

VII.C.8 Development of Transition Metal/Chalcogen Based Cathode Catalysts for PEM Fuel Cells

Stephen Campbell

Ballard Power Systems

9000 Glenlyon Parkway

Burnaby, BC, V5J 5J9 CANADA

Phone: (604) 412-3151; Fax: (604) 412-4704; E-mail: stephen.campbell@ballard.com

DOE Technology Development Manager: Donna Ho

Phone: (202) 586-8000; Fax: (202) 586-9811; E-mail: Donna.Ho@ee.doe.gov

DOE Project Officer: David Peterson

Phone: (303) 275-4956; Fax: (303) 275-4753; E-mail: David.Peterson@go.doe.gov

Contract Number: DE-FC36-03GO13107

Subcontractors:

Case Western Reserve University, Cleveland, OH

University of British Columbia, British Columbia, CANADA

Start Date: September 1, 2003

Projected End Date: August 31, 2006

Objectives

- To deliver a commercially viable non-precious metal catalyst which performs in a fuel cell stack at a power output equivalent to $200 \mu\text{gPtkW}^{-1}$ for a cost saving of 50%.
- Demonstrate performance for 2,000 hours with <10% degradation in power output
- To research and select preferred catalyst structure and composition for powder production process development and characterization.
- Transfer preferred powder catalysts to in-situ optimization of electrode structure in fuel cells
- Deliver optimized short stacks with desired performance and degradation characteristics

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Durability
- B. Cost
- C. Electrode performance

Technical Targets

This project is conducting fundamental studies on non-precious metal cathode catalysts for PEM fuel cells based upon Co, Fe, Cr, Se, S binary systems. The approach is to screen the compositions ex-situ using sputtered thin films on glassy carbon (GC) with a defined surface area to enable accurate activity comparisons.

The optimum composition will then be dispersed upon a carbon support and optimized structurally in fuel cells. Insights gained in the composition and structure of active, stable catalysts will be applied towards developing a catalyst that will meet the following 2010 targets:

- Cost: \$8/kW
- Non-Pt catalyst activity per volume of supported catalyst: $>130 \text{ Acm}^3 @ 800 \text{ mV (iR-free)}$
- Durability with cycling: 5,000 hrs at $\leq 80^\circ\text{C}$; 2,000 hrs at $\geq 80^\circ\text{C}$

Approach

- Develop methodology to sputter thin films of metal and chalcogen onto GC substrates
- Initial screening of Co, Fe, Cr, Se, S binary matrix to determine stability and activity for oxygen reduction reaction (ORR) in sulfuric acid
- Down-select preferred composition(s) for supported dispersion development
- Develop process for nano-dispersion of preferred composition(s) on a high surface area conductive support (carbon)
- Optimize fuel cell electrode catalyst layer structure with regard to catalyst loading, ionomer content and dispersion to maximize activity and stability in a fuel cell
- Demonstrate activity and durability in short stack

Accomplishments

- Methodology has been developed to sputter a wide range of binary metal/ selenium compositions onto the glassy carbon substrates. These have been assessed for stability and activity for ORR.
- The results indicate that the stable phases are 1:1 binary compounds and that the activity changes with the metal as $\text{Co} > \text{Fe} > \text{Cr}$. The activity of the CoSe thin film is close to that of a sputtered Pt thin film but at a potential which is $>150 \text{ mV}$ lower.
- While long term stability measurements are not scheduled until powder catalysts are developed, indications are that the mono-selenides are certainly stable during multiple cycling in sulfuric acid. Ex-situ testing at 50°C indicates that the CoSe material is stable at this temperature.
- Ex-situ x-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) analysis before and after electrochemical assessment indicate that the surface of the stable phase is very selenium rich and contains only trace amounts of oxygen. The amount of oxygen increases as $\text{Co} < \text{Fe} < \text{Cr}$ with the CrSe films containing oxygen from the sputter chamber.
- Initial data from the sulfide films suggest that, unlike the selenide films, the stable and active phase may be the disulfide. Work continues.
- Two chemical routes to dispersed, supported chalcogenide catalyst have been identified. It has been established that nanodispersed CoSe catalysts contain the same stable phase as the thin films. Activity comparisons are difficult without surface area measurements on the chalcogenide. This technique is to be developed in the latter half of 2005 at Case Western Reserve University (CWRU).

Future Directions

- Deposition and analysis of sulfide films is underway. A new method of making the sulfide targets has been developed.
- Work on the chemical processes to nanodisperse the chalcogenide materials on a carbon support will start in July 2005. The impact of conditions upon particle size and phase purity and the impact these parameters have on activity and stability will be determined ex-situ.

- The relationship between transmission electron microscopy particle size distribution and surface area will be determined to allow estimation of dispersed particle surface area from high-resolution transmission electron micrograph image analysis will be carried out at CWRU.
- A go/no go decision will be made near the end of 2005 with regard to the final phase which makes membrane electrode assemblies and stacks for fuel cell testing. A decision to continue with ex-situ development rather than build stacks will require a redirect at this time.

Introduction

One of the technical barriers to the commercialization of PEM fuel cells is that of cost. In order to produce an automotive system at a competitive cost the cost of individual components must be minimized. A significant cost component is that of the platinum catalyst used in the fuel cell to increase the rate of reaction and hence the power density of the stack. In recent years there has been a strong drive to reduce the Pt loading in the stack, while maintaining performance, by increasing the utilization of the Pt. In parallel, there has been a longer term field of research to find a much cheaper alternative material to replace the Pt, especially on the air reduction electrode, or cathode.

The aim of this project is to investigate the activity and durability of catalytic systems based upon non-precious metal- based, non-metallic materials involving transition metals and chalcogens such as sulfur and selenium. Literature and preliminary results suggested that these systems would be stable in acid and have significant activity for oxygen reduction. Such a catalyst would eliminate the need for Pt on the cathode of a fuel cell and thus greatly reduce the cost of a stack. This would reduce the overall cost of the automotive system, lowering one of the barriers to commercialization of hydrogen fuel cell powered vehicles.

Approach

The use of non-Pt materials means that the surface area of dispersed materials cannot be measured easily. Also, the surface composition of nano-disperse materials cannot be defined. Therefore it was decided to assess the activity and stability of the chalcogenide materials using sputtered thin films upon glassy carbon substrates. In this way the surface area is well defined and the

surface morphology can be determined by a range of surface analytical techniques such as XPS, AES, Raman, energy-dispersive x-ray (EDX), x-ray diffraction (XRD), etc., as well as electrochemical evaluation of the stability and activity of these materials. Initial screening will lead to a down-selection of the best combinations of metal and chalcogen. Only at this stage will nano-dispersed materials be developed which have similar composition and structure. These will also be assessed ex-situ before incorporation into single cells and stacks for demonstration. In parallel to this stage, efforts will be taken to develop a method of estimating the surface area of these materials from the HRTEM particle size distribution. In this way the effects of the dispersion upon activity and stability may be assessed.

Results

Cobalt (Co), chromium (Cr) and iron (Fe) have been evaluated in combination with selenium (Se) as thin films on GC. The Co-Se system was used to develop the methodology. A novel sputter target was developed in-house to enable the deposition of films with a widely varying, controlled Co-Se composition. It can be seen in Tables 1 and 2 that the films, after electrochemical evaluation, become Se rich on the surface, but remain stable in the acidic

Table 1. Catalyst Bulk Composition from EDX

Catalyst	Bulk Composition for 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

Table 2. Catalyst Composition from Scanning Auger Microscopy (SAM)

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

environment. The difference between the EDX (bulk) composition and the AES (surface) composition is quite clear. The formation of Co-Se compounds is supported by the high resolution Auger and XPS data shown in Figure 1. XRD data supported the compositional data and indicated that the stable and active phase was $\text{Co}_{0.85}\text{Se}$ as a single phase but with a Se rich surface (Auger). The open circuit potential (OCP) of the electrode was, however, low at 0.78V. In order to verify the method, a supported CoSe catalyst was made which was Co rich. Upon electrochemical evaluation the excess Co phase dissolved rapidly leaving a similar CoSe phase behind (XRD). This catalyst was also active and stable in the acidic environment with an activity that appears comparable with platinum (Figure 2). However, this cannot be verified without a method for determining the surface area of the CoSe phase.

The Fe-Se system behaved in a similar way with rapid dissolution of the iron leaving behind a FeSe phase which was active for ORR, but at an even lower potential than the CoSe at 0.59V. There was some difficulty in getting the Fe-Se films to adhere to the GC because of residual stresses in the films after deposition. It was found that a thin tantalum underlayer greatly improved the adherence and allowed full evaluation of the system. The Cr-Se system proved difficult to deposit without incorporation of oxygen from the chamber

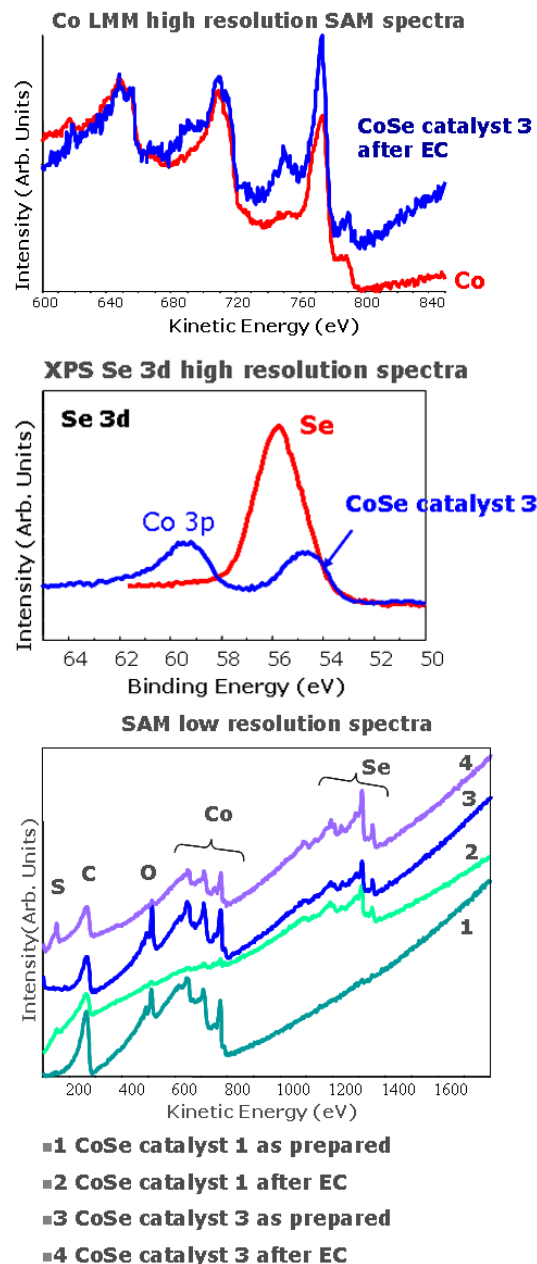


Figure 1. Auger and XPS spectra of Co-Se thin films #1 (Co rich) and #3 (Co:Se 1:1) showing the evolution of a Se rich surface after electrochemistry and evidence of compound formation with additional Auger transitions in the Co LMM and a shift to lower binding energies of the Se 3d XPS peak.

Cr oxide in the film. Even after this was reduced to 3% by lowering the chamber pressure, the Cr-Se films were stable but not very active with a very low OCP at 0.42V.

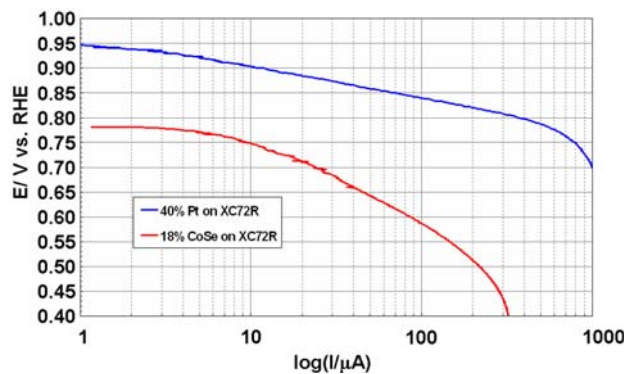


Figure 2. Comparison of the ORR activity of the carbon supported CoSe catalyst with supported platinum baseline (40% Pt on XC72R); 0.5M sulphuric acid, O₂ saturated at 30°C, on GC disc at 2,000 rpm, 5mVs⁻¹.

A summary of the activity of the thin films is shown in Figure 3. These are the best of each system tested. The comparison with the bare glassy carbon and a sputtered Pt thin film is also shown as uncorrected Tafel plots. It can be seen that the Co-Se thin film produced a reaction rate (current) of a similar magnitude to the Pt thin film, but at a lower potential. It was not possible to deposit stable diselenides for any of the metals tested.

These results indicate that the metal-chalcogen systems are active and stable in this environment and that activities similar to that of Pt are obtainable. It is of fundamental importance that the active phases appear to be narrow bandgap semiconductor materials with an active surface which is selenium rich. The nature of the active site and the related active site density is work which falls outside the scope of this project. Work proceeds to evaluate the sulfides of these metals. To date, only Fe has been studied. It appears that for the iron, the monosulfide is difficult to deposit and is not stable, whereas the pyrite phase disulfide is stable and active. Mixed chalcogenides involving S and Se are outside the scope of the project.

Preliminary work on the chemistry to nanodisperse the materials on a high surface area carbon has shown that this may be achieved with some control over the particle size. This may be an important factor in stability and activity of the supported catalysts. The OCP is still lower than ideal for current PEM fuel cell systems.

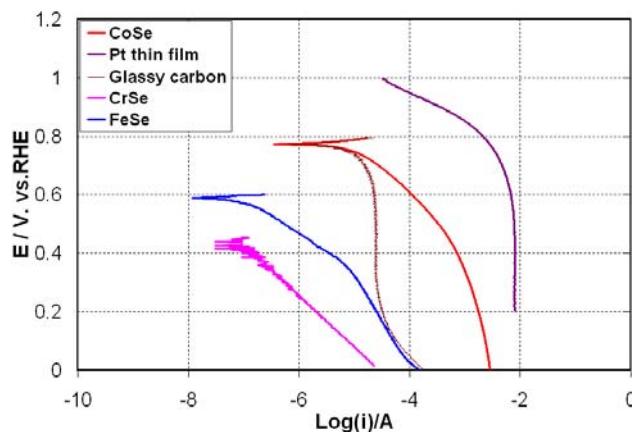


Figure 3. Comparison of polarization curves from Pt thin film, glassy carbon, Co-Se, Fe-Se/Ta and Cr-(O,Se) thin films. Conditions as in Figure 3.

Conclusions

- Co, Cr and Fe have been evaluated with Se as thin films.
- Indications from surface analysis (AES, XPS) for Co-Se and Fe-Se films are that excess metal dissolves leaving a stable selenide with a 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 well to GC and require a thin Ta underlayer to improve adhesion and allow evaluation.
- Cr-Se films contain oxygen (in the bulk of the film, not just on the surface) due to incorporation from the sputter chamber atmosphere. Even when reduced to 3% the activity of the Cr-Se films is poor.
- The CoSe thin films are stable and active and have a higher open circuit potential than those of Fe-Se and Cr-(O, Se) but this is still lower than Pt.
- Nanodispersed catalysts made using the Co-Se system develop a similar stable and active phase (Co_{0.85}Se) in which the activity may approach that of Pt. The OCP, however, remains low.
- Preliminary work with the Fe-S system indicates that the stable phase is a disulfide (pyrite) which has comparable activity with the Co-Se system.

FY 2005 Publications/Presentations

1. "A fundamental approach to non-precious metal catalysts for PEM fuel cells"; S. Campbell; PCAMM 2004 Conference, December 4th, 2004, Vancouver, BC, CANADA
2. "A fundamental approach towards the non-precious metal catalysts for oxygen reduction in PEM fuel cells"; D. Susac, L.Zhu, A. Sode, M. Teo, P.Wong, D. Bizzotto, K. Mitchell, R. Parsons and S. Campbell"; 88th Canadian Chemistry Conference, May 28th-June 1st, 2005, Saskatoon, SK, CANADA
3. " A fundamental approach towards the non-precious metal catalysts for oxygen reduction in PEM fuel cells"; S. Campbell, D. Susac, P. Wong, L. Zhu, A. Sode, M. Teo, D. Bizzotto, K. Mitchell, R. Parsons; 2nd International Conference on Polymer batteries and Fuel Cells, June 12th-17th, 2005, Las Vegas, NV
4. Four papers in preparation