

Combinatorial Screening and Characterisation of Platinum Based PEM Fuel Cell Catalysts.

GR/R50639/01: Individual Grant Review

The first and essential objective of this work was to develop a methodology for the combinatorial synthesis of thin film metal alloy catalysts. This goal was fully achieved and is encompassed in a patent application [1], has now been presented at a number of scientific meetings and will shortly be published [2]. The method allows, for the first time, simultaneous wedge growth of a number of elements (up to 6 in the present chamber) allowing the synthesis of alloys and oxides, nitrides and hydrides when combined with a plasma atom source.

Experiments have been carried out in a UHV system, base pressure 1×10^{-10} mBar (DCA) consisting of two cryo-pumped PVD chambers, an ion pumped surface analysis and reaction chamber, and a turbo-molecularly pumped LPCVD chamber, specifically designed to carry out high throughput synthesis of thin film materials. Facilities for mask transfer and a fast entry port are incorporated, and the synthesis and analysis chambers are interconnected by a series of ion pumped transfer tubes for substrates of up to 4" in diameter. The experiments described here have been carried out in a PVD chamber incorporating six off axis sources, three e-beam and three Knudson, cryo-panels and shields, a manipulator with heating in the range 300-900K, quartz crystal monitors for e-beam sources and a number of shutters for the control of material deposition. Shutters and source temperatures are computer controlled to allow automated deposition of predetermined thicknesses and composition gradients of the thin film materials. The use of a fixed shutter placed at a specific position within the molecular beam produced by a PVD source during the course of deposition give rise to a controllable gradient / spread of the evaporated material. Depending upon the shutter's position within the molecular beam, the gradient can be controlled from the natural profile of the source (which has been optimized to give as uniform profiles as possible without using rotation of the substrate) to a fully controlled gradient. The position of the shutter within the chamber and the molecular beam is crucial in order to give rise to the desired profile. The different gradients are obtained by changing the position of the shutter. The location of the shutter is such that it partially masks the source, leaving some portion of the substrate in line of sight of the source, and other parts to be shadowed. Each source is controlled individually; i.e. each material can be evaporated with its own gradient. Figure 1A shows a schematic of the geometry of the six source PVD chamber used for the simultaneous deposition of metals in this project. An aperture placed between the source and the substrate allows a graded ("wedge") deposition of each of the materials across the sample. The characteristic (gradient) of the wedge growth is determined by the position of the aperture with respect to the sample and the source. By using the wedge growth method on several sources simultaneously allows the deposition of a thin film of variable composition as a function of position across the sample. Figure 1B shows the concentration of Pt, Au and Pd measured by EDS across a thin film substrate deposited simultaneously using the source configuration in Figure 1A. There is a controllable concentration gradient perpendicular to the aperture, and a near constant concentration perpendicular to the aperture. The combination of the elements produces a range of ternary alloys across the substrate. The case shown in Figure 1B represents deposition of a wide range of ternary compositions, corresponding to variants of 5% per field on the 10x10 array (below). By varying the apertures and relative rates of elemental deposition one can control the ternary alloy concentration range obtained over the sample to regions of particular interest producing variants per 1mm electrode of less than 1% atomic composition.

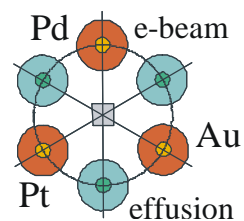


Figure 1A

The HT-PVD methodology has not only been successful in this project in producing continuous alloy thin films for electrocatalytic screening, but is suitable for the high throughput synthesis of a wide range of materials. We are investigating the scope for the synthesis of functional ceramics, chalcogenide glasses, dielectric materials and hydrogen storage materials. The intellectual property of this methodology has enabled the full exploitation of a high throughput physical vapour deposition system funded under the JIF initiative and provided a key IP component of a University of Southampton “spin out” company, Ilika Technologies Ltd.

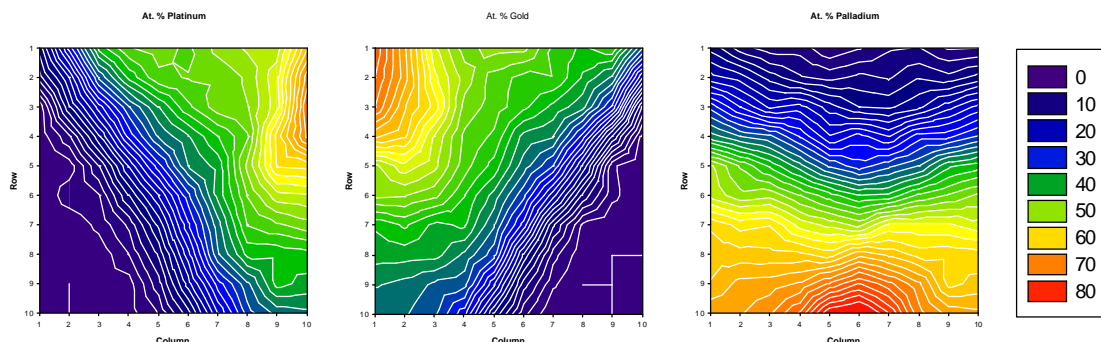
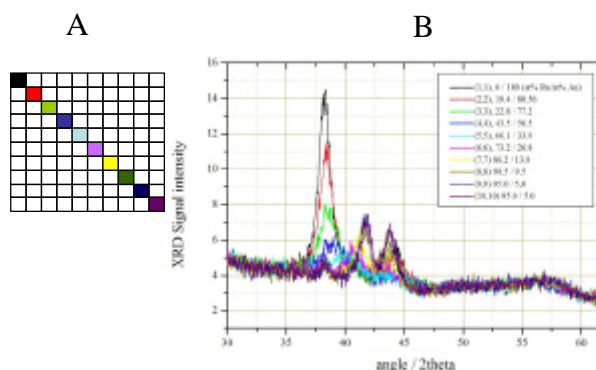


Figure 1B Shows the concentration of Pt, Au and Pd measured by EDS across a thin film substrate deposited using the source configuration in Figure 1A.

In order to obtain materials compositions, we have adapted EDS measured by electron excitation in a Jeol SEM to provide fast and automated measurements across the thin film arrays. The adaptation of the software allows compositions to be incorporated in the down stream analysis of additional figures of merit. Structural characterisation (Figure 2) has been achieved by automation of a Bruker C2 XRD (Cu Ka source ($\lambda = 1.54184 \text{ \AA}$)). High signal to noise in 2T mode (the spectrum shown is 2T from 29.4° deg to 62.4°) is achieved by integration λ from -108.1° deg to -72.7° . The result is that the spectra shown for a 75nm AuRu binary alloy film on Si with a spot size of $\sim 100\mu\text{m}$ to be obtained in 60s per sample.

Screening methods were developed in parallel to synthesis development which would allow the extraction of figures of merit relating to the activity and tolerance of thin film alloy materials for anode and cathode electrocatalysis in acid electrolyte. Two high throughput methods were developed, as described in the proposal. The first was a truly parallel screen using an optically responding counter electrode. This method is the subject of a patent application [3], the principles have been presented at scientific meetings and will be the subject of a future publication.

Figure 2 . HT-XRD of a 75nm AuRu binary alloy film on Si using an automated Bruker C2 XRD (Cu Ka source ($\lambda = 1.54184 \text{ \AA}$)). The spectra (B) shown are 2T from 29.4° deg to 62.4° integrating λ from -108.1° deg to -72.7° . The spot size was $\sim 100\mu\text{m}$ and measurement time was 60s per sample. The grid (A) shows the samples analysed on the array.



The principle of the new electrochromic counterelectrode is shown schematically in Figure 3. The cell consists of an array of working electrodes, where the test materials are deposited, and an electrochromic counterelectrode placed directly opposite. In this work we have chosen to investigate methanol oxidation on different amounts Pt catalyst, a reaction that produces protons. The

electrochromic counterelectrode is a WO_3 film on ITO-coated glass. WO_3 acts as an insertion electrode intercalating protons to balance those produced at the working electrode, this causes a colour change (colourless to blue) in the counterelectrode. A two electrode set-up is employed where the counterelectrode also functions as a pseudo-reference electrode.

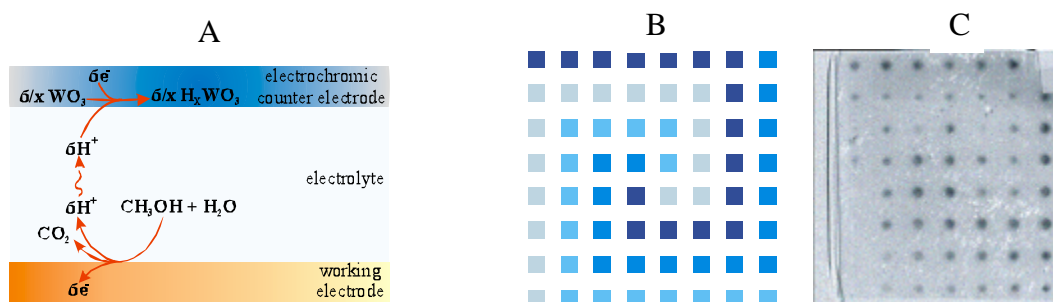


Figure 3 The principle of the electrochromic optical screen (A) is that protons generated at the working electrode (screened catalyst) during methanol oxidation are injected into WO_3 at the counterelectrode. Results of optical response (C) are shown for a series of patterned catalyst loadings shown in B. Reference [*]

This arrangement allows different points along the surface of the counterelectrode to have slightly different potentials at the same time and therefore differing intensities of blue colour are observed across the counter electrode, with darker shades indicating where more charge has been passed and hence more active catalysts. A charge (activity) distribution map of the whole array can be measured simultaneously. To maintain the local variation in the current distribution created at the array it is necessary that the electrolyte has a higher than normal resistivity. The rest of the counterelectrode is a transparent conducting oxide, and with the addition of a filter paper acting as diffuse reflector (and also cell separator) between the counter and working electrode, even small variations in the absorbance properties of the counterelectrode can be quantitatively measured using a digital camera in a single image. Such a cell eradicates the need for a separate current follower for each element of the array and hence greatly simplifies the electrochemical instrumentation required and eradicates the need for an electronically iterated array. However to demonstrate our optically screening counterelectrode we have performed the optical and electrochemical measurements simultaneously. Figure 4 shows the charge and change in absorbance of 4 loadings of Pt black on the array. The results demonstrate that the screen can be operated under conditions where there is a linear optical response with respect to the charge passed at the working electrode (catalyst) showing the method provides a realistic screening of activity.

A second screening method was developed which involved two key components for the thin film catalysts. The first was a multi-channel current follower coupled to a fast analogue multiplex interface, a potentiostat and ramp generator. This system was developed in house, together with fast and flexible control software to allow high throughput electrochemical screening of individual electrodes. The result was a fast sequential screen and characterisation which was first demonstrated on a series of supported catalysts in a 64 element screening array [4]. The second component was the design and micro-fabrication of a 10x10 gold pad electrode chip. Combined with the graded deposition method and using a contact mask, 100 thin film compositions could be deposited at the electrode fields and subsequently screened using the fast sequential methodology [4]. A photograph of the 10x10 array chip is shown. Electrodes are 1mm^2 and the over all chip size is ca. 30mm^2 . Two

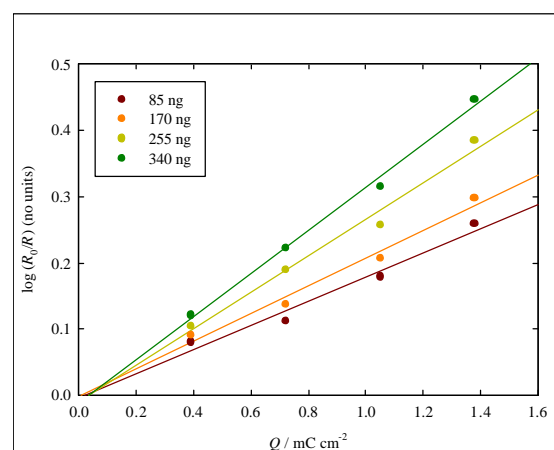


Figure 4 A linear optical response with respect to charge measured at the working electrode (catalyst) demonstrates the validity of the electrochromic screen (Figure 3).

64 channel current followers of higher sensitivity than those used for the high area catalyst screen [4] were used to carry out the measurements. The sensitivity was sufficient using this configuration to allow the 100 voltammograms at a sweep rate of 50mVs^{-1} to be recorded in ca. 60s.

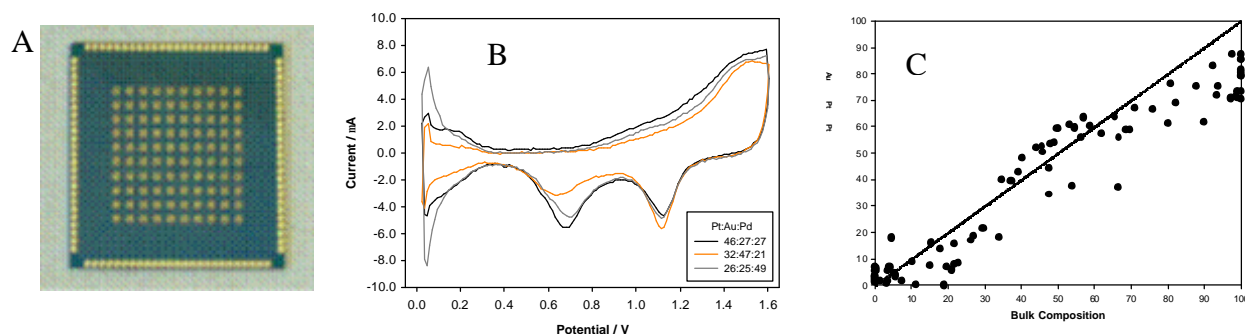


Figure 5 The 10x10 electrochemical chip (A) micro-fabricated on Si with 100 gold pads and insulated (silicon nitride) interconnect. The voltammograms (B) are taken from a set of 100 obtained in ca. 60s for three compositions of the ternary system PtPdAu. Integration of the reduction charge (C shows the binary PtAu) indicates that the surface and bulk compositions are the same within experimental error.

The ratio of the Pt and Au peaks may also be used to estimate the surface composition of Pt-Au films.[5] A correlation between the bulk composition (as measured by EDS) and the surface composition (as measured the ratio of surface oxide peak for Pt to the total of Pt and Au) is shown on the inset of Figure 3C and indicates that the surface and bulk composition of the thin film deposits are indeed the same under the deposition and electrochemical conditions. Surface analysis of the films by XPS also indicate that the surface and bulk compositions were the same.

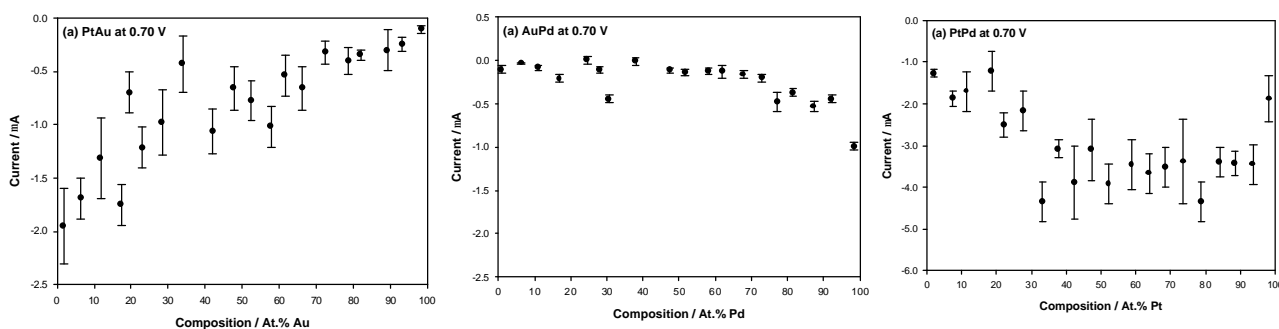


Figure 6 Steady State Oxygen Reduction on PtPdAu binary alloys at $0.7V_{RHE}$.

The steady-state activity of these thin film alloys towards the ORR at potentials between 0.7 and 0.9 V_{SHE} were evaluated in $O_2(g)$ saturated 0.5 M $HClO_4(aq)$ at 25 °C using potential step experiments. The average currents associated with the binary compositions in 5% composition ranges are shown in Figure 6 for $0.7V_{SHE}$. The trends in the variation of activity with composition are the same at both of these potentials. The activity of the individual components decreases in the order $Pt > Pd > Au$ which is of course expected. The addition of Au to Pt or Pd causes a monotonic decrease in ORR activity across the composition range. This suggests that Au is an inert diluent to the activity of Pt and Pd. The PdAu binary was the only one to show a significant interaction of the components leading to an additional PdAu alloy oxide reduction peak in the cyclic voltammograms. The activities across the PtPd binary composition space are also shown in Figures 6. There is clearly a maximum in the activity in the composition range of 50 to 90 % Pt. The activities of the ternary composition space are shown in Figure 7. It is evident from inspection of this plots that the highest activity towards the ORR is located along on nearer to the Pt-Pd axis, as one may expect from Figure 6. The addition of Au to the binary Pt-Pd compositions in the range of their maximum activities appears to draw the activity into the ternary space that contains significant quantities of Au. Indeed, it appears that addition of up to 30% Au to an optimum Pt-Pd range (70% Pt) produces a catalyst with similar activity to that of pure Pt. PtPd unfortunately may be unstable as a catalyst under operating conditions of a PEM cathode because of dissolution of the Pd component. It remains to be

determined if the addition of Au to the PtPd alloy system provides the additional stability required through the relatively strong alloying interaction with Pd. Recently the Bard group has reported that the addition of Au to a binary (PdCo) electrocatalyst improves its stability towards long term, steady-state oxygen reduction [6].

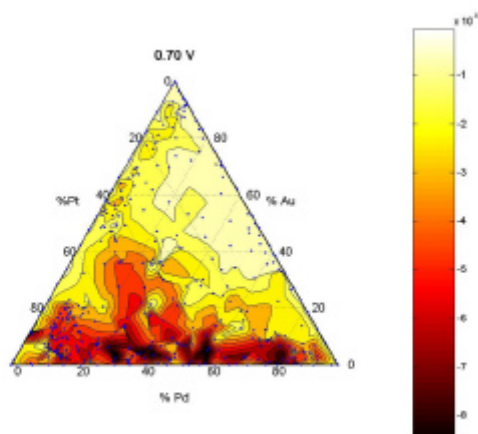


Figure 7. Steady State Oxygen Reduction on the PtPdAu binary alloys at $0.70V_{RHE}$ over the complete compositional range. The results presented are the combined measurements from ca. 700 samples ($7 \times (10 \times 10)$ arrays).

Since there is a clear interaction in the Pt-Pd components, we plot the peak potential of the Pt-Pd derived surface reduction feature as a function of the ternary components [7]. In the case of supported platinum catalysts of varying particle size, a correlation has been observed between the peak potential for surface reduction and the activity in ORR [4]. Such a correlation may be expected if the stability of the surface oxygen bond directly influences the rate of the ORR [8]. We believe that this shifting peak potential correlates with the

activity of the surface towards the ORR. It is apparent from this ternary plot that the increased peak potential attributable to Pt-Pd components extends into the composition space that includes Au.

It is disappointing not more of the work has been published at submission of this report, but this was in some part due to delays while Patent Applications were made and published because of the Spin-Out activity. The essence of the work has now been presented at a number of meetings, and we now will endeavour to publish a number of papers directly from the work in the open literature.

Meetings

IEA Annex XVI Fuel Cells (2003, 2004, 2005)
 Gordon Fuel Cell Conference (2003)
 ElectroChem, Southampton (2003)
 Trondheim Symposium, Norway (2003)
 Gordon Fuel Cell Conference (2004)
 RSC High Throughput Materials Chemistry, London (2004)
 Fuel Cell Institute, Yamanashi, Japan (2004)
 Third San Louis Symposium (2004)
 Catalysis from First Principles, Copenhagen (2004)
 Gordon Research Conference, Oxford (2005)

References

- [1] B. E. Hayden, S. Guerin. Vapour Deposition Method. *International Patent Application PCT/GB04/004255*, 2004.
- [2] S. Guerin, B. E. Hayden, C. E. Lee, C. Mormiche, Nature Materials to be submitted. (2005)
- [3] J. R. Owen, A. R. Russell, B. E. Hayden, P. N. Bartlett, K. Brace. Method for the Testing of Multiple Materials for Electrochemical Uses. In *International Patent Application PCT/GB04/000085*, 2004.
- [4] S. Guerin, B. E. Hayden, C. E. Lee, C. Mormiche, J. R. Owen, A. E. Russell, Journal of Combinatorial Chemistry. 6 (2004) 149.
- [5] R. Woods, Electrochimica Acta 16 (1971) 655.
- [6] J. L. Fernandez, D. A. Walsh, A. J. Bard, J. A. C. S. 127 (2005) 357.
- [7] S. Guerin, B. E. Hayden, C. E. Lee, C. Mormiche, to be submitted. (2005)
- [8] J. K. Norskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jonsson, J. Phys. Chem. B 108 (2004) 17886.