 cubic-feet per minute of air from the ceiling area of the lab. A air make-up system recirculates approximately 70% of the extracted air, and blends 30% fresh air. The lab facility is separated from the offices by a 2-hour fire separation. Ventilation in the offices is slightly positive-pressure relative to the lab.**
- **The lab facility has flammable gas detectors at the ceiling that are set to provide an audible warning alarm at 20% of the lower flammable limit (LFL) of hydrogen (0.8% hydrogen in air), and to shut down all electrical power to the lab at 40% of the LFL (1.6% hydrogen in air). If this shut down were to occur, electrical power for all equipment is shut off, and explosion-proof emergency lighting turns on. At the same time, the exhaust fans (which are outside of the lab, and are of explosion-proof design) ramp up to 250,000 cubic-feet per minute extraction, and the air make-up system switches to 100% fresh-air make-up (no recirculation). Simultaneously, the gas supplies to the facility are shut-down, and the gases in the distribution manifolds are vented (depressurized).**
- **This system has been in operation for over 9 years, and has never experienced a shut down incident.**