

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

Stephen Campbell

Ballard Power Systems
9000 Glenlyon Parkway
Burnaby, BC, CANADA V5J 5J8
Phone: (604) 412-3151; Fax: (604) 412-4704
E-mail: stephen.campbell@ballard.com

DOE Technology Development Manager:
Amy Manheim

Phone: (202) 586-1507; Fax: (202) 586-9811
E-mail: Amy.Manheim@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

Technical Advisor: Thomas Benjamin
Phone: (630) 252-1632; Fax: (630) 252-4176
E-mail: Benjamin@cmt.anl.gov

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Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Electrode Performance

Technical Targets

The 2010 technical targets at which this project is aimed are as follows:

- Cost: \$8/kW
- Non-Pt catalyst activity per unit volume of supported catalyst: $>130 \text{ A/cm}^3$ @ 0.8 V (iR free)
- Durability (with cycling) $\leq 80^\circ\text{C}$: 5,000 hours; $\geq 80^\circ\text{C}$: 2,000 hours

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. In recent months, the project has been redirected to include ternary systems to raise the open circuit potential. 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 2010 targets above.

Objectives

- To deliver a commercially viable non-precious metal catalyst which performs in a fuel cell stack at a power output equivalent to $200 \mu\text{gPt/kW}$ 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

Accomplishments

- The project has evaluated the metal-sulfur systems and found that, unlike the selenides, the stable and active forms are disulfides in the pyrite structure. These materials are more active and stable than the monoselenides with open circuit potentials above 0.8 V vs. RHE (e.g. 0.83 V for CoS_2).
- Initial stability studies show that the CoS_2 thin films are stable in acid under oxygen reduction conditions at ambient temperature.
- A method for accurately measuring the particle size distribution and therefore specific surface area for nanodispersed catalysts based upon high resolution transmission electron microscopy (HRTEM) image analysis has been developed. This is now being applied to dispersed, supported chalcogenide catalysts.

- Surface analysis by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) has indicated that before and after electrochemistry the surfaces of these pyrites are sulfur rich. XPS studies near the valence band edge indicate significant coupling of the S and metal electron densities for the more active materials.
- Ternary systems with mixed S and Se show no advantage but mixed metal systems may increase the open circuit potential (OCP) for oxygen reduction (ORR).

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 scanning electron microscopy (SEM), and surface composition by a range of surface analytical techniques such as XPS, AES, and Raman. The bulk compositions and structure can be investigated by EDX and XRD, while the stability and activity of these materials towards ORR is by

standard electrochemical methods. 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

In the past twelve months the focus of the project has moved forward from the metal-selenium system to that of metal - sulfur. In the last report, it was noted that chromium selenide contained oxygen that could not be removed and had a very low activity. For this reason, when considering sulfides, only iron and cobalt were considered. In order to avoid complications in assessing the electrochemical activity, the electrolyte has been changed from sulfuric acid to perchloric acid. The sputtered Pt thin film standard was also redone in the new electrolyte.

It was reported in previous work that the stable sputtered selenides were generally monoselenides but it has been our experience that the preferred sulfide stoichiometry is that of the disulfide which, in the cases of cobalt and iron, exhibit the pyrite structure in which the sulfur atoms are paired in the lattice in a complex S_2^{2-} anion. Sputtered thin films of both Co and Fe pyrite were fabricated using sputter targets made from pressed powder material. A small amount of sulfur was added as a binder. These targets performed well, depositing reproducible films with close to stoichiometric bulk compositions when used in radio frequency mode.

The films were evaluated electrochemically as before using a rotating disc electrode in oxygen saturated 0.1 M perchloric acid. The results for ORR are shown in Figure 1 with that for a sputtered Pt thin film for comparison. It should be noted that the surface area for these films is the same, allowing for direct comparison of their respective activities. It is clear that the activity increases as $FeS_2 < CoS_2 < Pt$ with the equilibrium, or crossover potential of the CoS_2 being greater than 0.8 V. This is the first time that the OCP has been >0.8 V in this project. The Tafel slope for CoS_2 is similar to that for Pt. The pyrite films appeared to be stable for the period of the experiments. Durability studies are not planned for the thin films but for the dispersed catalysts in fuel cells at a later date. However, preliminary results show a degree of stability of the CoS_2 films under ORR conditions extending up to 72 hours.

Ex-situ compositional studies of the Co-S thin films were carried out using XPS and AES and EDX.

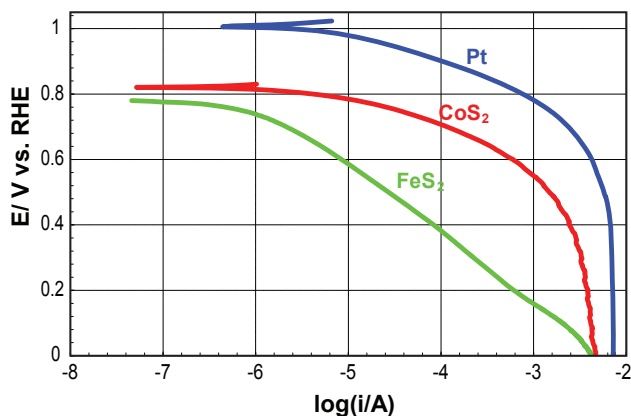


FIGURE 1. Tafel plots for oxygen reduction on sputtered thin films on glassy carbon in O_2 saturated $0.1M HClO_4$; $V = 5mVs^{-1}$; $\Omega = 2,000$ rpm; ambient temperature. Plots show that CoS_2 is significantly more active than FeS_2 but still less active than Pt.

The initial bulk compositions (from EDX) of the three films discussed here is shown in the table below. For comparison, a third film was analyzed with a much lower S content.

	Co (at%)	S(at%)	S/Co ratio
TF1	20.8	79.2	3.8
TF2	35.3	64.7	1.8
TF3	42.0	58.0	1.4

Figure 2 shows the XPS analysis of the S 2p peak from surface of Co-S thin films after electrochemical evaluation. The data for fresh films was similar as the films did not change noticeably during the electrochemical experiments. It can be seen that, in each case, the S 2p feature may be deconvoluted into three oxidation states of sulfur: elemental sulfur (S^0), S^{2-} and the pyrite form, S_2^{2-} . The films with a high S/Co ratio show a predominance of the S_2^{2-} form indicating that the major component is that of the CoS_2 pyrite with some CoS and elemental sulfur. For TF1 the monosulfide is the major component. No single component material was observed in any of the thin films studied, indicating the complexity involved in determining the mechanism of ORR on these surfaces. The surfaces of all three films are sulfur rich as determined by Auger spectroscopy. As in previous reports, it is proposed that this surface film may protect the underlying material from metal dissolution. Its role in the catalytic reduction of oxygen is unclear at this time.

The XPS spectra for S 3s and valence regions allow clear differentiation to be made between monosulfide and disulfide materials. This is shown in Figure 3 for the Fe-S films as an example. In films with a high bulk sulfur content, containing mostly pyrite, the S 3s peak is split into two peaks centered around a binding energy of

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

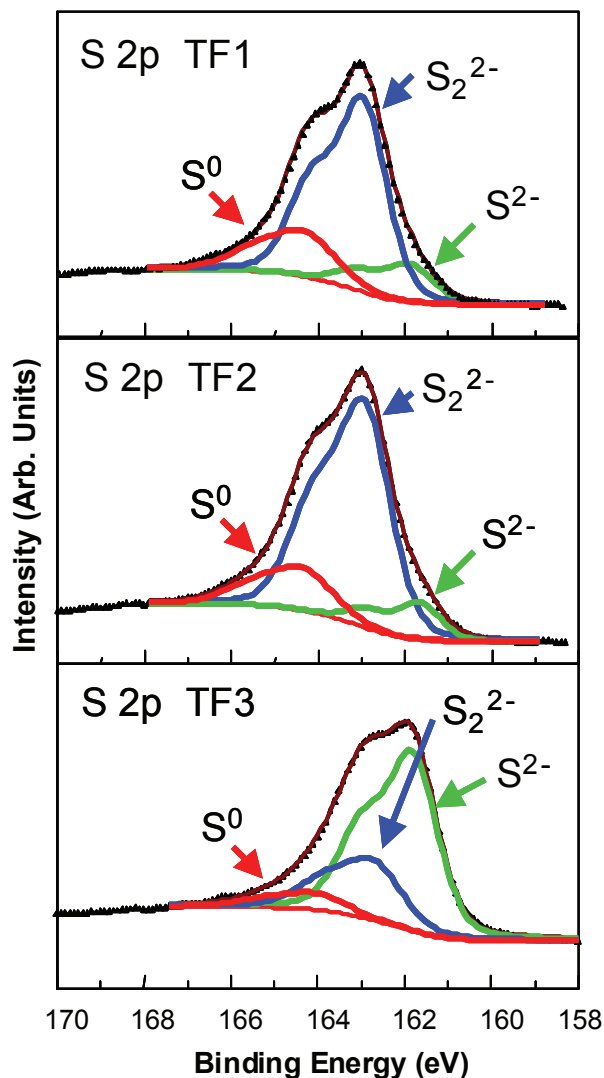


FIGURE 2. Analysis of S 2p XPS spectra for three different Co-S thin films after electrochemical evaluation showing the relative proportions of S oxidation states.

15 eV. For the film, which is mostly monosulfide, there is only a single S 3s peak at around 12 eV. There is also a significant difference in the electronic structure at the valence band edge. The monosulfide film does not show any Fe 3d states at the band edge but the FeS_2 film, with significantly less iron in the composition, shows a clear Fe 3d peak. It should be noted that the monosulfide was not stable in acid and had a poor OCP whereas the FeS_2

film was stable and had some activity for ORR albeit at a lower potential than the cobalt based materials.

This section of the work on the metal-sulfur systems showed that the pyrite CoS_2 structure was stable and the most active to date for ORR with an OCP of 0.83 V vs. RHE which is still significantly below the requirements for automotive applications. The films have a sulfur rich surface and there is a degree of electronic coupling near the valence band edge between the sulfur 3p electrons and the 3d electrons from the underlying metal which may be important in the mechanism of the ORR on these surfaces. In order to compare the activities of various powder catalysts, it is first necessary to be able to measure or estimate the surface area of the catalyst. This is not difficult for Pt catalysts as CO gas adsorption or CO stripping voltammetry may give accurate results. For non-metallic materials, however, the task is more challenging. It is possible to estimate the surface area from an accurate measurement of the particle size as it may be assumed that the particles are essentially spherical (valid for very small particles). XRD will yield a particle size using the Scherrer equation but this does not take into account the asymmetric particle size distribution that generally occurs in nano-dispersed fuel cell catalysts. HRTEM image analysis has been shown to enable accurate particle size distributions to be measured even if some agglomeration occurs. The impact of asymmetry in this distribution on the mean particle size has been demonstrated [1]. In addition to this work, HRTEM has recently been applied to the non-Pt catalysts developed in the project. To date, CoSe , FeS_2 and CoSe_2 dispersed catalysts have been produced and analyzed using HRTEM at CASE. Analysis is underway. Figure 4 shows the TEM micrograph of a single particle from the FeS_2 dispersed catalyst. It is larger than optimum with clear facets. At high resolution, the atom planes can be clearly seen. Fast

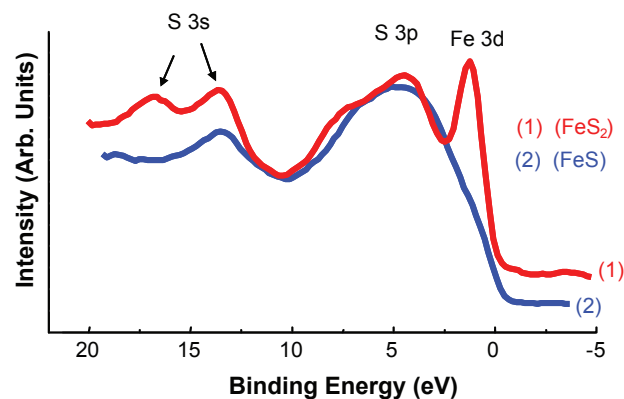


FIGURE 3. XPS S 3s spectra of two different Fe-S sputtered thin films showing the splitting of the S 3s into a doublet in the case of the pyrite structure along with the strong metal 3d states at the valence band edge.

fourier transform (FFT) of the image (Figure 4b) shows that the crystal is of iron pyrite.

In September, the project was redirected in scope. The data indicated that, although significant progress has been made, the OCP is still too low for automotive applications despite a significant reduction in cost. It was felt that if ternary systems were allowed, the focus would shift to adding additional metals to the best chalcogenide with the express purpose of raising the OCP. The base material was down selected as CoS_2 to which S and metals such as Ni and W were added. Metals such as Ni and Fe are known to form pyrite phases as Co and the W (along with Ta and Nb) have a more noble character. Figure 5 shows the Tafel plots for the addition of Fe and Mn to the Co-S system. It was found that the addition of Fe to CoS_2 did not enhance the activity for ORR. Mn did not form a pyrite but

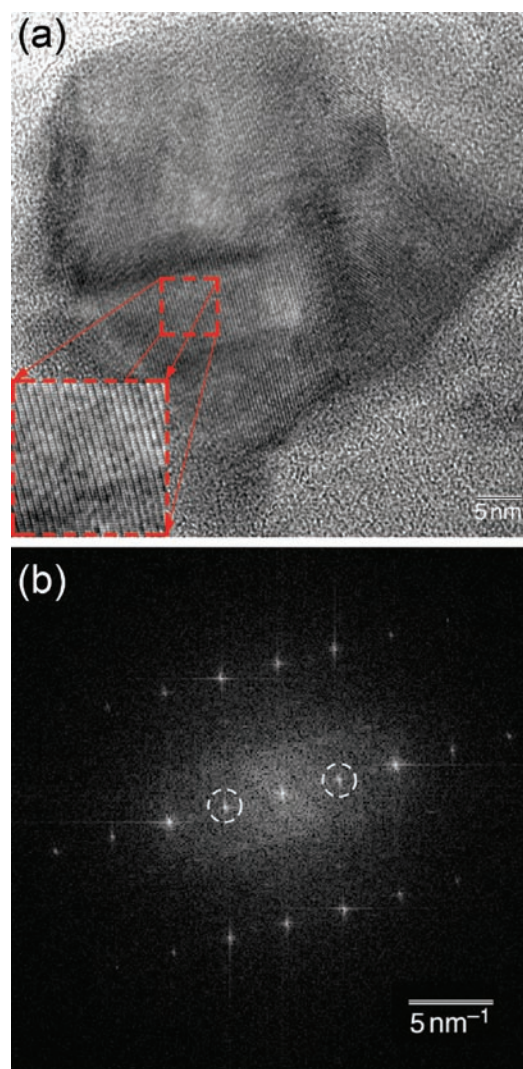


FIGURE 4. HRTEM image of a single FeS_2 particle deposited upon XC72R carbon.

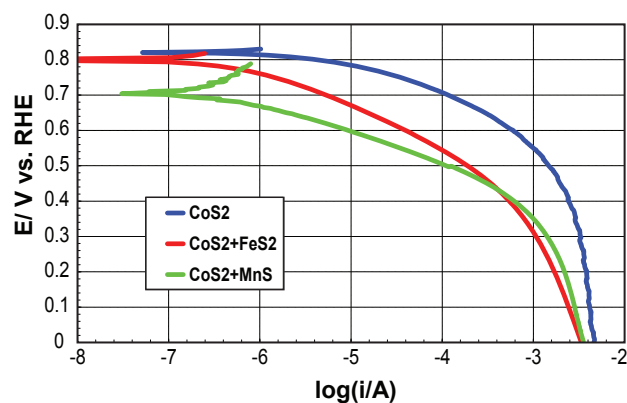


FIGURE 5. Tafel plots for oxygen reduction on sputtered thin films on glassy carbon in O_2 saturated $0.1M HClO_4$. $V = 5 mVs^{-1}$; $\omega = 2,000$ rpm; ambient temperature. Plots show the impact of adding Fe and Mn to the CoS_2 system.

precipitated as an unstable monosulfide MnS which dissolved in the acidic environment and produced a lower OCP. Work is currently underway to evaluate $(Co,W)S_2$ and $(Co, Ni)S_2$ systems. Preliminary data for the $(Co, Ni)S_2$ system indicate a significant increase in OCP. Further characterization is in progress.

Conclusions and Future Directions

- The project has evaluated the metal-sulfur systems and found that the stable and active forms are disulfides in the pyrite structure. These materials are more active and stable than the monoselenides with open circuit potentials above 0.8 V vs. RHE (e.g. 0.83 V for CoS_2).
- Initial stability studies show that the CoS_2 thin films are stable in acid under oxygen reduction conditions at ambient temperature.
- A method for accurately measuring the particle size distribution and therefore specific surface area for nanodispersed catalysts based upon HRTEM image analysis has been developed. This is now being applied to dispersed, supported chalcogenide catalysts.
- Surface analysis by XPS and Auger AES has indicated that before and after electrochemistry the surfaces of these pyrites are sulfur rich. XPS studies near the valence band edge indicate significant coupling of the S and metal electron densities for the more active materials.
- Adding a second metal to the CoS_2 system to increase the OCP above 0.83 V vs. RHE is in progress. Ni, W and Cu will be evaluated in the next few months.
- A synthesis process for nanodispersed disulfide catalysts is currently being developed. This will be

used to produce powder catalyst of the preferred, downselected composition to enable fuel cell evaluation to begin in the last quarter of 2006.

- Single cell demonstration of performance will begin in the 2007.

Publications

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