Final Scientific Report

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Working Partners: Ballard Power Systems, University of British Columbia,
Case Western Reserve University

Cost-Sharing Partners: Ballard Power Systems, Inc.

Contact: Stephen Campbell; 604-412-3151; stephen.campbell@ballard.com

DOE Managers: Nancy Garland, Technology Manager; David Peterson, Project Officer

Executive Summary

The aim of this project was to investigate the potential for using base metal sulfides and selenides as low cost replacements for precious metal catalysts, such as platinum, currently being used in PEM fuel cells. The approach was to deposit thin films of the materials to be evaluated onto inert electrodes and evaluate their activity for the cathode reaction (oxygen reduction) as well as ex-situ structural and compositional characterization. The most active materials identified are CoS_2 and the 50:50 solid solution $(\text{Co,Ni})\text{S}_2$. However, the OCP of these materials is still considered too low, at 0.83V and 0.89V vs. RHE respectively, for testing in fuel cells. The methods employed here were necessary to compare with the activity of platinum as, when nano-dispersed on carbon supports, the active surface area of these materials is difficult to measure, making comparisons inaccurate. This research adds to the knowledge of potential candidates for platinum replacement in order to reduce the cost of PEM fuel cell technology and promote commercialization. Although the fabrication methods

employed here are strictly experimental, methods were also developed to produce nano-dispersed catalysts with similar compositions, structure and activity. Cycling of these catalysts to highly oxidizing potentials resulted in an increase of the open circuit voltage to approach that of platinum, however, it proved difficult to determine why using these dispersed materials. The potential for non-precious, non-metallic, low cost, compound catalysts for PEM fuel cells has been investigated and demonstrated.

Project Objective: To deliver a commercially viable non-precious metal catalyst which performs in a fuel cell stack at a power output equivalent to $200\mu\text{gPt kW}^{-1}$ (peak) for a cost saving of 50%. The catalyst should be reliable and stable enough to perform for >2000 hours with <10% degradation in power output.

[1] Introduction

In recent years it has become apparent that there are issues with the use of platinum metal as a catalyst for oxygen reduction on the cathodes of PEM fuel cells despite their continued development. The most obvious one is the cost which has risen threefold since 2002 and shows no sign of levelling off; and this is without the impact of the commercialization of fuel cells. Platinum is now also known to be non-selective, catalyzing not only the desired reaction but also the oxidation of its own carbon support, leading to rapid performance degradation particularly in automotive applications where the load is continually varying and there are numerous start-up/ shutdown events. In addition, significant Pt dissolution is observed: it turns out Pt is not as "noble" as was originally thought. In the expansion of the effort to find cheaper alternatives that may have similar performance, on a $\text{\$/kW}^{-1}$ basis, and have at least similar durability, it has been determined that the transition metals of interest (Cr, Fe, Ni, Co, etc.) may not be used in their metallic state but only in the form of compounds in which the metal is in a higher oxidation state. The requirement that the catalyst, being part of an electrode, must also conduct electrons, limits the type of compound to carbides, nitrides, and chalcogenides.

There has been a great deal of effort put into the search for alternatives to platinum for the oxygen reduction reaction (ORR) in PEM fuel cells. In nearly all cases the approach was to develop nano-dispersed, carbon supported catalysts and then test them; usually in fuel cells but sometimes ex-situ using a rotating disc electrode (RDE). This approach would appear to work except that, unlike the case of Pt metal, it is difficult to compare catalysts for at least two reasons. Firstly, in all cases the active surface area of the dispersed materials cannot be measured using the established method for Pt, CO stripping voltammetry. In most cases CO does not specifically adsorb on the active surfaces. Without knowing the active surface area of each catalyst it is invalid to compare alternatives with Pt, or even with each other as often, even if the mass of material is similar the particles size distribution may differ considerably. Secondly, in the case of a non-elemental material, which is often the case for non-precious metal catalysts, the heterogeneous nature of the active surface opens the possibility of a wide range of possible active sites which will not have a surface density that is equal merely to the total surface area exposed to the reactants.

The approach taken in this work was different in that the effort was separated into two stages. Firstly, the identification of the most active and stable material composition took place on electrodes with similar surface morphologies and surface area. To achieve this, thin films of the various compositions were sputtered onto polished glassy carbon (GC) substrates. These films were then characterized using surface science methods such as X-ray photoelectron spectroscopy (XPS), scanning Auger microscopy (SAM) to determine the nature of the active surface and energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and Raman spectroscopy to determine the bulk composition. The substrates were designed to fit into a rotating disc electrode (RDE) holder for electrochemical evaluation for stability and ORR activity. The baseline was a sputtered platinum thin film which also served as a check on the cleanliness of the electrolyte. In this way direct comparisons of the activity of the various thin films could be established without having to make any assumptions on the surface areas. The SAM also served as a scanning electron microscope (SEM) allowing confirmation that the majority of the

materials were deposited as smooth, homogeneous films. The films were then analyzed further after electrochemical evaluation (EC) to determine what changes, if any, may have occurred.

Only when viable materials were identified was any attempt to develop a methodology for fabrication of nano-dispersed, carbon supported catalysts made. It should be noted that, as these chalcogenide materials were compounds the chemistry necessary to achieve this was often not straightforward. The objective was to establish that the supported catalysts behaved in a similar way to the thin films with the same composition before moving to actual fuel cell testing. At this stage there also had to be a parallel effort to develop a method to use high resolution transmission electron microscopy (HRTEM) to determine the particle size distribution and hence enable an estimation of the catalyst surface area. In the end, this remains a hurdle to be overcome before fuel cell testing has any validity. While this approach was not new, it is the first time it has been applied to chalcogenide catalysts.

Metal chalcogenide thin films were fabricated from chromium, iron, nickel, tungsten, molybdenum and cobalt with selenium or sulfur. It was found that the bulk composition of the films generally consisted of mostly mono- or dichalcogenide regardless of the atomic proportions of metal and chalcogen. The dichalcogenides, especially the pyrite disulfides, exhibited good activity with an open circuit potential (OCP) of between 0.82V and 0.89V vs. RHE (compared with 1.02V for Pt) with currents that were approximately one order of magnitude lower than Pt at 0.7V. The synthesis of these materials as powder catalysts proved to be problematic owing to safety issues with using H₂S gas and fuel cell testing was not carried out as it was felt that the low OCP did not meet the requirements of the automotive application. Nevertheless, this methodology has proven to give real insights into the electrocatalytic activity of non-metals for oxygen reduction at a fundamental level despite the exclusion of a detailed mechanistic study due to time constraints.

This report will show that cobalt disulfide (CoS_2) with an OCP of 0.83V vs. RHE is capable of catalyzing ORR at a considerable rate. Adding Ni to form a solid solution has raised the OCP to 0.89V. The surfaces of these sulfides are S-rich and this seems to be important in the ORR mechanism although the impact of the metal is clear. This may be due to coupling of the metal 3d states with the S 2p states at the valence band edge. Powder catalysts did not perform in the same way having an OCP that did not vary with the Ni content. There is spectroscopic evidence that the thin films made by sputtering may have metal polysulfide species on the surface which are absent in the chemically prepared powder catalysts. This may be significant.

[2] Experimental

(a) Thin film deposition

The sputter coater used in this study is shown in figure 1. There are two magnetron targets at the top right of the cylindrical chamber. The box below it is a glove box for introducing substrates to the chamber. The substrates for deposition were glassy carbon (GC) machined as shown in figure 2a below. The deposition was done using an RF power supply (13.6MHz) operating at between 35 and 45W. The distance between target and substrate was 11cm. The targets were 2" in diameter and between 3 and 5mm thick attached to a Cu backing plate with silver loaded epoxy adhesive. In the case of FeS_2 a commercial target was available. For all other films targets were fabricated by cold pressing (35MPa) commercially available powders. A small quantity of elemental sulfur was generally added as a binder. The base pressure of the deposition chamber was established by a turbomolecular pump at

Figure 1: A view of the magnetron sputter-coater used to deposit the chalcogenide thin films studied in this project.

3.5×10^{-6} Torr. The plasma discharge was operated at 3.5×10^{-3} Torr with a continuous, throttled flow of argon. Targets were pre-sputtered for 10 minutes prior to moving the substrate into the deposition zone. An initial bias of -180V was applied to the substrate for the first minute to ensure a strong adhesion of the film material. Following this the bias was reduced to -75V. The deposition time varied due to variations in the sputtering rate for the different materials but was continued until the film was around $0.3 \mu\text{m}$ thick. Following deposition the films were removed from the chamber and transported to the surface science equipment in air.

(b) Powder catalyst fabrication

The Co selenide catalysts were produced by adding $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and SeO_2 to an aqueous slurry of XC72R to which a solution of NaBH_4 was slowly added to precipitate

the metal and the elemental selenium onto the carbon. The mixture was filtered and washed with ultra pure water and dried before reacting the Co and Se at 600°C for 4 hours in an argon atmosphere. The selenium was always in excess as some was lost as condensate on the cooler parts of the quartz furnace tube.

For the sulfide based catalysts, the monosulfide was precipitated onto the carbon by adding $(\text{NH}_4)_2\text{S}$ solution to a slurry of carbon in a metal nitrate solution ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) or a mixture of Co and Ni nitrates. This was then filtered, washed and dried before reacting in H_2S gas in a tube furnace at 250°C for 6 hours. An attempt was made to avoid using H_2S gas by sulfidation with elemental sulfur vapour in a vacuum furnace at 250°C. This was only partially successful.

(c) Ex-situ characterization

EDX spectra were measured with a Hitachi 3000 N/X spectrometer (20keV incident electron beam), and the elemental peaks were converted to atomic percentages using Xone software. A Leybold MAX200 spectrometer with Mg $K\alpha$ source ($h\nu = 1253.6\text{eV}$) operated at 15kV and 20mA was used to measure XPS survey scans and higher-resolution spectra with pass energies of 192eV and 48eV respectively. Binding energies were referenced to the Au $4f_{7/2}$ peak at 84.0eV. Elemental amounts were estimated from peak areas using sensitivity factors provided by the manufacturer. A Microlab 350 spectrometer (Thermo Electron Corp.), equipped with a field emission source and a hemispherical energy analyzer, was used to measure local surface composition by SAM; this instrument also gave SEM images for assessing surface topography. The Auger electron spectroscopy (AES) measurements were performed on different surface micro-regions, with the primary electron beam set at 10keV and 3.5nA, and the analyzer operated in the constant retardation ratio mode with CRR values of 4 and 10 for the survey and higher-resolution spectra respectively.

X-ray diffraction measurements were performed using a Bruker D8 advanced diffractometer with Cu $K\alpha$ radiation source ($\lambda = 1.5418\text{\AA}$), and intensities were recorded

as the scattering angle, 2θ , varied from 5 to 90° at 0.02°s^{-1} . Raman spectra were acquired using the 632.8 nm line of a helium-neon (HeNe) laser (Renishaw inVia Raman Microscope) with a 20x objective (numerical aperture of 0.40). Each spectrum was acquired using 10% of the maximum laser power ($<0.5\text{mW}$ on the sample surface), and co-adding individual scans for a total exposure of 500s. Before each measurement, the instrument was calibrated with a standard Si sample (520cm^{-1}).

(d) Electrochemical evaluation

The activity of the sputtered thin films for ORR was assessed in O_2 -saturated 0.1M HClO_4 electrolyte using a potentiostat. The initial characterization of each thin film was done by measuring the cyclic voltammograms at a stationary electrode in a standard three-electrode glass cell with a reversible hydrogen electrode (RHE) as the reference electrode and a Pt wire as the counter electrode. The potential on the stationary thin-film working electrode was scanned from OCP to 0V vs. RHE and then back to OCP with the sweep rates ranging from 10 mVs^{-1} to 1100mVs^{-1} . This has been considered as a pre-treatment step to remove any dissolvable species, and to assess the stability of the film.

Thin film samples were further characterized electrochemically in fresh O_2 -saturated electrolyte using the RDE approach. The RDE holder, was specially designed to accommodate the GC substrate (top-hat shape) and to allow sample transfer between the electrochemical and surface science characterization systems (figure 2). The surface of each thin film was leveled with the holder to prevent any hydrodynamic artifacts during the rotation (500-2000rpm). The three-compartment electrochemical cell used a RHE reference electrode connected to a Luggin capillary with Pt gauze as the counter electrode. The electrolyte was fresh 0.1M HClO_4 or 0.1M H_2SO_4 which was O_2 saturated by bubbling. The electrode was swept, linearly, from 100mV positive of the OCP to 0.0V vs. RHE at 5mVs^{-1} .

Solution cleanliness was regularly assessed by measuring the voltammogram for an analytical Pt RDE (diameter 3 mm, Ω Metrohm), and checking that it closely matched literature reports. The catalytic activities of the thin films were evaluated against the performance of an electrode formed by a thin film of Pt sputtered onto the GC substrate. The purity of the Pt thin film was confirmed by EDX and XPS measurements and by assessments of its electrochemical response compared with that of the analytical Pt electrode.

Figure 2: [a] a sketch of the RDE design with a removable GC disc, [b] A photograph of the RDE used in this study.

Powder catalysts were evaluated in a similar electrochemical cell. 20mg of catalyst was dispersed in 2mls glacial ethanoic acid by ultrasound for 10 minutes. 5 μ l of this suspension was then pipetted onto a 5mm diameter glassy carbon RDE and was then dried carefully with an air gun so that the catalyst was deposited as a disc in the centre of the disc. The RDE was rotated at 2000rpm in an O₂ saturated 0.1M HClO₄ electrolyte heated by a water jacket around the cell maintained at 30°C by a circulating water bath. Linear sweep voltammetry was carried out as for the thin films and the current response recorded.

[3] Results and discussion

(a) Metal- selenium thin films

Three metals were chosen for this study based upon literature that indicated that, based upon volcano-type plots of activity, these were the more active metals of the non-precious transition metals. They are chromium, iron and cobalt. Metal-selenium thin films were sputtered onto glassy carbon discs, as described above, characterized and evaluated for ORR activity. An in-house Cr-Se sputtering target from Cr powder and Se chunks was made and used together with a Cr sputtering target to prepare films with different composition (table 1). SAM analysis indicated that Cr-Se thin film 1 is Cr rich on its surface, while Cr-Se thin film 2 is Se rich with Se/Cr atomic ratio being equal to 6.02 (table 1b). In addition their morphologies were different, with Cr-Se film 1 being smooth (Figure 3a), while Cr-Se film 2 is granular, with particle size $\sim 0.1\mu\text{m}$ (figure 4a).

Electrochemical and subsequent SAM characterization proved that these films are very stable in acidic environment. There are no observable morphological changes for both films after EC2 treatment (figure 3b for film 1 and figure 4b for film 2). The Se content at the surface of Cr-Se film 1 is reduced below the detection level after EC2 (figure 3c spectrum 2), but the composition of Cr-Se film 2 remains practically unchanged (figure 4c spectrum 2). The high resolution of Cr LMM Auger transition measured from both thin films (figure 9) shows that oxygen is present even after the electrochemical characterization, which is in contrast with observations recorded from Co-Se and Fe-Se systems. The depth profile taken from Cr-Se thin film 2 after EC2 indicated that oxygen is incorporated into the bulk of the film, since it has not been removed after 841 s of Ar^+ sputtering.

[a]

EDX elemental composition (atomic %)	Cr-Se Thin Film 1	Cr-Se Thin Film 2
Cr	75.28	13.47
Se	24.72	86.53
Se/Cr	0.33	6.42

[b]

elements	Thin film 1 EDX: Se 13.47 atomic %		Thin film 2 EDX: Se 86.53 atomic %	
	As prepared	After EC2	As prepared	After EC2
C	69.07	81.20	65.57	80.57
O	4.70	2.97	0.44	0.25
Cr	22.16	15.82	4.84	2.58
Se	4.06	Traces	29.15	16.61
Se/Cr	0.18	N/A	6.02	6.44

Table 1: [a] EDX elemental analysis of the Cr-Se thin films (as prepared); [b] Auger surface composition of the same films before and after electrochemical evaluation.

Polarization curves measured from Cr-Se thin films (figure 6) show poor catalytic activity. Linear current response is observed at potentials less than 0.2 V vs. RHE, and current values are for order of magnitude smaller compared to that from polished glassy carbon. The OCP of these films was very low, perhaps because of the incorporated oxygen. Attempts to eliminate this oxygen by reducing the Ar pressure in the deposition chamber and adding a cold trap to the pumping system reduced the oxygen content but had little effect upon the activity of these films. Work on Cr-Se films was terminated at this time.

Figure 3: (a) SEM micrograph of Cr-Se film 1 as prepared, (b) its morphology after EC2 and (c) SAM spectra before (1) and after EC2 (2).

Figure 4: (a) SEM micrograph of Cr-Se thin film 2 as prepared, (b) its morphology after EC2 and (c) SAM spectra before (1) and after EC2 (2).

Figure 5: [a] high resolution Auger Cr LMM spectra for Cr-Se film 1 before (1) and after (2) electrochemical evaluation; [b] the same for Cr-Se film 2.

Figure 6 : Tafel plots for the two CrSe films tested compared with a bare GC substrate and a sputtered thin film. O_2 saturated 0.1M H_2SO_4 , $\omega = 2000\text{rpm}$, $v = 35\text{mVs}^{-1}$, $T = \text{ambient } (20^\circ\text{C})$, electrode area 1.23cm^2

The deposition of Fe-Se films proved difficult as residual stress in the films and poor adhesion to the GC substrate caused the films to flake off the substrate during electrochemical evaluation. It was found that a very thin tantalum underlayer greatly improved adhesion and allowed effective evaluation of two Fe-Se films. As before, the bulk composition of the film was determined by EDX and the surface composition by SAM. Both films were stable in acid and adhered well to the Ta underlayer. The compositional analysis (bulk and surface) is shown in table 2 below.

element	FeSe/Ta 1			FeSe/Ta 2			
	EDX (bulk) Atomic %	SAM as prepared Atomic %	SAM after EC2 Atomic %	EDX (bulk) Atomic %	SAM as prepared Atomic %	SAM after EC1 Atomic %	SAM after EC2 Atomic %
C	ND	92.00	79.26	ND	90.05	87.72	79.39
O	ND	3.20	ND	ND	3.36	1.41	0.56
Fe	40.56	4.80	5.22	27.44	3.93	2.34	1.99
Se	36.90	ND	15.52	54.11	2.67	8.53	18.05
Se/Fe	0.90	N/A	2.97	1.97	0.68	3.65	9.07
Ta	22.54	ND	ND	18.45	ND	ND	ND

•FeSe/Ta film 1 was covered with a thin hydrocarbon layer after EC1 and EC2 that prevented Fe and Se detection by SAM. The SAM elemental composition after EC2 was obtained after the sputtering by Ar⁺ for 4 min.

Table 2: Compositional analysis for the Fe-Se films deposited on a Ta underlayer on a GC disc.

The electrochemical oxygen reduction polarizations for the Fe-Se system are shown below (figure 7). The ORR on the two films is similar despite the different bulk composition. It is perhaps dominated by the Se rich surface. Nevertheless, the potential is lower than for pure Se suggesting that there is an electronic effect of the

underlying metal. This is more promising than it looks as it means that the catalytic surface may be stable in acid, due to the selenium overlayer, yet may still be modified electronically by the choice of the right metal or combination of metals. It is noted that the mass transport limited current is not reached at 0.0V vs. RHE. Literature reports similar results with mineral pyrites.

The SAM data below (figure 8) shows in detail there is clear evidence for the compound formation in the sputtered films. After EC there is a clear change to a Se rich surface and a loss of bound oxygen. Taken with the Cr-Se data from previous work, there is a suggestion that the surface oxygen binds to the metal sites on the surface. This oxygen is not present on the stable, active, Se rich surfaces.

Figure 7: ORR Tafel plots for the two FeSe thin films (TF1 and TF2 refers to Table 2). The data for a Pt sputtered thin film of the same area is shown for comparison. (T=ambient, O₂ saturated 0.1M H₂SO₄, sweep rate = 35mVs⁻¹; rotation rate 2000rpm.)

Figure 8: Auger analysis of Fe-Se films on a tantalum underlayer to improve adhesion. [a] survey scan for TF2 (1) as prepared, (2) after EC; [b] high resolution Fe LMM spectra for TF2 (1) as prepared, (2) after EC.

In order to sputter Co-Se thin films a new sputtering target was designed that used a single RF source with a target made of Co powder and Se powder. Upon heating in inert gas the Se melted and produced, upon cooling, a composite Co-Se target. Three films with bulk Se/Co ratios varying from 0.38 to 1.23 were made and tested. The bulk compositions, from EDX, and the surface compositions, by Auger, both before and after electrochemical evaluation, are shown in table 3 below. It can be seen that film #1 was very Co rich in the bulk and at the surface. After electrochemical testing the bulk composition became Se rich. The surface composition was originally very close to that of the bulk, being Co rich but after EC it became very Se rich presumably as a result of Co dissolution from the surface. The high Se surface would account for the apparent change in bulk composition by EDX. Films #2 and #3, being just below and just above stoichiometry respectively, both behaved in a similar way. Both films were Se rich on the surface after EC but not by as much as film #1.

The Auger survey scans shown in figure 9 clearly show how the surfaces changed during electrochemical evaluation for ORR. Film 1 (figure 9a) shows that the surface

was initially dominated by Co and, after EC, was dominated by Se. It is useful to note that, initially, there was oxygen detected on the surface (O KLL) but that this was

Catalyst	Bulk composition and Se/Co (atomic ratio) by EDX			Bulk composition and Se/Co (atomic ratio) by EDX after EC			Surface Se/Co ratio by Auger	Surface Se/Co ratio by Auger after EC
	Co at%	Se at%	Se/Co	Co at%	Se at%	Se/Co		
#1	72.47	27.53	0.38	16.51 [*]	79.37	4.81	0.42	23.40
#2	51.58	48.42	0.94	40.79	59.40	1.46	3.94	5.91
#3	44.86	55.14	1.23	36.49	63.51	1.74	2.21	5.13

^{*} For catalyst # 1 after EC, 4.12 atomic % of S has been detected by EDX

Table 3: Composition of the Co-Se thin films tested: bulk by EDX and surface by SAM before and after electrochemical evaluation.

removed by electrochemistry with the surface Co. It is interesting to note that no oxygen is found bound to the Se rich surface. In figure 9b & 9c the surfaces contain both Co and Se before and after EC as quantified in table 3. Again, oxygen is removed after electrochemistry. These two films also developed a sulfur LMM peak at very low kinetic energy. There is some evidence in the literature for chalcogen exchange; a process by which the Se in the film may be exchanged for S in solution. This caused us to switch from sulfuric acid to perchloric acid for the electrolyte in later studies.

The high resolution Auger spectra shown in figure 10 below indicate that, as in the case of FeSe (figure 8) there are additional peaks at the low kinetic energy side of the

transitions for the cobalt metal suggestive of Co-Se interaction. Even though XRD is difficult on such thin films this is evidence of the formation of a monoselenide phase.

Figure 9: Survey scan Auger spectra of the three Co-Se films. [a] film #1, [b] film #2, [c] film #3. Note the appearance of S LMM and the absence of O KLL after EC2.

Figure 10: High resolution Co Auger spectrum showing peaks corresponding to Co interaction with Se (arrowed) when compared to pure Co.

Figure 11: XPS Se 3d spectrum for thin film #3 compared with pure elemental Se. The Se 3d peak shifts to lower BE. The Co 3p also shows up at 59.4eV.

Figure 11 shows the XPS Se 3d peaks for elemental Se and CoSe film #3. The Se 3d peak shifts to a lower binding energy (BE) than elemental selenium indicating that it is in a lower oxidation state (Se^{2-}) and it is joined by the 3p peak from the metal.

Figure 12: Tafel plot summary of the three Co-Se thin films tested. The composition of these films is tabulated in Table qq. (Ambient T; O_2 saturated 0.1M H_2SO_4 ; sweep rate 35mVs^{-1} ; rotation rate 2000rpm.)

The results from the electrochemical evaluations are shown in figure 12 as Tafel plots for ORR. The films show some ORR activity but there is no correlation between the surface Se/Co ratio and the activity or the OCP. This suggests that there are other factors involved. The SAM images indicated that all three films were physically smooth both before and after electrochemistry. It was thought that there may be features within the structure of the films which was a determinant for activity. To investigate this an HRTEM study was carried out on a microtome section through a Co-Se thin film. The

section is shown at low resolution by SEM in figure 13. It can be seen that the film appears to consist of particles embedded in a matrix. After microtoming a section was studied in TEM as shown in figure 14 & 15 below. The 'fish scale' appearance is an artifact of the microtoming process. Figures 15b & c indicate that the particles embedded are nanocrystals of $\text{Co}_{0.85}\text{Se}$.

Figure 13: SEM micrograph of a section through a CoSe thin film (56%Se). There appear to be particles embedded in a matrix.

Figure 14: TEM micrograph of the microtomed CoSe (56%Se) thin film. The "fish scale" effect is an artifact of the microtome process. (The GC substrate is on the left.)

Figure 15: Increasingly higher magnification micrographs of the CoSe section. [a] edge of the thin film showing area in [b]. The particles in [b] are shown to be crystalline $\text{Co}_{0.85}\text{Se}$ by the diffraction pattern inserted in [c].

This study has identified that thin films made by sputtering transition metals and selenium are active for oxygen reduction despite the surface becoming very Se rich due to the initial dissolution of the surface metal. The most active of the three metal-selenium systems tested (chromium, iron and cobalt) was the cobalt selenide with an OCP of 0.78V vs. RHE. The methodology has proven useful in that detailed analysis of the bulk composition of the film and the catalytically active surface have been carried out using TEM, AES and XPS. This has shown that the surfaces are often very different from the bulk composition leading to questions about what is controlling the OCP and what is the ORR mechanism on the Se surfaces. A mechanistic study was outside the scope of this project but it is clear that although the surface is Se rich, it is conductive and is affected by the nature of the underlying metal. In a later section covering the work done on powder catalysts it will be shown that powders may be fabricated that behave as the corresponding thin films. Summary Tafel plots are shown in figure 16 below. It can be seen that there is a clear trend in activity in the order $\text{CrSe} < \text{FeSe} < \text{CoSe} < \text{Pt}$.

Figure 16: Summary Tafel plot for the sputtered metal- selenide thin films tested with a comparison with a sputtered Pt film on the same substrate. O_2 saturated 0.1M H_2SO_4 , $\omega = 2000\text{rpm}$, $\nu = 35\text{mVs}^{-1}$, $T = \text{ambient } (20^\circ\text{C})$, electrode area 1.23cm^2 .

(b) Metal- sulfur thin films

Following the work on Co and Fe selenides the project switched to consider sulfides. An iron disulfide (FeS₂) target was purchased and a monosulfide (FeS) target was fabricated from pressed powder. In order to vary the composition of the films deposited, a second, iron target was also used in dc mode. The bulk composition of these films was determined using EDX and the surface was analyzed using SAM both before and after electrochemical evaluation (EC1 & EC2). The data is summarized in Table 4 below.

Fe-S system								
Targets used for film preparation	TF 1 (FeS ₂)		TF 2 (FeS ₂)		TF 3 (FeS ₂)		TF 4 (FeS)	
	FeS ₂ target		FeS ₂ target + Fe target		FeS ₂ target + Fe target		Target pressed using FeS powder	
Bulk Composition from EDX (atomic %)								
element	As prepared		As prepared		As prepared		As prepared*	
S	69.74		67.11		66.28		54.20	
Fe	30.26		32.89		33.72		27.80	
S/Fe (EDX)	2.30		2.04		1.96		1.94	
Surface composition from SAM (atomic %)								
Electrolyte used for EC analysis	Thin film 1 (FeS ₂)		Thin film 2 (FeS ₂)		Thin Film 3 (FeS ₂)		Thin Film 4 (FeS)	
	0.1 M H ₂ SO ₄		0.1 M HClO ₄		0.1 M HClO ₄		0.1 M HClO ₄	
element	As prepared	EC2	As prepared	EC2	As prepared	EC2	As prepared	EC2
S	51.50	32.46	24.04	61.88	7.50	63.43	12.01	films dissolve after EC1
C	43.89	64.43	69.20	33.79	81.20	33.33	72.69	
O	0.78	0.57	3.96	ND	6.12	ND	8.85	
Fe	3.83	2.54	2.81	4.33	5.26	3.24	6.44	
S/Fe (SAM)	13.45	12.78	8.55	14.29	1.43	19.57	1.86	

ND = not detected

* 18.00 atomic % of Ta present. Ta is used as underlayer to improve adhesion

Table 4: Composition of iron-sulfur sputtered thin films.

Analysis of the thin films by XRD proved difficult but XPS, SAM and Raman spectroscopy were employed to characterize the films. The Raman spectrum for TF2 (figure 17) shows the expected peaks for a pyrite structure. XPS spectra near the

valence band edge clearly show the difference between TF2 (predominantly FeS₂ pyrite) and TF4 (predominantly FeS) (figure 18). For the pyrite TF2 there is a clear coupling between the S 3p electrons and the Fe 3d and a splitting of the S 3s level due to the dimeric nature of the S (S₂²⁻). These features are not present in the FeS (TF4) spectrum.

Figure 17: Raman spectrum obtained for TF2 showing the bands associated with FeS₂ pyrite.

The Fe 2p XPS spectra for these films is shown in figure 19. The Fe 2p_{3/2} peak at 708eV binding energy is consistent with a pyrite structure for TF2. The shifting to higher binding energies for both the Fe 2p_{1/2} and Fe 2p_{3/2} peaks is indicative of a monosulfide and may also indicate some Fe-O bonding. After electrochemistry, the TF2 spectrum remains largely unchanged but the TF4 FeS film dissolved in the electrolyte. The

splitting of the S 3s in TF2 is indicative of a pyrite structure. The Fe 3d feature is absent in the FeS film (TF4).

Figure 18: XPS S 3s and valence region for TF2 and TF4 as prepared.

Figure 19: XPS Fe 2p spectra for the two thin films. No spectrum was possible after EC2 for TF4 as the film dissolved in the electrolyte.

The electrochemical evaluation of the FeS₂ thin films was initially carried out as before in 0.1M H₂SO₄ but our concerns with chalcogen exchange with the selenide films reported above suggested that we switch to 0.1M HClO₄. Of the three primarily FeS₂ films (TF1,2 & 3) TF1 was tested in sulfuric acid and TF2 & TF3 were tested in perchloric acid. In figure 20 below, only the results for TF1 & 2 are shown as TF3 behaved in a way very similar to TF2. Compared to the Pt thin film the performance is low, with an OCP of 0.79V which is similar to the monoselenide thin films. TF2 & 3 in perchloric acid (not shown) had a greater current at the same potential that TF1 in sulfuric acid. For comparison, a piece of mineral FeS₂ pyrite from Zacatecas, Mexico was made into an electrode by wrapping a fine Cu wire around it and potting it in epoxy resin at the end of a glass tube. The surface was polished using increasingly finer grade of polishing alumina until a mirror finish was achieved. This material had been analyzed by XRD and XPS found to be crystalline iron pyrite with trace amounts of Ca and Si commonly found in mineral deposits. It can be seen that the electrochemical behaviour of the mineral pyrite is very different from that of the sputtered thin films. The OCP is much lower at 0.51V which is lower than literature values of around 0.6V. This difference may be explained by careful analysis of the surfaces of the thin films and mineral pyrite.

Figure 21a compares normalized S 2p spectra measured from the cleaved Zacatecas pyrite and from the as-prepared thin film. The spectral shapes differ, indicating that the surface of the sputtered film is not identical to that of the natural sample. The latter is used as a reference for assessing the extra components required for the thin-film sample, as outlined in the following. The S 2p spectrum from the natural pyrite was fitted (figure 21b) with a 2p_{3/2} and 2p_{1/2} doublet (binding energies 162.6 and 163.8eV respectively) consistent with S₂²⁻ dimers fully coordinated by iron and a broad component at 165.6 eV associated with energy loss processes. Although the sample was exposed to air after cleavage, no sulfate species could be detected at around 168eV. These spectral characteristics were then used to fit the S 2p spectrum from the

sputtered film (figure 21c). The fit using curves 1 and 2 from the natural sample required two additional components (with $2p_{3/2}$ at 161.8 and 163.6 eV for curves 3 and 4 respectively, where the peak widths and spin-orbit splittings are fixed by values for curve 1). Previous reports have interpreted the first additional component to arise from surface S_2^{2-} dimers with less than the full Fe coordination, while that at 163.6eV is consistent with the presence of short-chain polysulfides S_n^{2-} ($2 < n < 8$). As a point of reference, the curve fitting using these components for the as-prepared thin film gave the relative contributions 86% bulk S_2^{2-} , 10% surface S_2^{2-} and 4% polysulfide. Mycroft et al. reported that polysulfide species occur at pyrite surfaces only after severe electrochemical oxidation. In contrast, the characterization of our sputtered samples point to polysulfides being present at the surface of the as-prepared thin film (i.e. had not undergone any electrochemical treatment), and thereby suggests that the formation of these species relates to the specific method of thin film preparation. In other work, short-chain polysulfides have been reported to form when S vapor is exposed to an electrical discharge. Similar conditions exist during the sputtering process, since S vaporization occurs as the Ar^+ bombardment heats the target to around 60-80°C. Additionally, sputtered S dimers may interact while on the substrate to form polysulfides during the film growth.

Figure 20: Tafel plots of the ORR behaviour of FeS_2 thin films compared with that of a sputtered Pt thin film and an electrode of natural mineral pyrite. [a] TF1 in 0.1M H_2SO_4 ; [b] TF2 in 0.1M $HClO_4$; [c] mineral pyrite; [d] Pt thin film. In all cases, ambient T, O_2 saturated acids, rotation rate 2000rpm, sweep rate $35mVs^{-1}$.

Figure 21: S 2p spectra: (a) comparison of normalized spectra for Zacatecas pyrite and as-prepared FeS₂ thin film; (b) curve fitting for Zacatecas pyrite with components for bulk S₂²⁻ (curve 1) and energy loss peak (curve 2) as noted in main text; (c) curve fitting for as-prepared FeS₂ thin film with two components in (b) plus those for surface S₂²⁻ (curve 3) and polysulfide (curve 4) and (d) FeS₂ thin film after electrochemical analysis.

It was found that sputtering of CoS films from a CoS target was not possible due to the extremely low sputtering rate of this material. CoS₂ films were successfully fabricated using a target composed of CoS₂ powder with added sulfur to act as a binder and as an additional source of S. Using this type of target it proved possible to deposit films with compositions varying from S-rich to Co-rich. Table 5 below shows the compositional analysis for the three films tested. The bulk composition was determined by EDX and the surface composition by SAM both before and after electrochemical evaluation. The morphology of the S-rich film (TF1) was wrinkled but there was no indication that the film contained residual compressive stress as it was very stable in the electrolyte.

Co – S system						
Thin film	TF1		TF2		TF3	
Sputtering target	pressed CoS ₂ + S		pressed CoS ₂ + S		pressed CoS ₂ + S	
Morphology	Wrinkled		smooth		smooth	
Bulk composition (from EDX atomic %)						
Element	As prepared		As prepared		As prepared	
Co	20.8		35.3		42.0	
S	79.2		64.7		58.0	
S/Co	3.8		1.8		1.4	
Surface composition (from SAM atomic %)						
Thin Film	TF1		TF2		TF3	
electrolyte	0.1 M HClO ₄		0.1 M HClO ₄		0.1 M HClO ₄	
element	As prepared	After EC2	As prepared	After EC2	As prepared	After EC2
S	64.26	57.6	52.04	45.10	49.17	53.1
C	34.02	38.9	45.20	52.81	46.93	41.4
O	ND	1.19	ND	ND	ND	1.82
Co	1.72	2.21	2.77	2.17	3.91	3.68
S/Co	37.36	26.06	18.79	20.39	12.58	14.43

ND= not detected

Table 5: Bulk and surface composition of the three Co-S films studied.

SEM images of the films showing the differences in morphology are shown below in figure 22.

Figure 22: SEM images of the three Co-S films before and after electrochemical evaluation (EC1 & EC2).

A wrinkled thin film morphology in TF1 (and other films not reported here) seems to be dependent upon a high S content. This kind of thin film structure has been reported in films where one component is more mobile than the other during deposition. Although the carbon substrates are not heated, the temperature does rise to a point where the S species may be assumed to be mobile. In the other films with a lower S content (TF2 & TF3 as examples) the morphology is smooth. The wrinkled surface morphology is preserved during electrochemical evaluation as shown in figure 22 and analysis by SAM indicates that the film surface composition is uniform.

The results of the electrochemical evaluation of the Co-S films for ORR are shown in figure 23. TF2 shows the highest OCP of any of the films evaluated to this point at

0.83V vs. RHE. The wrinkled TF1 is slightly lower but has a higher turnover rate (current) at 0.7V due to the larger surface area than geometric electrode area.

Figure 23: ORR Tafel plots for the Co-S films in Table 5 and figure 22 compared with a Pt thin film. O_2 saturated 0.1M HClO_4 ; ambient T; $\omega = 2000\text{rpm}$; $\nu = 35\text{mVs}^{-1}$

TF3, which was shown to have a much lower S content close to a stoichiometry for CoS , is much less active with an OCP of only 0.53V. In all cases, as with the FeS_2 films, the limiting current converges with that of Pt indicating the predominance of a four electron pathway for oxygen reduction. Following the electrochemistry a detailed surface analysis was carried out on all three films using XPS and Raman spectroscopy.

Figure 24: XPS S 3s and valence band edge spectra for the three Co-S films after electrochemical evaluation.

Figure 24 shows the S 3s XPS spectra for the three Co-S films (TF1-3). TF1 and TF2, as noted with regard to the Fe-S work, exhibit a splitting of the S 3s peak between 13 and 18 eV indicating a predominance of a S_2^{2-} pyrite structure. TF3 does not show this splitting suggesting a monosulfide (S^{2-}) structure is the dominant phase present. Near the valence band edge there is also considerably less coupling between the S 3p and Co 3d electron density for TF3 than is the case for the other two films. A high degree of coupling was found important for ORR activity in the metal selenide work that preceded these results. The poor activity of the TF3 is therefore possibly due to the preponderance of the cobalt monosulfide (CoS) rather than the more active pyrite (CoS_2) found in TF1 and TF2.

A detailed curve fitting of the S 2p XPS peak for these three films is difficult to carry out in the same way as was done for the Fe-S films (figure 21) as detailed measurements of a mineral CoS_2 are not available. Also, the component in the Fe-S films corresponding to the low coordinated surface S_2^{2-} overlaps with the S^{2-} peak in Co-S. When curve fitting the Co-S spectra, the component fitted as S^{2-} may contain contributions from the surface S_2^{2-} . Nevertheless the detailed analysis, shown in figure 25 and tabulated in table 6, do support the EDX compositions reported in table 5 and the S 3s spectra in figure 24. TF1 and TF2 are predominantly S_2^{2-} (pyrite) whereas TF3 is predominantly CoS. In TF1 and TF2 there is a significant proportion (13-14%) of a polysulfide species (S_n^{2-}) which is not present in TF3. The polysulfide component is significantly larger than that found in the FeS_2 sample discussed above.

Raman spectroscopy of the CoS_2 thin films (figure 26) indicates the presence of polysulfides in the appearance of a broad feature at $460\text{-}470\text{cm}^{-1}$ which is not present in the case of the commercially available CoS_2 used as the sputter target. These are not attributed to elemental sulfur due to the absence of intense multiple peaks below 300cm^{-1} . Taken together, the Raman and XPS data for the CoS_2 films indicate a significant presence of polysulfides (S_n^{2-}) at the electrode/ electrolyte interface in which $n>2$. In films which have a high surface S content without the presence of polysulfides, ORR activity is much lower.

Figure 25: XPS S 2p spectra of the surfaces of the three CoS_2 thin films in figure B above showing the curve fit used to determine the relative proportions of the sulfur species as tabulated in table AA below.

Sulfur species	TF1	TF2	TF3
S_2^{2-}	73%	70%	28%
S^{2-}	14%	16%	71%
S_n^{2-}	13%	14%	1%

Table 6: Relative proportions of the sulfur species on the surface of the three CoS_2 thin films.

Figure 26: Raman spectrum of the predominantly cobalt disulfide TF2.

In September 2005 the project was redirected to find a way to increase the OCP above 0.83V before initiating fuel cell testing as it was felt that the OCP was too low for practical automotive fuel cells following comments from the FreedomCar Technical Team during a review in the first quarter of that year. It was decided to study ternary systems based upon the best candidate at that time, cobalt disulfide (CoS_2). The systems to be investigated were (i) mixed chalcogen (Se/S) and (ii) mixed metals. The metals to be mixed with the Co were identified as Fe, Ni, Mn and W. Fe, Mn and Ni are known to form pyrites and so may be assumed to form single phase solid solutions. W is not a pyrite but is included as it may have a higher potential in oxygen saturated acid.

Thin films of $\text{Co}(\text{Se},\text{S})_2$ were deposited from a single target using RF sputtering in which the Se:S ratio is 50:50. The OCP of these films were lower than either CoSe or CoS_2 possibly because a simple crystal structure was not produced due to differences in size of the chalcogen atoms. This approach was therefore abandoned and work progressed to the addition of transition metals. Using composite targets of the individual metal disulfides (e.g. CoS_2 and FeS_2) thin films were fabricated containing nominally equal amounts of the two metals. The first two additional metals studied were Mn and Fe added to CoS_2 and the electrochemical evaluations for ORR are shown as Tafel plots in figure 27 below. The plots for CoS_2 , FeS_2 and Pt are included for comparison. It can be seen that the $(\text{Co}+\text{Mn})\text{S}_2$ thin film had a lower OCP than either FeS_2 or CoS_2 (0.70V vs. RHE) and that the performance for the $(\text{Co}+\text{Fe})\text{S}_2$ thin film is midway between pure FeS_2 and pure CoS_2 . Although neither indicated an advantage and were not pursued further, some XPS analysis of the films after EC was carried out.

Figure 27: ORR Tafel plots for the mixed Co+Fe and Co+Mn sulfide thin films. O_2 sat'd 0.1M HClO_4 ; 2000rpm; 5mVs^{-1} ; ambient T

The S 3s and valence band edge regions of the XPS spectra are shown in figure 28. The splitting of the S 3s characteristic of a pyrite is observed for the $(\text{Co+Fe})\text{S}_2$ thin film and in fact the spectrum looks similar to both the FeS_2 and CoS_2 also shown (figure 28[a]). The $(\text{Co+Mn})\text{S}_2$ thin film spectrum (figure 28[b]), however, looks quite different; before EC there is significantly less splitting of the S 3s peak and less contribution from the metal 3d coupling with the S 3p near the band edge. After EC the pyrite structure becomes more pronounced. This has been interpreted as indicating that the manganese sulfide forms as a separate monosulfide phase which is unstable and dissolves during the electrochemistry.

Figure 28: Valence band-edge XPS spectra for [a] the Co-Fe-S system and [b] the Co-Mn-S system (see text for details).

In order to investigate the activity and OCP of mixed CoS₂ + WS₂ thin films two films were fabricated using targets made from pressed powders with some added S to act as a binder; one pure WS₂ and one 50:50 CoS₂:WS₂. The bulk and surface compositions of these films is shown in table 7. For the WS₂ film the initial bulk composition by EDX was surprisingly S rich. This may be explained by a slow sputtering rate of tungsten compared to that of S. After EC the surface S/W ratio did not change significantly suggesting that, although the OCP was low, the film was stable under the EC conditions. The mixed metal sulfide film had a bulk Co/W ratio of close to 1. Surprisingly, the surface S/ metal ratio (by XPS) was low initially but rose after EC. The surface Co/W ratio was only 0.4, considerably less than the bulk value suggesting some surface segregation. After EC this was reversed, rising from 0.4 to 6.2 indicating that the W dissolved during the ORR experiments in perchloric acid.

The W 4f and S 2p narrow scan XPS spectra in figure 29 help to explain this phenomenon. The W 4f spectrum of the WS₂ film compares well with that of the standard powder from which the target was made but the mixed Co/W disulfide exhibits a clear shift of the W 4f doublet to higher binding energies characteristic of tungsten

oxide (WO_3) rather than the sulfide. It would appear, therefore, that, like the CrSe films, the W in these films has sequestered oxygen from the chamber atmosphere and formed a surface oxide. It was this that dissolved during the electrochemical evaluation. The S 2p spectrum for the WS_2 thin films shows a single, broad peak rather than the expected doublet seen in the standard WS_2 powder. This may be due to a high degree of disorder in the as-prepared film. The peak for the Co/W sulfide thin film is shifted to a lower binding energy similar that for a monosulfide. This is expected from a very metal rich film (see table 7). After EC the sulfur level was increased to that expected for a CoS_2 film after the surface W oxide dissolved.

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

Table 7: Bulk (EDX) and surface (XPS) compositional analysis of the WS_2 and W-Co-S thin films.

Figure 29: XPS narrow scan spectra of the W 4f and S 2p peaks in both the WS₂ and Co-W-S thin films compared to a reference commercial WS₂ powder.

The oxygen reduction Tafel plots are shown below in figure 30. Clearly, there is no advantage to adding W to the CoS₂ thin films although the possibility of this result being confounded by the presence of oxides in the film cannot be ruled out. The poor performance of the WS₂ film suggested that the OCP could not be raised by adding W to the CoS₂ and this work was not pursued further.

Figure 30: ORR Tafel plots for [a] Pt thin film, [b] CoS₂, [c] Co-W-S, [d] WS₂

In order to study the addition of Ni to the CoS₂ pyrite thin films, composite sputtering targets containing both NiS₂ and CoS₂ were fabricated as before. In order to assess the activity of the pure NiS₂, itself a pyrite, a pure NiS₂ target was also made. Thin films were deposited of both NiS₂ and (Co,Ni)-S. The surface composition of the first two (Co,Ni)-S films are shown in table 8 below. The proportions of the sulfur species were obtained by curve fitting the S 2p peaks as before in the analyses of the FeS₂ and CoS₂ thin films. The NiS₂ thin film was identified as being primarily pyrite disulfide with 15% surface polysulfides as was the first (Co,Ni)-S film but the second ternary thin film was predominantly monosulfide with less polysulfides on the surface (8%). The surface of this film was also found to be Ni-rich. This analysis was supported by the S 3s and valence band edge spectra shown in figure 31. Compared with the spectrum S 3s spectrum for CoS₂ the NiS₂ shows the splitting of the S 3s peak indicative of a S₂²⁻ pyrite structure but there appears to be less coupling of the metal 3d and S 3p near the band edge. The first (Co,Ni)-S film shows a similar spectrum to that for CoS₂ but the

other displays a single S 3s peak supporting the S 2p curve fit in indicating a predominately monosulfide structure. It is worth noting that this films also has significantly less coupling of the metal 3d states and the S 3p. There are indications from the earlier work that this coupling is important in determining the catalytic activity of the thin films.

Thin film compositions determined using XPS			
Magnetron sputtering	Target: pressed NiS ₂ powder + elemental S	Target: pressed NiS ₂ , CoS ₂ powders & elemental S	Target: sintered NiS ₂ , CoS ₂ powders & elemental S
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

Table 8: Thin film compositions (by XPS) of three films in the (Co,Ni)-S system. The proportions of the sulfur species were obtained by curve fitting as in the previous FeS₂ and CoS₂ films. The pure NiS₂ is also shown for comparison.

Figure 31: S 3s and valence band edge XPS spectra for the (Co,Ni)-S system thin films studied initially.

The ORR Tafel plots for these three films are shown in figure 32 below. It can be seen that the OCP of the pure NiS₂ thin film, at 0.80V vs. RHE, is lower than that for the CoS₂ but higher than for FeS₂ shown above in figure DD. The current at 0.7V is more than an order of magnitude lower than CoS₂. This may be because of the poor metal 3d/ S 3p coupling discussed above. The ternary monosulfide film is very similar (curve e) but that of the ternary Co-Ni disulfide (curve b) is 80mV higher than CoS₂ and at 0.8V the current is an order of magnitude larger than the CoS₂ thin film. It must be remembered when discussing the thin films' activity that the surface areas are similar as the geometric areas are identical. This is not the case for dispersed powder catalysts whether supported or not.

Figure 32: ORR Tafel plots of the films studied in the (Co,Ni)-S system [b] disulfide, [e] monosulfide. . The plots for Pt [a], CoS₂ [c], and NiS₂ [d] are also shown for comparison.

O₂ saturated 0.1M HClO₄; ambient T; $\omega = 2000\text{rpm}$; $\nu = 5\text{mVs}^{-1}$

In order to understand the surprising activity of this film which exceeds that of either NiS₂ or CoS₂ and comes close to the required activity for fuel cell testing, further characterization of this film was carried out after electrochemistry (EC) using XPS, XRD, Auger and Raman spectroscopies. The Auger spectra of the films before and after EC are shown in figures 33 (survey scan) and 34 (narrow scan). The survey scans for NiS₂ and (Co,Ni)S₂ films are shown in figure 33 below. All the expected features are present: sulfur LMM and KLL peaks, carbon KLL due to adventitious carbon (the film is too thick to detect the GC substrate), and the Co and Ni LMM features between 600 and 900eV. The NiS₂ film as prepared had a small amount of oxygen on the surface but this was not detected after EC; apart from this, for both films, there is little change in the nature of

Figure 33: XPS survey scans for the NiS_2 film before [a] and after [b] EC and for the Co,Ni disulfide film before [c] and after [d] EC.

Figure 34: Narrow scan Auger spectra of the metal LMM region for [a] the CoS_2 [b] NiS_2 and [c] Co+Ni in the Co,Ni disulfide thin films.

the surfaces of the two films as a result of the electrochemical evaluation indicating the stability of the films. Unfortunately, the Ni and Co peaks overlap severely making it impossible to determine the Co:Ni ratio using AES. XPS, however, was able to provide the data in table 8 above. In figure 34 the metal LMM features for the CoS₂, NiS₂ and (Co,Ni)S₂ films are shown in more detail. In all three cases the additional peaks (arrowed) indicative of bonding of the metal to sulfur can be seen.

The Raman spectrum for the high performing (Co,Ni)S₂ thin film is shown in the centre of figure 35 below where it is compared with the spectra for the commercial CoS₂ and NiS₂ from which the sputter target was made. It can be seen that the spectrum for the CoS₂ has two prominent peaks at 287 and 389cm⁻¹ and a shoulder at 410cm⁻¹ which is in agreement with literature values for CoS₂ and the NiS₂ spectrum shows a small peak at 282cm⁻¹ and a sharp peak at 477cm⁻¹ with a shoulder at 488cm⁻¹ corresponding to literature values for NiS₂ single crystals. The spectrum for the (Co,Ni)S₂ thin film does not show the characteristic peaks for both CoS₂ and NiS₂ superimposed as would be expected for a simple mixture of the two phases. There is a broad peak centred at 409cm⁻¹ in between the CoS₂ peak at 389cm⁻¹ and the NiS₂ peak at 477cm⁻¹. The broad peak in between these two peaks are indicative of a solid solution and, as the peak extends into the region of 460-470cm⁻¹ where polysulfides are found, the presence of these species cannot be dismissed.

High-resolution X-ray diffractograms measured for the CoS₂, NiS₂ and (Co,Ni)S₂ like thin films after electrochemical measurements are shown in figure 36. Some broader peaks seen are associated with glassy carbon (marked GC), but the characteristic peaks located at $\theta=18.13^\circ$ in the CoS₂ pattern and at $\theta=17.60^\circ$ in the NiS₂ pattern are in good agreement with the (210) peaks for respectively bulk CoS₂ and NiS₂. By applying the Scherrer equation to the characteristic peaks of the CoS₂ and NiS₂ thin films, the average particle sizes were estimated to be ca 25 and 34 nm respectively. An additional structure, comprising of a shoulder at ca $\theta=11.00^\circ$, is detected in the diffractograms measured for all three thin-film samples, and this could indicate the presence of elemental S and/or anionic polysulfide species.

Figure 35: Raman spectrum of the $(\text{Co,Ni})\text{S}_2$ thin film compared with those of the commercial powders used to make the sputter target from which it was made.

The XRD pattern obtained from the $(\text{Co,Ni})\text{S}_2$ thin-film sample shows two small peaks at $\theta=17.41^\circ$ and 17.96° , and hence differences from the characteristic peaks identified for the CoS_2 and NiS_2 thin film. An examination using an XRD simulation package (Powdercell, Powder Cell for Windows, Version 2.4, Federal Institute for Materials Research and Testing, Germany) excluded the two small peaks observed for the $(\text{Co,Ni})\text{S}_2$ thin film as arising from elemental components (formed by Co, Ni and S) or from binary compounds formed by Co and S, or by Ni and S. On the other hand, these small peaks are within the fingerprint region identified for recognizing a $(\text{Co,Ni})\text{S}_2$ solid

solution (or alloy formation). Their smallness indicates that the (Co,Ni)S₂-like film has low crystallinity compared with the CoS₂ and NiS₂like thin films, although the Scherrer equation applied to these peaks suggests that the contributing particles have an average dimension around 40nm. We conclude this sample is basically composed of an amorphous matrix with interspersed nanocrystallites.

The peak at $\theta=17.96^\circ$ is positioned between the (210) peaks of CoS₂ and NiS₂ (both have the pyrite structure), which could be consistent with the (210) peak from a (Co,Ni)S₂ solid solution. That hypothesis was pursued according to the following discussion. Assuming that it originates with reflections from the (210) planes of a pyrite structure, the lattice constant for the experimental peak at $\theta=17.96^\circ$ is established to be 5.5860 Å, a value that can be compared with the two parent lattice constants (5.5350 Å CoS₂ and 5.6700 Å for NiS₂), assuming those for the Co_xNi_{1-x}S₂ series of alloys follow a linear relation between x and lattice constant. On that assumption, x is estimated to be about 0.6, and fortuitously Bouchard *et al.* reported the value 5.5861 ± 0.0005 Å for Co_{0.6}Ni_{0.4}S₂, suggesting an overall consistency with our assumption for the origin of the peak at $\theta=17.96^\circ$. We are not aware of a XRD database that covers the wider (Co,Ni)S₂ series of solid solutions, and background data are lacking for identifying the origin of the small experimental peak at $\theta=17.41^\circ$. Nevertheless, the consistent argument given here for the small peak at $\theta=17.96^\circ$ does provide *prime facie* support for the belief that the (Co,Ni)S₂like thin film studied involves solid solution (alloy) formation, rather than a mixture of the separate parent compounds.

Figure 36: XRD data for the $(\text{Co,Ni})\text{S}_2$ thin film compared with CoS_2 and NiS_2 thin films.

Following the success of the $(\text{Co,Ni})\text{S}_2$ thin film which gave an OCP of 0.89V vs. RHE several new films were made to vary the Co:Ni ratio to see what effect it had on the activity. The 1:1 ratio was also repeated. A summary of the films that were subjected to analysis is shown in table 9 below. Film #1 is the one with the high OCP discussed above. Film #11 is a similar film with the same Co:Ni ratio. As far as possible, the deposition conditions were identical for all the films shown. Film #6 has a high Ni content and #9 a high Co content. All had a similar surface S/metal ratio as determined from XPS and were stable, with little change in surface composition after EC.

CoNiS ₂ thin films				
Thin Film	# 1	# 11	# 6	# 9
E _{eq} (V vs. RHE)	0.89	0.80	0.77	0.80
Bulk atomic ratio Co/Ni from EDX	1.5	1.5	0.4	6.6
Surface S/M atomic ratio from XPS (as prepared)	3.1	3.4	3.0	2.8
Surface Co/Ni atomic ratio from XPS (as prepared)	1.1	1.6	0.4	4.9
Surface S/M atomic ratio from XPS (after EC)	3.8	3.8	3.6	3.2
Surface Co/Ni atomic ratio from XPS (after EC)	1.5	1.6	0.5	7.6

Table 9: Bulk composition (EDX) and surface composition (XPS) of the various (Co,Ni)S₂ thin films tested. The OCPs are also shown.

Table 9 also shows the OCPs of the films tested. It can be seen that the OCP of 0.89V is not repeated even by film #11 which has a very similar composition deposited under similar conditions. Figure 37 shows the ORR Tafel plots for these films compared with the other data already discussed. It would appear that the high OCP could not be repeated and all films gave an OCP around 0.8V which is similar to CoS₂ without the added Ni. An explanation must be sought as to why this is the case. There is considerable spectroscopic evidence for the presence of polysulfides on the surface of these pyrite films regardless of the metals used. It may be posited that these species play a major rôle in the ORR mechanism on these catalytic surfaces. It is known that these species may be formed in S vapour during an electrical discharge similar to the plasma environment in the deposition chamber. Also, when the sputtering is stopped there may be considerable amounts of S vapour left in the chamber which may condense on the surface of the thin films in an uncontrolled way. With no clear indication of these conditions it would be very difficult to reproduce the precise

environment necessary to deposit the surface species responsible for the high OCP. Transition metal polysulfides are not widely studied and have certainly never been considered as electrocatalysts.

Figure 37: ORR Tafel plots for the (Co,Ni)S₂ films in table 9. The plots for Pt, CoS₂ and NiS₂ are included for comparison. Oxygen saturated 0.1M HClO₄; ambient T; $\omega = 2000\text{rpm}$; $v = 5\text{mVs}^{-1}$.

It has been demonstrated here that sputtering thin films is an effective tool in the study of the ORR activity of non-metallic materials. Detailed surface compositional analysis is possible and direct comparisons between samples and standards are straightforward as the electrode areas may be considered equal. This is an advantage over the study of novel catalytic systems prematurely developed as nanodispersed catalysts.

(c) The development of powder catalysts

The initial plan defined the development of powder catalysts as being carried out with the downselected compositions after the thin film stage of the project. Timelines, however, became under pressure and, early on in the project, it was decided to carry out some parallel work to validate the approach of the thin films. At the same time it was planned that work at CASE using HRTEM would investigate and develop accurate methods to estimate catalyst surface area from particle size distribution measurements so that the activity of nanodispersed catalytic materials could be compared with Pt baselines once fuel cell testing was underway.

Initial work at CASE concerned the development of HRTEM methods to determine the particle size of nano-dispersed catalysts and this was done using commercially available Pt catalyst (Johnson Matthey HiSpec4000). It was noted that a significant proportion of the Pt particles were not spherical but faceted and steps and faults were visible in many cases. It was also noted that rather than the particles sitting on the carbon surface with no more than a tangential contact, there appeared to be a significant portion of the Pt particle completely occluded by a "neck" of carbon that formed the actual support. These features are illustrated in the HRTEM brightfield image in figure 38 below. In order to develop an automated image processing method it is important to be able to differentiate between Pt particles and the carbon. It was found that a scanning transmission electron microscope (STEM) using a high angle annular dark-field (HAADF) detector the high atomic number of Pt meant that the contrast between the Pt and the carbon was easy to differentiate with appropriate thresholds. In many images the Pt particles appear to overlap even when not clustered because of the transparency of the carbon support. These overlapping particles would appear, in STEM-HAADF mode, to be a single large, irregular particle making accurate measurements difficult. It was found that it was possible to differentiate between overlapping particles by Fourier transformation of the lattice fringes of a particular crystal orientation. The bright spot corresponding to the FT of these fringes can be mapped and all the background intensity set to zero. Then, by performing an inverse

Fourier transform, the original image may be produced of only the one particle. Figure 39 shows how, after this process (referred to as "selected Fourier component imaging" or SFCI) the image, after inverse Fourier transformation back into real space and the application of false colour with appropriate thresholds, may yield a simple outline of the particle which is easy to process to measure its area. This area may be converted to a "diameter" by calculating the diameter of a spherical particle with the same cross-sectional area. This does involve the introduction of an error due to faceting observed and it is possible that with more detailed work, it may be possible to adjust for a faceted crystal shape. Nevertheless, it was possible to measure a large number of particles and develop a mean particle size (3.2 ± 0.99) nm within which the specified particle size of 3.7 nm falls. This asymmetry leads to a discrepancy between the mean particle size measured by TEM and that determined from XRD as the higher scattered intensity from larger particles tends to skew the mean to higher values using XRD than by statistical analysis of TEM images. Having the image treatment methodology developed, the group at CASE waited for samples of non-precious metal catalysts to study.

Figure 38: HRTEM image of a single Pt particle. The viewing direction corresponds to the $\langle 110 \rangle$.

Figure 39: [a] shows a STEM-HAADF image of a single Pt particle. [b] shows the image after SFCI and false colour have been applied. Application of suitable thresholds in [c] produce a simple outline of the particle.

The first carbon supported non-precious catalyst fabricated in this project was the same nominal composition as the first thin film; CoSe. The volatility of the Se vapour used in the fabrication, as described in the experimental section, led to an incomplete reaction with the cobalt metal. TEM images of the catalyst in figure 40 and XRD data in figure 41 indicate that two phases were initially present. A CoC phase, a result of the heat treatment on the unreacted Co was mixed with distinct crystallites containing only Co and Se and with a crystal structure similar to $\text{Co}_{0.85}\text{Se}$.

Figure 40: TEM images of different samples of the CoSe catalyst. Analysis at point [1] indicates 42.5at% Co, 57.5at% Se; point [2] shows only a trace of Se with Co, C and O; point [3] shows only Co, C, & O.

The conditions of fabrication of this catalyst were not optimized and it is believed that it would be possible to obtain a complete conversion of the Co to the $\text{Co}_{0.85}\text{Se}$ phase. The electrochemical activity of this catalyst is shown in figure 42. The OCP was 0.78V and a clear Tafel slope was obtained although this was found to be 182mV/decade which is much steeper than for the Pt catalyst which was 63mV/decade which is close to the expected value at 30°C. It is not clear why the Tafel slope is so high as no mechanistic study is possible without a very accurate measurement of the surface area and a detailed characterization of that surface which is not feasible for nano-dispersed catalysts.

Figure 41: X-ray diffractogram from the CoSe powder catalyst (Cu K α radiation).

Figure 42: [a] ORR Tafel plot of 88.5 μ g of the catalyst (nominally 50%wt Co),
[b] similar plot for 50 μ g 40% Pt on XC72R (Johnson Matthey).

O₂ saturated 0.5M H₂SO₄, ω = 2000rpm, v = 5mVs⁻¹, T = 30°C

It should be noted here also that the ORR currents in figure 42 may not be as comparable as they look; the surface area of the CoSe is at least an order of magnitude smaller than the Pt.

Attempts to increase the interaction of the Se with the Co led, unexpectedly, to the fabrication of a CoSe_2 supported catalyst. Given the results with pyritic disulfide catalysts we were given the opportunity to evaluate a catalyst composition we were unable to sputter as a thin film.

Figure 43: (a) X-ray diffractogram from the carbon supported catalyst and (b) the powder file data for CoSe_2 pyrite (International Center for Diffraction Database, PDF 00-065-3327).

Figure 43 above shows that the XRD data for this material matches closely the peak positions and intensities for the CoSe_2 crystal structure, confirming that this catalyst is the pyritic disulfide and not the expected monosulfide. HRTEM analysis at CASE indicated that the CoSe_2 forms large, faceted crystals upon the carbon support (figure 44). EDX measurements confirmed that the Se:Co ratio was 2 as expected. Image analysis was used to determine the particle size distribution as shown in figure 45. The particle size was much larger than for commercial Pt catalysts at predominantly between 100 and 240nm.

Figure 44: TEM image of the CoSe_2 supported catalyst showing agglomerations of large, faceted crystals.

Figure 45: Histogram of the particle size distribution represented by the Heywood diameter for a sample of 300 particles of the CoSe₂ powder catalyst.

Figure 46: ORR Tafel plots for the carbon supported Co-Se catalysts studied in this project. [a] XC72R without catalyst; [b] Co_{0.85}Se on XC72R; [c] CoSe₂ on XC72R and [d] Pt on XC72R (Johnson Matthey HiSpec4000).

It can be seen in figure 46 that the activity of the CoSe_2 powder catalyst has an OCP which is 90mV higher than the $\text{Co}_{0.85}\text{Se}$ catalyst. The ORR current at 0.7V is 2 orders of magnitude smaller than that of the Pt catalyst but the catalyst size is also much larger indicating that the turnover rate in terms of current density at the catalytic surface may be similar. Unfortunately, agglomeration and the faceting of the particles made an estimation of the catalyst surface area fraught with inaccuracies. Also, without a detailed mechanistic study on better defined surfaces, such as sputtered films, it is not possible to equate the active site density to the surface as in the case of platinum. Analysis of the catalyst, before and after electrochemical evaluation, indicates the catalyst is stable over this timeframe in an acidic electrochemical environment. The improvement of the pyrite, diselenide structure over the monoselenide is expected following the difference between the predominantly monosulfide thin film and the disulfide thin film in figure 23 above.

Powder disulfide catalysts were made based upon a catalyst loading on XC72R based upon a nominal 50 wt% Co metal. The synthesis as described in section 2(b) above was used to produce a number of catalysts comprising CoS_2 or the solid solution $(\text{Co,Ni})\text{S}_2$ to match the work done on thin films. The latter was made by co-precipitating the monosulfide with Na_2S solution prior to the reaction with H_2S gas at 250°C . Figure 47 below shows HRTEM images for the CoS_2 and $(\text{Co,Ni})\text{S}_2$ supported catalysts. Micrography proved challenging for these samples, nevertheless, against the background of the essentially amorphous carbon black, the crystallinity of the sulfide materials was established using the Fourier transform of the images (shown in the inserts). Safety issues with the use of H_2S gas at Ballard prompted us to seek an alternative approach to synthesis using S vapour in a vacuum furnace. Unfortunately, optimization of this process eluded the team until the project ended. The electrochemical evaluation of these catalyst was carried out using a GC RDE as described above. The results are shown in figure 48 where it can be seen that the catalysts all have similar OCPs. The impact of the Ni is more subdued than with the thin films but it can be seen that the supported catalysts are higher than the unsupported materials, probably due to a higher dispersion, and the $(\text{Co,Ni})\text{S}_2$ is slightly

Figure 47: HRTEM images of [a] CoS_2 on XC72R and [b] $(\text{Co,Ni})\text{S}_2$ on XC72R. The inserts show the Fourier transform of the image indicating the crystallinity of the catalyst material.

Figure 48: ORR Tafel plots of for the XC72R supported disulfide catalysts evaluated. O_2 saturated 0.1M HClO_4 ; $T = 30^\circ\text{C}$; $\omega = 2000\text{rpm}$; $v = 5\text{mVs}^{-1}$.

higher than the CoS_2 catalyst. The activity in terms of the current cannot be easily compared as the materials have very different active surface areas. The particle size distribution of these materials proved difficult and was not measured. The difference between the thin film behaviour of the $(\text{Co,Ni})\text{S}_2$ and the powder catalyst is noted. The evidence for the presence and relative importance of the polysulfides on the surface of the sputtered thin films suggests that these species may form an active site on the catalyst surface. The powder catalysts were fabricated using a wet chemical approach followed by a gas phase reaction. These reactions are based upon chemical equilibria and so are unlikely to form polysulfides. The fact that the powders, albeit with similar bulk structure and composition, do not behave in the same way lends support to the importance of polysulfides in the ORR activity of these dichalcogenide surfaces that would warrant further study.

In order to get an idea of the stability of these catalyst materials under normal operation each catalyst was cycled at 100mVs^{-1} from 0.1V to 1.4V for 100 cycles and the ORR activity was measured again. The results are shown on figure 49 below. It can be seen that the OCP of both the CoS_2 and the $(\text{Co,Ni})\text{S}_2$ catalysts rise significantly upon cycling. The highest OCP is for the CoS_2 which rises to 0.98V vs. RHE, a potential much higher than previously recorded for a cobalt sulfide catalyst. Unfortunately, this is associated, in both catalysts, with an increase in the apparent Tafel slope leading to a significant drop in turnover rate as the overpotential increases. The changes that must be occurring on the catalyst surface cannot be understood using nanodisperse catalysts. Unfortunately, the thin films were not cycled to such a high potential as durability was not planned until powder catalysts were fabricated and fuel cell testing could begin. The increase in Tafel slope means that, even with the high OCP, the overall activity of these catalysts was not high enough to start fuel cell testing. It has been reported in the literature that it is possible to generate polysulfide species electrochemically and it is possible that this is what is occurring on these catalysts during cycling.

Figure 49: ORR Tafel plots for carbon supported disulfide catalysts showing the effect of cycling to 1.4V.

[4] Further Work

It is indicated in figure 49 that cycling the dichalcogenide catalysts modifies the surfaces of these materials to raise the OCP by 180mV. The effect of this sort of treatment on sputtered thin films should be studied so that the changes occurring may be understood. It is possible that this may lead to an understanding of the role of polysulfides in the ORR reaction. A mechanistic study was considered outside the scope of this project due to the limited time available. A detailed mechanistic study should be carried out on single crystal disulfides and perhaps on sputtered, epitaxial films grown on pyrite single crystals so that the active sites and the impact of the presence of polysulfides may be studied. In parallel, cobalt polysulfide materials should be manufactured and studied in isolation. It has long been considered that polymeric polymorphs of sulfur are well understood but the ionic polysulfides, where the anionic charge may be shared between as many as 8 sulfur atoms, even in ring structures, has not been widely studied in relation to their electrochemistry.

[5] Summary

The ORR activity of non-precious transition metal chalcogenides has been studied as possible low-cost alternatives to platinum in PEMFCs. A novel approach has been developed in which the catalyst materials are sputtered onto polished GC substrates so that the surface areas of each material studied has a similar surface area, including the baseline Pt thin film which was also sputtered in a similar way. This enables the activity to be directly compared without complications that normally arise when comparing the activity of non-platinum nanodisperse catalysts where the active surface area is unknown.

The activity of mono- and diselenides and mono- and disulfides has been studied. The most active materials identified are CoS_2 and the 50:50 solid solution $(\text{Co,Ni})\text{S}_2$. However, the OCP of these materials is still considered too low, at 0.83V and 0.89V vs. RHE respectively, for testing in fuel cells. Spectroscopic evidence has been found for the presence of metal polysulfides on the surfaces of these sputtered films which may play a role in the ORR mechanism. This is supported by the results obtained for the same materials nanodispersed on XC72R carbon and tested ex-situ using an RDE. The high potential of the $(\text{Co,Ni})\text{S}_2$ thin film was not reproduced although an OCP of 0.81V was produced by the CoS_2 catalyst. When these catalysts were cycled to 1.4V in 0.1M HClO_4 the OCP rose significantly (to 0.98V vs. RHE in the case of the CoS_2 catalyst) although the activity fell due to an apparent increase in the Tafel slope. This effect is not understood at this time.

The project was redirected in September 2005 to delay fuel cell testing and focus on ternary systems to increase the OCP. This was successful with the introduction of Ni to the CoS_2 thin films. Fuel cell testing was not carried out and the OCP was considered too low for the project to continue. The project was not extended beyond its planned completion date.