Co-sputtered Pt_xPd_yAl_z thin film electrocatalysts for the production of hydrogen via SO₂(aq) electro-oxidation

A. Falch^a, V.A. Badets^b, C. Labrugère^c, R.J. Kriek^{a*}

^aElectrochemistry for Energy & Environment Group, Research Focus Area: Chemical Resource Beneficiation (CRB), North-West University, Private Bag X6001, Potchefstroom, 2520, South Africa

^bISM, CNRS UMR 5255, University of Bordeaux, F-33400 Talence, France

^cPLACAMAT UMS 3626 CNRS, University of Bordeaux, 87 av. Albert SCHWEITZER, 33608 PESSAC Cédex-FRANCE

Abstract

A co-sputtered Pt_xPd_yAl_z ternary system was investigated for potential use as anode catalyst for the electro-oxidation of aqueous sulphur dioxide (SO₂), a key reaction in the hybrid sulphur (HyS) process for splitting water into hydrogen and oxygen. Combining the noble metals Pt and Pd with Al resulted in no significant improvement in onset potential, however, current output was improved for the majority of the electrocatalysts evaluated. Of these electrocatalysts only a single ternary composition exhibited improved stability when compared to pure Pt. It was found that a combination of Pt₄₀Pd₅₇Al₃ (annealed at 900 °C) exhibited superior performance when compared to pure Pt and the previously determined best binary electrocatalyst, i.e. Pt₃Pd₂. Current density (mA.mg Pt⁻¹) increased from 108.11 to 181.21 and finally to 396.73 for Pt, Pt₃Pd₂ and Pt₄₀Pd₅₇Al₃ respectively, indicating an increase in activity that correlates with a decrease in Pt content. Atomic force microscopy (AFM) revealed an increase in surface roughness for Pt, Pt₃Pd₂ and Pt₄₀Pd₅₇Al₃, while the occurrence of metal interaction and certain degrees of Al migration (a result of annealing) was confirmed for Pt₄₀Pd₅₇Al₃ by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction analysis (XRD).

Keywords: SO₂ electro-oxidation, hydrogen production, electrocatalyst, high-throughput screening

*Corresponding Author: E-mail: cobus.kriek@nwu.ac.za, Tel no: +27 (0)18 299 2345

1. Introduction

Hydrogen, the only non-carbon containing energy carrier, is the most abundant atom on earth ¹ and is considered as the ultimate clean energy carrier to be generated from renewable resources ². The range of hydrogen production processes can roughly be divided into hydrocarbon-based (steam-methane reforming and coal gasification), non-hydrocarbon based (water electrolysis and thermochemical water decomposition) and integrated (steam-methane reforming linked to non-hydrocarbon based) ³. As hydrogen is only found as part of compounds on earth, it is fairly energy intensive to separate hydrogen into its molecular form ¹, and goes hand in hand with huge amounts of environmental pollutants being emitted to the atmosphere. If, however, hydrogen can be returned/produced as part of a remediation process of these detrimental environmental pollutants, a portion of the energy input for the remediation process can be returned in the form hydrogen. This is exactly what the hybrid sulphur (HyS) cycle, a thermo-electrochemical water splitting process, accomplishes, through the electrochemical oxidation of aqueous sulphur dioxide (Figure 1). Thermochemical processes produce hydrogen through a series of chemical reactions with water-splitting being the net reaction. Since hydrocarbons are not used in these thermochemical processes no harmful emissions such as carbon dioxide (CO₂) are produced, with the hydrogen produced being extremely pure ⁴. There are various thermochemical cycles (a combination of thermochemical and electrochemical reactions ⁵) that can produce hydrogen from water with the HyS cycle (reactions 1 – 4) being the most promising ^{4, 6-8}.

Figure 1: The thermo-electrochemical HyS cycle for the splitting of water.

The HyS cycle undergone extensive development in the 1970s^{9, 10} and 1980s^{10, 11}. For the subsequent 20 years, further development nearly ceased as advanced nuclear technologies gained increased interest¹⁰. After this period, interest in the HyS cycle revived and the HyS cycle was subsequently rated first among 115 thermochemical cycles considered¹². Interest in the HyS cycle results from the fact that, whereas the anodic reaction for regular water electrolysis occurs at a standard potential of 1.23 V (SHE)¹³, the anodic reaction for SO_2 depolarised electrolysis (SDE) occurs at a standard potential of 0.17 V (SHE)¹⁴, which translates into an energy gain of more than one volt^{7, 15}. In SDE the rate determining step occurs at the anode, which results in the anode attributing to the inefficiencies of the SDE¹⁶. To this regard, an optimal operational target of 500 mA.cm⁻², at a cell potential of approximately 0.6 V, has been proposed for SDE by Gorenssek and Summers^{7, 17}. This target can potentially be achieved through the development of an effective electrocatalyst for the anodic electro-oxidation of SO_2 and to that regard the properties of the anode is regarded as pivotal for improving the entire HyS process^{18, 19}.

While platinum is generally considered the standard anode catalyst for the SDE^{8, 16}, efforts are underway to identify an electrocatalyst other than platinum (see^{20, 21} for a detailed list of investigated catalysts). As Pt is costly the development and implementation of a catalyst with increased or equal catalytic activity and reduced cost (less Pt) will be advantageous. Platinum content could be reduced by alloying/combining it with either a more cost effective noble metal or base metals in an effort to still maintain acceptable catalytic activity^{20, 21}. An earlier investigation by us (employing sputtered thin films) has shown that Pt content can indeed be reduced by combination with Pd, i.e. Pt_xPd_y , without sacrificing electrocatalytic activity²¹. A thin film combination of Pt_3Pd_2 has specifically been found to exhibit competitive performance compared to pure Pt for the electro-oxidation of aqueous SO_2 with annealing further improving performance²¹. For this study aluminium (Al) was introduced as a third component in an attempt to lower the content of both Pt and Pd (both noble metals). Al is considered a metal of great electrochemical potential²² and a study by Lee²³ on Pt and Al combinations proved that only small amounts of Al is effective in improving catalytic performance towards aqueous SO_2 electro-oxidation. This study by Lee was brief and no subsequent investigations were pursued²⁴. For this investigation we employed combinatorial evaporative sputtering and high-throughput parallel screening in search of $\text{Pt}_x\text{Pd}_y\text{Al}_z$ electrocatalysts for the electro-oxidation of SO_2 . Identified compositions that merit more thorough investigation were evaluated employing conventional methods.

2. Experimental

2.1. Preparation, deposition, screening and annealing of thin films

The wafer and glassy carbon preparation, thin film deposition and electrochemical testing have previously been described in-depth^{20, 21}. Employing a built-in quartz crystal microbalance (QCM)²⁰ and Pt, Pd and Al targets, all with a purity of 99.99 % (ACI alloys), the conditions for physical vapor deposition (PVD) were derived for the chosen compositions. The thin films (~60 nm) were subsequently deposited in triplicate by PVD, onto an annular arrangement (Patent Application No. 2015/08424) of 64 square working electrode pads (0.09 cm² each), developed through photolithography²⁰ (Figure 2). The electrode pads were connected by a network of traces to individual rectangular pin pads on the outer perimeter of the wafer. The network of traces were provided with reinforced bending points to prevent braking of the lines/traces. For the conventional electrochemical testing glassy carbon inserts (0.196 cm² each) were employed as substrate onto which the thin metal films were deposited.

Electrochemical testing was performed on the wafer containing the various thin film compositions, in a dedicated electrochemical cell ²⁰, with each working electrode connected individually to a multichannel potentiostat (Arbin MSTAT) for high-throughput screening while conventional testing commenced in a standard three electrode setup ²¹. Preconditioning was conducted in degassed 0.1 mol.L⁻¹ HClO₄ (Merck), scanning from 0.041 V vs SHE to 1.441 V vs SHE starting at E_{ocp} (open circuit potential) for 25 cycles, followed by 3 cycles up to 1.741 V vs SHE and finally the first step was repeated but only for three cycles, employing a scan rate of 50 mV.s⁻¹ respectively. Linear polarisation (LP) was conducted in 1 mol.L⁻¹ H₂SO₄ (Merck, pH = 0.55) in the potential window 0.2 V vs SHE to 1.441 V vs SHE at a scan rate of 10 mV.s⁻¹. This solution was degassed with N₂ for 15 min prior to linear polarisation. A stock solution of 1 mol.L⁻¹ Na₂SO₃ (Sigma Aldrich) was used as an in-situ SO₂ source ²⁰. These electrochemistry testing parameters were identical for the thin films deposited onto the wafer and the glassy carbon inserts. In addition internal resistance (i-R) drop was measured to be 46 Ω for the conventional electrochemical setup employing the various combination of thin films sputtered onto glassy carbon inserts. i-R compensation was intentionally not applied to LP scans as it damps current oscillations (as is observed for our catalyst (not shown)) which is specific to catalytic activity and relates to mechanistic phenomena ²⁵ (mechanistic investigation was not part of the scope). Subsequent to the deposition of the selected thin film combinations onto the glassy carbon substrates (designated with letters of the alphabet as a means to ease comprehension throughout the article), some were kept as fresh (as-deposited) thin films while the rest of the thin films were annealed ex-situ under an Ar atmosphere, employing a rapid thermal annealing oven (Accuthermo AW610), with the maximum temperatures ranging from 600 °C to 900 °C with intervals of 100 °C ²¹.

Figure 2: Annular arrangement of 64 square working electrode pads (Patent Application No. 2015/08424).

2.2. Physical characterisation of thin films

Energy-dispersive X-ray spectroscopy (EDX, employing INCA software) analysis, in moving average mode employing a collection time of 100 s and a 15 keV electron source, was conducted in triplicate before and after electrochemical testing, so as to evaluate thin film composition. Atomic force microscopy (AFM, Nanoscope V Multimode from Veeco) was used to investigate surface roughness, deriving various surface roughness parameters by employing Nanoscope Analysis (Veeco) software. In addition, surface properties of the thin films were characterised employing X-ray photoelectron spectroscopy (XPS). A Thermo Fisher Scientific K-ALPHA spectrometer was used for surface analysis with a monochromatised Al K α source ($h\nu = 1486.6$ eV) and a 200 micrometer spot size. A pressure of 10⁻⁷ Pa was reached in the chamber when transferring the samples. The full spectra (0-1100 eV) were obtained with a constant pass energy of 200 eV and high resolution spectra (C1s, Pd3p-O1s, Al2p-Pt4f, Pd3d, Al2s) at a constant pass energy of 40 eV. Charge neutralisation was applied during analysis. Sputtering was performed with Ar⁺ ions at 500 eV. High resolution spectra were fitted and quantified (Scofield sensitivity factors used for quantification) using the AVANTAGE software provided by Thermo Fisher Scientific.

3. Results and discussion

3.1. Combinatorial sputtering and high-throughput screening of the $\text{Pt}_x\text{Pd}_y\text{Al}_z$ system

With the focus on identifying a possible ternary anode composition for application in the electro-oxidation of SO_2 , Pt_xPd_y compositions were evaluated previously^{20, 21} and characterised so as to establish a standard for comparison with ternary $\text{Pt}_x\text{Pd}_y\text{Al}_z$ anode compositions²⁶. The initial binary combinations investigated include a wide compositional range (Pt_xPd_y) that spanned from pure Pt to pure Pd using mainly 10 % content increments (refer to reference²⁰ for in-depth details). Pt_3Pd_2 was identified to be the optimum binary composition and extensive characterisation was conducted on it²¹, with annealed Pt_3Pd_2 (at 800 °C) proving to be a worthy contender to compete with pure Pt for the electro-oxidation of SO_2 . In producing a ternary electrocatalyst the combination of Pt and Pd with a base metal will result in an electrocatalyst containing less noble metal with Al making up the balance. Due to the vast number of electrocatalyst combinations which can statistically be formulated using the three components, Pt, Pd, and Al, our selection of electrocatalysts to be subjected to high-throughput screening was aligned with the high-throughput experimental planning categorized by R. Potyrailo²⁷. This includes hierarchical developing the experiment with increasing focus covering a space of interest²⁷. Employing the finding of our previous work, that a Pt_3Pd_2 annealed at 800 °C exhibited competing performance, as a guideline for a possible ternary anode composition which contains a base metal, ternary compositions were mainly focused but not limited to the area where Pt is less than 60 %, Pd less than 40% (i.e. Pt_3Pd_2) and random Al content. Al, however, could not be increased above 60 % as (i) Al deposits at a much lower rate in contrast to Pt and Pd resulting in very long deposition times, while operating the PVD apparatus at its limit, (ii) Al is not very resistant in strong acidic environments with degradation being almost immediate in sulphuric acid, and (iii) a report found in literature, on Pt and Al combinations, proved that only small amounts of Al is effective in improving catalytic performance²³. Linear polarisation response of the various compositions were obtained through high-throughput parallel screening, which is a simple means of quickly identifying an active composition that may work well in the SDE environment. The average of the polarisation graphs (conducted in triplicate) were used to determine the onset potential for each ratio employing the method reported by Cooper & McGinn with the current density based on (a) geometric area^{20, 26, 28}, and (b) mass Pt present in the thin film.

Before and immediately subsequent to electrochemical testing each of the catalyst pads were visually evaluated for signs of corrosion. Some of the compositions did corrode during electrochemical testing (Figure 3), which was also observed by Cooper & McGinn for their Pt-Ru-W thin film anode catalysts for direct methanol fuel cells²⁶.

Figure 3: Examples of varying degrees of corrosion occurring after linear polarisation for (a) $\text{Pt}_{34}\text{Pd}_{22}\text{Al}_{44}$, (b) $\text{Pt}_{43}\text{Pd}_{46}\text{Al}_{11}$, and (c) Al.

In the event that the greatest portion of the pad revealed corrosion, it was not included in the results, as it would in essence be the gold circuit that participated in the electro-oxidative reaction. Gold shows a high onset potential for SO_2 electro-oxidation, hence obtaining low onset potentials eliminated the possible interference of gold. Onset potential, as a means of evaluating catalyst activity, is a suitable measure in the event of possible corrosion as it is not influenced by any change in surface roughness²⁶. As only some catalyst pads revealed severe signs of corrosion, which were subsequently eliminated, current density based on geometric area and mass of Pt present in the thin film were also employed to evaluate thin film combinations. Current density, in contrast to onset potential, is influenced by both surface roughness and composition and by applying both these parameters to

identify thin film candidates during the screening phase, limited any systematic errors made. Screening of the various thin film combinations, for the electro-oxidation of SO_2 , are summarised in Figure 4 as ternary contour plots in terms of (a) onset potential (V), (b) current density ($\text{mA}\cdot\text{cm}^{-2}$), and (c) mass-specific current density ($\text{mA}\cdot\mu\text{g Pt}^{-1}$). Employing these criteria eight thin film composition, three based on lowest onset potential value, three based on highest geometric current density (normalised by geometric area), and two based on highest mass-specific current density (normalised by Pt mass), were selected for additional testing employing conventional testing techniques with glassy carbon inserts as substrate.

Figure 4: Ternary contour plots for (a) onset potential, (b) current density normalised by geometric area, and (c) mass-specific normalised current density, towards SO_2 electro-oxidation for the $\text{Pt}_x\text{Pd}_y\text{Al}_z$ system.

3.2. Composition of the thin films prior to conventional electrochemical testing

The bulk stoichiometry of the eight best electrocatalysts was investigated in triplicate by EDX, both before and after annealing. EDX analysis revealed that the expected theoretical compositions, predicted by employing the built-in QCM, correlate well with the actual sputtered bulk stoichiometry (Figure 5). No difference between as-deposited thin films and their corresponding annealed states were observed.

Figure 5: EDX after sputtering verifying that the actual sputtered ratios correlate with the expected sputtered ratios of (A)-Pt₄₂Pd₂₃Al₃₅, (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, (G)-Pt₂₃Pd₂₆Al₅₁, and (H)-Pt₂₃Pd₅₈Al₁₉.

3.3. Conventional electrochemical evaluation

3.3.1. Linear polarisation and subsequent EDX characterisation

Employing physical vapour deposition and high-throughput screening accelerates the complex process of new catalyst design and improves performance identification. However, it is not sufficiently suited for in-depth investigation and characterisation, and conventional methods, such as rotating disk electrode (RDE) linear polarisation, are more suitable. Hence, Figure 6 exhibits the electrocatalytic performance of the eight selected thin films (in the as-deposited (AD) and annealed state (on glassy carbon as substrate)) that did not show signs of corrosion (mainly in the form of delamination) during/after electrochemical testing. (I)-700 °C, referring to Pt, and previously identified (J)-800 °C, referring to Pt₃Pd₂, are taken as the baseline to which all ternary combinations are compared against. In general, it is evident that no significant improvement in onset potential was achieved, with the majority of electrocatalysts exhibiting similar onset potentials (within error), when compared to (I)-700 °C and (J)-800 °C. However, (E)-AD, 700 °C, 800 °C and (D)-AD performed well. As the results obtained from onset potential are not sufficient for identifying an alternative electrocatalyst, mass-specific current density was also investigated. From Figure 6 it is evident that the majority of the ternary electrocatalysts exhibits an increase in current density. Compared to the baseline, i.e. Pt and Pt₃Pd₂, Pt₄₀Pd₅₇Al₃ (annealed at 900 °C) performed the best in that current density (mA.mg Pt⁻¹) increased from 108.11, to 181.21 and finally to 396.73 for Pt, Pt₃Pd₂ and Pt₄₀Pd₅₇Al₃ respectively, indicating an increase in activity that correlates with a decrease in Pt content (Figure 7).

Figure 6: Onset potential values (a) and mass-specific current density values (b) for (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, (H)-Pt₂₃Pd₅₈Al₁₉, (I)-Pt, and (J)-Pt₃Pd₂.

Subsequent to electrochemical testing (Figure 6) the thin film electrocatalysts were analysed by EDX so as to evaluate any change in composition that could not be visually detected (an indication of short term stability). Overall, all the catalysts exhibit a slight change in compositional ratio with no specific trend (Figure 8), when compared to the compositional ratios directly after sputtering (Figure 5), with (B)-AD, (F)-AD, (H)-600 °C and (H)-700 °C showing the largest deviation in compositional ratio. This is however not sufficient in identifying a stable electrocatalyst, and additional evaluation on the stability is required. In an attempt to identify a stable electrocatalyst, in conjunction with having a low onset potential and acceptable current output, consecutive cycling in a sulphuric acid environment was conducted (Figure 9). For all the electrocatalysts under investigation, the only electrocatalyst that exhibited improved stability, compared to (I)-700 °C and (J)-800 °C, was (B)-900 °C, lasting about 1.4 times longer. Taking all three parameters (onset potential, mass-specific activity, and stability) into consideration that are indicative of an improved electrocatalyst, (B)-900 °C can therefore be considered the ternary candidate exhibiting the most potential in competing with (I)-700 °C and (J)-800 °C.

Figure 7: Correlation of current density (mA.mg Pt⁻¹) with Pt content (%).

Figure 8: EDX analysis subsequent to LP runs for (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, and (H)-Pt₂₃Pd₅₈Al₁₉.

To put (B)-900 °C further to the test, it was subsequently evaluated under an increased electrolyte temperature of 60 °C (using a SCE reference electrode above this temperature is not advised, due to the instability of Hg₂Cl₂) with the results also being depicted in Figure 6 and Figure 9. At this elevated temperature the same phenomena was observed for (B)-900 °C, (I)-700 °C and (J)-800 °C as in the case of 25 °C, with no significant difference in onset potential having been observed. However, an improved performance was evident in terms of current output and durability. The (B)-900 °C thin film (at 25 °C) furthermore exhibited totally different behavior in terms of visible signs of corrosion when compared to all the other tested electrocatalysts. This was evident in that the (B)-900 °C thin film (at 25 °C) dissolved gradually into solution (visually monitored until the film was so thin, that glassy carbon started to appear), keeping its active surface (Figure 10a) as only the thin film thickness decreased, while all the other electrocatalysts, including the target electrocatalysts ²¹, clearly delaminated. (B)-900 °C (at 60 °C), in contrast, only started to exhibit the normal signs of delamination nearer to the end of its stability lifetime, with the last cycle subsequently being lower in the hydrogen adsorption/desorption region than the first cycle (Figure 10b), as a part of the thin film delaminated from the surface.

Figure 9: Consecutive cycling of thin film electrocatalyst for stability evaluation with (B)-Pt₄₀Pd₅₇Al₃, (C)-Pt₃₃Pd₄₀Al₂₇, (D)-Pt₄₃Pd₄₆Al₁₁, (E)-Pt₄₈Pd₂₃Al₂₉, (F)-Pt₆₀Al₄₀, (H)-Pt₂₃Pd₅₈Al₁₉, (I)-Pt, and (J)-Pt₃Pd₂. Conditions: scan rate of 100 mV.s⁻¹ and potential window of 0.041 V vs SHE to 1.441 V vs SHE at 25 °C and 60 °C.

Figure 10: Consecutive cycling of (B)-Pt₄₀Pd₅₇Al₃ annealed at 900 °C in H₂SO₄ at (a) 25 °C, and (b) 60 °C.

3.4. Further characterisation and discussion

AFM and XPS analysis were conducted on the most promising binary²¹ and ternary thin film electrocatalysts in competing with pure Pt for SO₂ electro-oxidation, with the aim being to gain more insight into the physical and electronic properties of these thin films. Pt thin films (as-deposited and the best performing annealed form) were also included in these analyses, serving as the primary reference/target electrocatalyst.

3.4.1. AFM analysis

AFM allows, among other things, meticulous observation and evaluation of the morphological and topographical characteristics of thin film surfaces. Three-dimensional (3D) AFM scans were recorded over a substrate area of 2 µm x 2 µm, for each sample, at three different locations on the thin film. Roughness parameters were calculated from 2 different positions within each of the three individual locations so as to provide reliable average roughness values representative of the whole thin film surface. From the 2D and 3D AFM images shown in Table 1, it is clear that the thin films in the as-deposited form all exhibit a fine distribution of metal particles, adapting the profile of the underlying glassy carbon surface, with unavoidable grooves clearly visible resulting from polishing. Upon annealing the as-deposited thin films evolved from exhibiting a finely distributed appearance to clearly exhibiting different degrees of crystal formation with the least amount of change being visible for (I)-700 °C. (J)-800 °C transformed into a surface with clearly defined grain boundaries, evident of a polycrystalline nature²¹. (B)-900 °C exhibited crystal growth of a totally different nature when compared to (J)-800 °C, with a type of random agglomerated distribution of small ‘sheets’ of crystals varying in orientation with sharp corners emerging from the surface. It is remarkable how only ~3 % Al metal content can induce such an extreme difference in surface/bulk structure upon annealing. This type of crystal growth might be one of the reasons for observing a prominent improvement in catalyst performance for (B)-900 °C, especially the stability performance observed for this electrocatalyst in a sulphuric acid environment for both 25 °C and 60 °C (Figure 9), when compared to (I)-700 °C and (J)-800 °C.

Table 1: 2D and 3D AFM images for electrocatalysts (I)-Pt, (J)-Pt₃Pd₂, and (B)-Pt₄₀Pd₅₇Al₃

2D	As-deposited	Annealed
(I)-Pt

In addition to 2D and 3D imaging, the following surface roughness profile parameters (Figure 11) were acquired: (i) average roughness (R_a), which is based on mean height roughness, (ii) vertical distance between the highest and lowest points (R_t), and (iii) root mean square (RMS) of the distribution of surface height making it a bit more sensitive than R_a ²⁹.

Figure 11: Surface roughness profile parameters of (I)- Pt as-deposited (I AD) and annealed at 700 °C, (J)- Pt₃Pd₂ as-deposited (J AD) and annealed at 800 °C, and (B)- Pt₄₀Pd₅₇Al₃ as-deposited (B AD) and annealed at 900 °C.

In general, as is evident from Figure 11, (I)-700 °C and (J)-800 °C exhibited similar values for all the roughness parameters with (B)-AD showing a smoother surface (lower values) overall. As for the different annealed forms of the individual thin films, the roughness parameters all increased from the as-deposited state to the specific annealed form, with (B)-900 °C being the most influenced by annealing treatment and also exhibiting totally different crystal growth compared to (I)-700 °C and (J)-800 °C (Table 1 2D). Overall, (B)-900 °C exhibited the highest roughness values for all three roughness parameters acquired, which has a direct and positive effect on

the higher current output observed when compared to (I)-700 °C and (J)-800 °C. The rapid thermal annealing of catalyst (B)-900 °C has a positive influence on the performance and stability of this catalyst towards SO₂ electro-oxidation in a sulphuric acid environment.

3.4.2. XPS

In an attempt to further elucidate the observed electrocatalytic performance of the most promising binary ²¹ and ternary thin film electrocatalysts, in competing with pure Pt for SO₂ electro-oxidation, XPS surface analysis and depth profiling on the thin film samples were conducted so as to gain information regarding their composition and chemical environment. Knowing the overlapping that occurs between Pd3p3-O1s and Al2p-Pt4f peaks, high resolution spectra were collected to ensure that the best fitted quantified results are obtained, especially for materials J and B (cf. Electronic Supplementary Information (EIS) Figure S1 and S2 for fitted XPS spectra after 10s Ar⁺ etching for (B)-AD and (B)-900°C). The fits were conducted subsequent to linear background subtraction using a product of Gaussian and Lorentzian functions, as defined in the AVANTAGE software. Figure 12 reveals comparative information for the AD and annealed states with regard to the extreme surface (top outer layer) of the thin films for Pt4f, Pd3d and Al2s. Figure 13 exhibits compositional information (derived from the C1s, O1s, Pt4f_{7/2}, Pd3d_{3/2} and Al2s peak areas), related to the depth of the metallic Pt and Pt-based thin films deposited on glassy carbon as substrate. It must be kept in mind that (i) XPS remains a semi-quantitative analysis to follow atomic compositional change with depth (not to be directly correlated with previous EDX results), and (ii) XPS has an accuracy within 5 to 10 % of absolute atomic % compositional information ³⁰.

In the as-deposited state, no shift in the Pt4f_{7/2} peak at ~71.15 eV was observed for (I), (J) and (B), which is a direct indication that no significant change in the chemical environment occurred during/as a result of physical vapour deposition. Upon annealing, again no shift in the Pt4f_{7/2} binding energy was observed for (I)-700 °C and (J)-800 °C, however a clear change was observed for (B)-900 °C, exhibiting a slight negative shift in the Pt4f_{7/2} (Figure 11d) and Pd3d_{5/2} peaks (Figure 11e), which could possibly be ascribed to the occurrence of metal-metal interactions as a result of annealing temperature ³¹. In addition, (B)-900 °C (Figure 12f) exhibited an increase in Al content at the surface (15 at. %) when compared to (B)-AD (only 2 at. %), which is expected if explained in terms of fundamental properties of monometallic metals (atomic radius) ³². For the metals present in (B)-900 °C, the order of decreasing size with regard to atomic radii is Al (143 pm) > Pt (139 pm) > Pd (137 pm) ³³. In general, lattice strain is expected to contribute to the segregation/migration of the atom with the largest atomic radius to the surface, which in the case of (B)-900 °C is Al. This supports the observation obtained from XPS data that Al2s mainly appears on the extreme surface subsequent to annealing (Figure 11f), which clearly points towards the migration of Al to the surface upon annealing.

Figure 12: Pt4f, Pd3d and Al2s XPS spectra on the extreme surface, i.e. the top outer layer, of both the as-deposited (AD) (black curve) and annealed states (red curve) of (I)-Pt (a), (J)-Pt₃Pd₂, (b, c) and (B)-Pt₄₀Pd₅₇Al₃ (d, e, f).

While the previous XPS measurements (Figure 12) focused on the surface, depth profiles of the Pt and Pt-based samples (Figure 13) were obtained by combining a sequence of Ar⁺ ion gun etch cycles with XPS measurements from the current exposed surface. The objective of obtaining depth profiles was to validate that the observed electrocatalytic performance was not as a result of a ‘skin’ formed, as a result of severe segregation/migration to the surface, but rather being the result of a homogeneous composition throughout the depth of the thin film. The first observation for all the electrocatalysts, in both the as-deposited and annealed states, is (i) the presence of unescapable C, N, Si and Cl impurities, due to ambient pollution on the metal surface layer, disappearing after only 10 s of Ar⁺ etching, and (ii) a constant ~55 nm thin metallic layer (validating the calibrated sputtered layer of ~60 nm) recorded by XPS etching for all the analysed thin films. Subsequent to Ar⁺ etching through the thin metallic film, it is clear that at a depth of ~40 nm carbon from the substrate appears. Carbon, however, is present almost throughout the depth of the annealed surfaces (especially sample (B)-900°C), which can be explained either by possible diffusion of the substrate through the Pt/Pd/Al thin film at high temperature (which is unlikely as these specific glassy carbon inserts are stable under high temperatures) or as a result of XPS detecting possible ‘exposed’ substrate carbon as a result of the roughness of the (B)-900°C thin film (R_t around 30 nm, Figure 11). It is furthermore evident that contraction of the different sputtered layers occur upon annealing with increased contraction as the temperature increases.

Figure 13: Depth profiles of (I)-Pt, (J)-Pt₃Pd₂ and (B)-Pt₄₀Pd₅₇Al₃, for both the as-deposited (AD) and annealed states. The etch-rate was estimated 0.2 nm/s on each material.

For (B), Al seems to be in the oxidised state throughout the entire thickness of the layer (118.5 eV binding energy Figure 12f, only data for the top layer is shown). As Al gets oxidised easily in air, it is very probable that the samples were oxidised from the moment when the thin films were exposed to air. In addition, XPS depth profiling for (B)-900°C supports the previous observation (Figure 12f) of a degree of migration of Al towards the surface after annealing and that all three metals are present throughout the depth of the thin film. Concerning Pd3d_{5/2} peak fitting (cf. EIS Figure S1 and S2), the absence of PdO bonding usually located at 337 eV is confirmed³⁴ as the maximum component is Pd metal at around 335 eV, while another 1 eV higher (~336 eV) could be attributed to Pd-O-X bonding namely Pd-O-Al.

As thin film (B), i.e. Pt₄₀Pd₅₇Al₃, presented itself as being a competitive electrocatalyst for SO₂ electro-oxidation, measured against Pt and the previously identified Pt₃Pd₂ composition, XRD spectra were furthermore recorded

for (B)-AD and (B)-900°C (cf. EIS Figure S3). (B)-AD is concluded to consist of a PtPd cubic phase, whereas (B)-900°C consist of a possible $\text{Pt}_{2.84}\text{Al}_{1.16}$ cubic phase that may support the slight negative shift observed for the $\text{Pt}_{4f_{7/2}}$ (Figure 11d) and $\text{Pd}_{3d_{5/2}}$ peaks (Figure 11e), which are indicative of alloy formation.

4. Conclusion

As is evident from literature, only a limited number of surfaces have been investigated thus far for catalysing the electro-oxidation of aqueous SO_2 . It is furthermore clear that widespread disagreement and non-reproducible behavior exist²⁴, as this reaction is very sensitive and highly influenced by the prevailing conditions (electrode material, pH, temperature, preconditioning, pressure, applied anodic potential, etc.). From our investigation, identifying a possible alternative anode catalyst that can compete with pure Pt, it is clear that a lot of scope and room for improvement still exist for improving the catalytic activity and stability of the electrocatalyst. In general, it is primarily the surface properties of a catalyst in conjunction with the secondary bulk effects, which are credited for any observed catalytic improvements/weakening. We have highlighted the influence that a secondary/tertiary metal, in conjunction with annealing, can have on the catalytic performance of the thin film by effecting only slight changes in composition and temperature treatment.

The addition of a third component to the noble metals Pt and Pd, in the form of Al, i.e. $\text{Pt}_x\text{Pd}_y\text{Al}_z$, enhanced the electrocatalytic performance towards the electro-oxidation of aqueous SO_2 with the Al content kept below ~3 %. In excess of ~3 % Al the electrocatalytic performance was severely hampered. Overall onset potential, however, did not improve significantly for any of the evaluated electrocatalysts, while improvements in current output and stability (lasting ~1.4 times longer than both pure Pt (the (I)-700 °C sample) and Pt_3Pd_2 (the (J)-800 °C sample)) was achieved specifically for $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ (the (B)-900 °C sample), both in 25 °C and 60 °C testing environments. We have shown that electrocatalytic activity for the electro-oxidation of aqueous SO_2 can be achieved by substantially lowering the Pt content in that current density (mA.mg Pt^{-1}) increased from 108.11 to 181.21 and finally to 396.73 for Pt, Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ respectively, indicating an increase in activity that correlates with a decrease in Pt content.

Furthermore, additional information obtained from XPS analysis has shown that $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ ((B)-900 °C) exhibited an increase in Al content at the surface (~15 at. %) when compared to (B)-AD (only ~2 at. %) although no sign of a distinctive skin of one metal (or more in the case of $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$) was present near the surface for the Pt_3Pd_2 and $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ thin films (as-deposited and annealed). This confirmed that the observed activity of the thin films was a result of all the metals being present in the thin film surface. XRD analysis of the annealed $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ thin film ((B)-900 °C) has highlighted the presence of some degree of alloy formation.

The power of alternately employing combinatorial and high-throughput methods with conventional electrochemical and characterisation methods, for electrocatalysts development, has clearly been shown, and resulted in the identification of a catalyst that contains a lot less platinum while exhibiting increased catalytic activity and stability. Combining, among other things, the sensitivity of this reaction to the surface where oxidation occurs, with the mechanistic complexity of this reaction³⁵ (proposed mechanisms include, indirect oxidation via (i) a dithionate intermediate³⁶⁻³⁸ or (ii) involving bulk SO_2 and an unspecified S(VI) intermediate³⁹, and direct oxidation via adsorbed reactant³⁷), a specific active catalysts of interest will be better understood by in depth mechanistic investigation taking into account various factors such as temperature, acid concentration, sulphur coverage etc. It is however relevant to mention, that the majority of mechanistic studies on SO_2 oxidation were conducted on platinum and single component electrode materials. Based on the amount of effort devoted to the mechanistic understanding of Pt catalysing SO_2 oxidation, do these studies reveal the complexity of this reaction, proving that the necessary mechanistic characterisation of this identified multi-component $\text{Pt}_{40}\text{Pd}_{57}\text{Al}_3$ electrocatalyst evident to be challenging and will require meticulous and repeatable evidence to be fundamentally sound.

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