Dealloying and Synthesis of Nanoporous Pt and Au from AgPt and AgAu Binary Alloys

By

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i. ABSTRACT

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A study is presented on the synthesis and characterization of nanoporous AgPt and AgAu alloys after annealing and dealloying in 5% HClO₄. Dealloying removes the less-noble atom from the alloy surface to produce nanoporous, highly-interconnected ligaments. Voltammetry of AgPt and AgAu shows the critical potential, E_c, at various potential scan rates. Potential hold current decay experiments on Ag-23Pt and Ag-23Au further show the intrinsic E_c to be 275 mV and 290 mV, respectively. E_c was governed by thermodynamic clustering in the alloys as opposed to dissolution-diffusion kinetic effects. EDX shows the starting 77Ag-23Pt material changes composition after dealloying to about 12Ag-88Pt. XRD indicates the presence of ordering in AgPt via a superlattice (100)-peak for a specific anneal treatment. EIS measurements done on as-annealed and dealloyed AgPt and AgAu samples show the onset of bulk porosity and show that capacitance increase is equal for both alloys at two different dealloying potentials.
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vi. List of Symbols Used

- $A_pB_{1-p}$: Binary alloy A-B with atomic fraction $p$ of A and $(1-p)$ of B.
- $p_c(m)$: Site percolation threshold. A site percolation threshold in a randomly populated binary lattice is the critical occupancy of one component A at which long-range (in principle infinitely long-range) connectivity of A-occupied sites abruptly appears. Below this threshold, dealloying is negligible or passivated but above it dealloying occurs with the more active element being selectively dissolved to form an interconnected structure with a porous network. $m$ is the # of like nearest neighbours.
- $E_c$: Critical potential. The potential above which bulk porosity formation occurs in an alloy.
- $E_A^\circ, E_B^\circ$: The equilibrium metal-metal ion electrode potentials of A and B respectively.
- $\Delta G = \text{change in Gibbs free energy}; R = \text{gas constant} = 8.314472 \frac{J}{\text{mol} \cdot \text{K}}$; $T = \text{absolute temperature (K)}$; $\ln = \text{natural logarithm}; N_i = \text{mole fraction of the component}; n = \text{number of electrons per mole product}; F = \text{Faraday constant} = 96,485.3399 \frac{C}{\text{mol}}$; $\Delta E = \text{change in electric potential of a reaction}; K = \text{Boltzmann constant} = 1.38 \times 10^{-23} \text{J/K}; i = \text{current density A/cm}^2$.
- $\gamma = \text{solid liquid interfacial free energy}; V_{at} = \text{atomic volume}; \kappa = \text{Curvature}$. Can be positive (blobs on surface of alloy) or negative (pores); $q = \text{electronic charge} = 1.602 \times 10^{-19} \text{C}$.
- $\xi$: Average cluster size (or percolation backbone diameter) in percolation.
- $\Omega$: Molar volume; $a = \text{nearest - neighbour lattice spacing}; E_b = \text{nearest - neighbour bond energy}$
- $i_{\text{diss}} = \text{dissolution current density}; \Delta G_{\text{diss}} = \text{Gibbs free energy of activation for dissolution}; D_{\text{diff}} = \text{surface diffusion coefficient of the more noble element}; \Delta G_{\text{diff}} = \text{Gibbs free energy of activation for diffusion}$.
- AgPt: Silver-Platinum alloy with composition 77 at% Ag – 23 at% Pt. Also written as Ag-23Pt.
- AgAu: Silver-Gold alloy with composition 77 at% Ag – 23 at% Au. Also written as Ag-23Au (or Ag-20Au according to the alloy used)
- EIS: Electrochemical impedance spectroscopy
- $C_{\text{dl}}$: Double layer capacitance of dealloyed material (in F/cm$^2$)
1 INTRODUCTION

1.1 Application and synthesis of nanoscale materials

Nanochemistry has made it possible to synthesize materials from building blocks the size of atom clusters, which exhibit enhanced chemical, magnetic, electronic, and optical properties. Enhanced properties of nanomaterials, which most often are powders and materials optimized at the nanoscale (1–100 nm), afford tremendous potential beyond their immediate physical properties made possible by geometric miniaturization. At the nanosize, the assumptions used to derive the theories of classical and quantum mechanics are no longer valid making unexpected properties to be possible. Nanomaterials have grain size on the order of $10^{-9}$ m, large specific surface areas, strength and ductility and are generally very active chemically\textsuperscript{1}. Dealloying is the selective dissolution of homogeneous metallic alloys such as AgAu or AgPt. When a significant anodic overpotential is applied to such an alloy, the electrochemically more active elements are removed which results in the formation of a highly porous nanostructure composed of densely-interconnected highly-curved nanoscale tunnels completely random in direction\textsuperscript{2}, with the nanostructure consisting predominantly of the more noble metal of the alloy. For dealloyed materials, while the grain sizes are not on the order of 1 nm, the ligaments are however, nanoscale.

While the various common methods of preparing nanoscale materials will not be covered in detail here, the following is a brief listing.

- Plasma arcing: High temperatures form an arc or plasma to separate atoms which recombine outside the plasma to form nanosized particles.
- Chemical vapour deposition: Precursor gases are reacted and decomposed on a substrate. CVD conditions can be controlled to obtain the desired film product with certain properties on the substrate.
- Electro-deposition: While this process is similar to CVD, the controlled film is deposited from solution by applying an electric field.
- Sol–gel synthesis: A chemical precursor solution is hydrolyzed into an integrated network/gel of network polymers or either discrete nanoparticles on a suitable substrate.
• High intensity ball milling: A physical process where macrocrystalline material is ground into nanocrystalline structures without chemical structural change.

• Dealloying: An electrochemical process which is the selective dissolution of one or more components of a solid solution alloy. It is also called parting, selective leaching or selective attack with potential difference acting as the driving force for the preferential attack on the more "active" element in the alloy. Dealloying can be used to create nanoporous metals with a high degree of mechanical integrity, and will be expanded on in this work.

Some examples of where nanotechnology is being used today include functional polymers, nanowire arrays for electromagnetic radiation shielding, chemical gas sensing, biomedical and biomaterial sensor applications, marine anti-fouling, coatings and as catalyst materials in fuel cells.

1.2 Dealloying, nanoporous metals and characterization techniques

Dealloying has been observed in common metallic alloy systems such as brasses, copper-aluminium alloys and more recently in stainless steels. The mechanical properties of the porous overlayer are different from the bulk alloy beneath it, and studies in the past have focused on understanding undesirable materials failure aspects such as brittle crack propagation and stress corrosion cracking.

The binary metal alloy AgAu has been the standard of comparison and experiments because it is easily available and displays a single-phase solid solubility across an entire range of composition for all temperatures (see AgAu phase diagrams in APPENDIX B). Parameters of the synthesized nanoporous “sponge-like” structure can be controlled by varying the post-annealing temperature and applied dealloying potential; this includes pore size and curvature properties. The figures shown below are representative of homogeneous AgAu nanostructures after dealloying.
Dealloying has historically been used by in ancient times to dissolve the more active element from dilute gold alloys to create the illusion of a pure gold artifact. This was known as depletion gilding, used by the Incan civilization with CuAu to create an Au surface layer, and as cementation, used by European artisans with AgAu. Depletion gilding typically proceeds via selective gaseous oxidation followed by dissolution of the base metal oxide whereas actual dealloying occurs in a liquid.

Binary alloys such as CuPt, AgPt and AgAu, along with similar ternary alloys like AgAuPt, can have potentially useful applications in the area of biomedical sensors. Pt has a value of surface diffusivity that is at least 3–4 orders of magnitude lower than that of Au under their respective electrochemical environments, which allows us to make a comparison of the two systems and to understand how surface diffusivity affects dealloying. Further such nanomaterials can potentially be used for applications in optics, electronics, optoelectronics, catalysis, sensing, clinical diagnostics, surface-enhanced Raman scattering (SERS), information storage, and energy conversion/storage. Because of their low density and high surface area, an interesting application is making conductive composites by using metallic fillers in the form of hollow nanostructures.
In theory, an alloy with elements which have a significant difference in their metal ion/metal equilibrium potential can be dealloyed by anodic dissolution. The following alloys have been dealloyed by anodic dissolution: NiAu\(^7\), AgAu\(^2, 38, 18\), CuPt\(^8,9,10\), CuAu\(^11,12\), AuCd\(^7,13\), CdMg\(^14\), ZnPt\(^15\), CuZn\(^16\), CuMn\(^16\) and AgPt. This process is also exploited in material synthesis of catalytic Ni particles by the Raney process\(^17\).

Early work by Pickering\(^28\) and Forty\(^18\) showed the structure of the nanoporous gold formed as a result of dealloying AgAu thin films. Erlebacher\(^2\) has previously shown via scanning electron microscopy (SEM) that dealloying AgAu produces pore size around 5 nm and ligaments around 10 nm wide (see Figure 1). Subsequent work done on AgAu alloys reproduced these results with the same order of magnitude for pore size and ligament size, which is tunable based on post-dealloying heat treatment\(^3\).
Figure 3: SEM images showing pore and ligament structure in Ag-24at%Au for a series of post-dealloying heat treatment. Dealloying was done in 1 M HClO₄. (a) – (f): The samples were annealed for 10 minutes at 100 °C, 300 °C, 500 °C, 600 °C, 700 °C and 800 °C. The increasing pore size and ligament coarsening with temperature is clearly shown. All markers are 1 µm. Image modified from reference [3].

Work by Dursun and Corcoran⁴¹ showed that the average pore size and distribution depended on several controllable factors: alloy composition, electrolyte composition, rate of dealloying, applied potential, dealloying time and temperature treatment post-dealloying. Kelly, Young and Newman¹⁹ also showed that the porosity significantly coarsened at room temperature during the corrosion process and this coarsening was highly dependent upon the applied potential. It was proposed that the potential dependence of coarsening was due to surface diffusion. Four mechanisms have been proposed to date to explain dealloying in a binary alloy AₚB₁₋ₚ:

(i) The *ionization-redeposition* mechanism²⁰ in which both elements A and B of the binary alloy dissolve but the more noble element is redeposited. However, experimental works show that only one of the elements is preferentially dissolved. In most experimental conditions leading to nanoporosity formation, the dealloying potential is generally much below the potential required for the dissolution of the more noble component of the alloy.
(ii) The surface diffusion mechanism$^{21,22}$ whereby only the more active element is dissolved and the remaining more noble element aggregates by surface diffusion.

(iii) The volume diffusion mechanism$^{23,24}$ where the more active element is dissolved but both atoms move in the solid phase by volume diffusion. This creates a supersaturation of vacancies at the surface, formed as a result of the superficial dealloying of the more active element. Injection of divacancies into bulk alloy maintains the transport of the more active element to the surface, thereby propagating the dealloying process.

(iv) The percolation model of selective dissolution$^{31,43}$ expands upon the surface diffusion model to account for the pre-existing of like elements in the binary alloy. There is some surface diffusion of the more noble atoms. These interconnected paths or cluster backbone containing the majority of the cluster is precursor to the nanoporous structure evolved during dealloying.

Small angle neutron scattering (SANS)$^{25,26}$ and scanning tunneling microscopy (STM)$^{26}$ have been used to investigate the controlling mechanisms in 3D porosity formation. SANS scattering peak data confirmed that pore size becomes more defined with dealloying time (shown as a well defined peak in scattering data graphs of intensity versus scattering vector). STM measurements also showed that increasing the Ag$^+$ ion concentration in electrolyte when dealloying AgAu increased the overall Ag dissolution rate by increasing the exchange current density for the Ag dissolution reaction. It was also shown that the average ligament width increased with dealloying time in AgAu alloys. However, using the STM presents some challenges in investigating the morphology of bulk dealloyed materials due to depth of field and tip convolution issues where the tip is larger than the pore, evident by comparing Figure 3 and Figure 4, i.e. we are unable to distinguish between porosity versus a nanometer roughened surface. Another limitation here is that we are limited to characterizing the surface and then speculating on the relationship to the fully developed 3D structure.
Work by Renner et al. showed atomic scale detail of the initial stages of corrosion. This was reported in Cu₃Au (111) single crystal alloys dealloyed in H₂SO₄. In situ X-ray diffraction experiments on the Cu₃Au (111) surface showed that the (111) planes exhibited the average Cu₃Au composition showing that the corrosion process was independent of disordering and ordering phenomena within the alloy.
The CuAu system exhibits a continuous series of solid solutions, with various ordered intermetallic structures below 410°C, as shown in Figure 5. This feature has made the CuAu alloy gain popularity for studying kinetics and transformation of the ordered equilibrium structures from the disordered state. In 1989, work done by Parks Jr., Fritz and Pickering showed differences in the electrochemical behavior of ordered and disordered phases of CuAu. They showed that $E_{c\text{ (ordered)}} > E_{c\text{ (disordered)}}$ which is consistent with percolation arguments covered in section 1.6. The simple explanation is that in disordered alloys, there exist more cluster structures of less noble atoms with dissolution paths having many like neighbours, facilitating penetration by the electrolyte.

X-ray diffraction patterns showed that ordered and disordered states were reached in Cu-25at%Au samples. The X-ray diffraction pattern for a quenched sample is a typical face-centered-cubic pattern for this alloy in the disordered state. A slowly cooled sample reveals the superlattice structure of Cu$_3$Au, which is indicative of the ordered state, as shown below. Figure 6 shows the average polarization curves for ordered and disordered samples of Cu-25at%Au. It can be seen that the critical potential ($E_{c1}$) for the disordered samples is approximately 250 mV less oxidizing than the critical potential ($E_{c2}$) for the ordered samples, effectively showing that $E_{c\text{ (ordered)}} > E_{c\text{ (disordered)}}$. The disordered alloy also has a higher limiting current between the two critical potentials, $E_{c1}$ and $E_{c2}$, but both the ordered and disordered states exhibit the same limiting current above $E_{c2}$.

It is clear from Figure 6 that the disordered sample does not show the superlattice (110) peaks due to destructive interference, which are evident in the ordered sample.
Structurally, the difference between ordered and disordered states is the number of Cu-Cu and Cu-Au bonds per unit cell. In the ordered state there are 24 Cu-Cu bonds and 24 Cu-Au bonds or each Cu atom has 4 Au atoms as nearest neighbors (~CuAu). For the disordered state, on average there are 27 Cu-Cu bonds, 18 Cu-Au bonds, and 3 Au-Au bonds per unit cell.

One idea to explain this phenomenon in the literature is that $E_c$ marks the onset of dissolving Cu atoms directly from terrace positions, rather than via kink positions as shown in Figure 13. The
binding energy for Cu-Cu bonds is less than the binding energy for Cu-Au bonds. If this trend for
diatomic binding energies holds true in the alloy, it would result in a more oxidizing \( E_c \) for Cu
dissolution from the ordered than disordered Cu\(_3\)Au phases. \( E_c \) also shifts to more oxidizing
potentials as the Au content of the alloy increases. The AgAu system follows the same
dissolution and bond-strength patterns. However, as early as 1989, Sieradzki, Corderman,
Shukla and Newman\(^{31}\) proposed a model where \( E_c \) depends solely on clustering and percolation
arguments. This was further developed in subsequent years by Rugolo, Erlebacher and Sieradzki
in 2006\(^{42}\), which will be covered in detail in section 1.6.
1.3 Anodic polarization curves

In a seminal paper, Pickering postulated four distinct regions for the anodic polarization curves of alloys which were not seen in pure metals. This was typically seen in alloy samples which had a marked difference in the standard potentials of the elements of the alloy, i.e. where $\Delta E^o >> RT/F$, where $R$, $T$ and $F$ are the gas constant, temperature and Faraday constant, respectively – the larger the potential difference $\Delta E^o$ between the alloy constituents, the more pronounced the alloy features. This behavior is not commonly observed in base metal alloys since other side reactions such as hydrogen evolution obscure it, or the onset of strong passivity precludes the existence of an active region. As illustrated in the figure below, Pickering’s original study showed the following regions for the anodic polarization of binary metal alloys.

- Region (a) is a low current region where only the less noble element A dissolves slowly. Dissolution of A here is hindered by a protective passive layer of B.
- Region (b), above the critical potential $E_c$, is where the dissolution rate of A increases sharply. Only A is dissolved here, and only when the potential increases to above $E_B^o$ does B start dissolving with A. In curve 3b, A-B still exists as an alloy, but dissolution of the components is simultaneous.
• Region (c) shows non-preferential dissolution of both A and B. The degree of preferential
dissolution decreases with time until the alloy surface reaches a certain level of
enrichment in the more noble metal at which point the mode of dissolution becomes non-
selective. For some alloys, this region is obscured since it occurs at high potentials at
which oxygen evolution also occurs.

1.4 Percolation theory and computer modeling

In their book *Introduction to Percolation theory*, the authors explain how percolation theory
deals with clustering, criticality, diffusion, phase transitions and disordered systems. It is often
used to provide a conceptual and quantitative model for understanding these phenomena and
therefore presents a statistical, theoretical footing to the area of dealloying in which there is
inherent randomness.

Applying percolation theory to dealloying allows us to study and explore quantitatively the
connectedness of different atomic clusters in a random homogeneous alloy. For a given alloy, if
the alloy components have sufficiently different reactivity, the parting limit will be close to the
site percolation threshold, $p_c$. The parting limit is the alloy composition beyond which (in
theory) no porosity can be formed by dealloying, regardless of how oxidizing the applied
potential. In percolation theory, site percolation threshold refers to a limit of a critical mass or
critical concentration. Below the threshold, dealloying is negligible or passivated but above it
dealloying occurs with the more active alloy element being selectively dissolved to form an
interconnected structure with a porous network.

Dealloying occurs successfully at a large enough given potential when percolation clusters –
random groupings of the more active element that occur naturally – exist to form a “path of least
resistance” or a penetration path from one side of the alloy to the other. These percolation
clusters do not exist for alloy compositions smaller than $p_c$ and complete penetration occurs for
compositions above $p_c$. It should be noted that regardless of alloy composition being over $p_c$, if
the applied potential is not suitable, no dealloying can occur (i.e. it needs to be above the metal
ion/metal equilibrium potential of the active element for dealloying to occur). This applied potential is referred to as the critical potential and is expanded on in the next section.

Sieradzki, Corderman et. al\textsuperscript{31} presented a new framework in 1989 to better understand corrosion in alloy systems. Based on percolation theory, the Monte Carlo (MC) computer simulations developed with simple rules for 2-D planar and 3-D simple cubic lattices were able to account for all the known features and phenomena in dealloying. A Monte Carlo method is a stochastic technique\textsuperscript{32}, which uses random numbers and probability to simulate experiments. It can be simple to understand the interactions occurring between two atoms but when applied to thousands of atoms it becomes more complex. MC methods allow sampling of a system with a specified number of random configurations and conditions. The data produced can then be used to describe the system as a whole. The results of the MC simulations showed that de-alloying thresholds in real systems should be close to the relevant site percolation thresholds. This was simplistic in approach but MC could not simulate the time evolution process in dealloying and the computing power required for 3D simulations two decades ago was also lacking.

The improved Kinetic Monte Carlo approach\textsuperscript{2, 33} (KMC) in 2001, however, made it possible to simulate dealloying including diffusion of surface atoms and dissolution of the more active element. KMC differed from MC in that KMC simulations factored in time scales more efficiently (due to advances in computing power) and so were able to accurately predict the changing dealloying surface morphology over time. KMC simulations expanding on the continuum model revealed a qualitative picture of porosity formation: it begins when the active element atom is dissolved from a flat surface, leaving behind a terrace vacancy on a planar (111) orientation. Other active element atoms surrounding this vacancy become more susceptible to attack because there are now fewer lateral neighbor atoms. Subsequently the terrace becomes enriched with noble adatoms with no lateral coordination. The noble adatoms chemically diffuse to cluster together at the sample-electrolyte interface. This diffusion results in nucleation and growth of gold-rich islands possibly at preferred surface sites such as slip steps, structural fault boundaries and micro-twins. This was reported as early as 1967 by Pickering and Wagner\textsuperscript{34} who investigated transport mechanisms in the dealloying of CuZn and CuAu alloys. This is an interesting phenomenon – rather than a uniform layer of noble atoms dispersed across the
dealloying sample, we get distinct areas of pure noble atoms clustered into islands which passivate the surface, and areas of un-dealloyed material exposed to the electrolyte. Pickering and Wagner thought bulk diffusion was causing the formation of the porous structure, but more modern studies showed otherwise (as covered in the next few sections). This process continues as un-dealloyed material is exposed and attacked by the electrolyte, forming a porous structure and pit formation. The diagrams below show a time-lapse sequence of images for the dealloying of AgAu. See section 2.5 for SEM images of AgPt displaying this behaviour.

Figure 9: Monte Carlo Simulation of the dealloying of AgAu over time. Left to right: (a) shows the alloy at the start, with gold atoms shown in orange and silver atoms in white. (b) shows the surface diffusion of gold atoms to form clusters. Pores are allowed to grow and increase in total surface area and at the same time keep the pits from becoming clogged up with gold. (c) shows the final result of dealloying. Agglomeration of the gold atoms to the channel walls is due to thermodynamics which favours the clustering of adatoms on the alloy/electrolyte interface via a spinodal decomposition process. Images taken from the video clip found at http://www.deas.harvard.edu/matsci/downdata/downdata.html.

Figure 10: Images from http://www.sandia.gov/~sjplimp/spparks/pictures.html#nanoporous. This shows a 3D cube structure of an alloy that has undergone selective dealloying (b). Surface diffusion and pore formation evolve a characteristic length scale. This set shows a bulk diffusion model with a 50% porosity factor.
1.5 \( E_c \) – Critical potential for dealloying

Critical potential \( E_c \), mentioned in section 1.3, is the potential at which porosity formation occurs in an alloy, regardless of whether other dealloying conditions (like alloy composition) are met. On a plot of current density versus potential, the critical potential is defined by a sharp increase in current density with increasing potential which represents the transition from alloy passivity to porosity formation. Pickering\(^{28}\) has suggested that \( E_c \) corresponds to the potential at which a 'pitting' type of attack occurs on the surface. In a system \( A_pB_{1-p} \), the value of the critical potential is composition dependent and the value of \( p \) is referred to as the parting limit. Dealloying occurs if the concentration of the more active component exceeds the parting limit. The parting limit is expressed as a critical atom percentage of the more reactive component above which that component can be removed from the alloy by electrochemical dissolution in an oxidizing environment such as HNO\(_3\). Parting limits range from about 20 – 60 at %. For a homogeneous face centered cubic binary alloy this is usually 50 – 60 at %. Dissolution of Ag from AgAu occurs at a parting limit close to 55 at % Ag\(^{35}\).

The typical steady-state polarization curve for a binary alloy is shown in figure 5. \( E_{A^\circ} \) and \( E_{B^\circ} \) represent the equilibrium metal-metal ion electrode potentials of A and B respectively. At potentials less than \( E_c \), the current-potential curve is flat. The surface morphology was initially thought to be a smooth barrier layer, but was later shown\(^{36}\) to be a nanoporous structure. In potentiodynamic scans, not the whole of the flat region seen is ‘subcritical’. Porosity starts to form, over long times, below \( E_c \) as explained in the next paragraph. However, there is still a true subcritical region at lower potentials.
The dealloying process has been treated as a combination of a kinetically controlled morphological transition and as a phase separation process \(^{2,37}\). On a current density vs. potential plot, \(E_c\) is typically determined by locating the onset of the rapidly rising current during an anodic polarization scan through extrapolation to the baseline current of the passivation region (as shown in Figure 11a). The low current region below \(E_c\) during a polarization scan has been described as potential independent \(^{11}\).

\(E_c\) has traditionally been calculated \(^{38}\) by measuring the potential at which the current density reaches the 1 mA cm\(^{-2}\) threshold. The dealloying process has been described as a kinetically controlled morphological transition dependent on parameters such as alloy and electrolyte composition, potential scan rate \(^{39}\); and as a phase separation process \(^{2}\). At potentials below the critical potential the noble component covers the active dissolution sites leading to surface diffusion-limited current density and thereby a macroscopically flat porous surface. Above the critical potential, however, the rate of alloy dissolution overcomes the rate of surface diffusion of noble component and the current increases steeply with the potential forming a porous structure.

At \(E_c\), sustained anodic dissolution of the more active element occurs and is often associated with a kinetic competition between chemical dissolution (tending to roughen the surface) and
capillary forces that drive smoothening and passivation by the remaining, more noble component.

Thermodynamically, a simpler definition (which we are testing) is that at $E_c$, the more active element would rather be dissolved in electrolyte than bound up in the surface. With the thermodynamic definition, the existence of the critical potential can be found on theoretical grounds via an energy balance between the various species and the interfacial free energies associated with creation of new surface during the removal of material from the bulk during dissolution. Experimentally, $E_c$ can be found by a slow potentiodynamic scan where one looks for a sharp turn-on in the dissolution current. This technique works if the scan rate is slow enough (usually $< 0.01 \text{ mV/s}$). However, a better (if more tedious) method is to hold the potential of a fresh sample at a fixed value and to see if the current density reaches a steady-state current which indicates sustained dissolution or decays forever which indicates surface passivation via site blocking by the more noble component enriched in the near surface layer. Published results of this are shown in Figure 12.

There is a certain ambiguity in measuring critical potential using polarization curves. In figure 5 (b), the two dotted lines indicate this clearly. The first dotted line shows the “knee” in the polarization curve and the second dotted line shows the onset of rapid current increase. Sieradzki et. al presented a complete set of data for critical potentials as a function of alloy and electrolyte composition (dissolved cation content) as well as potential scan rate for samples of AgAu.

A potential hold below (but close to) $E_c$ results in a potential independent current transient which follows a power law decay ($i \propto t^n$ with $-0.5 \leq n \leq -1$). In 2003, however, Dursun, Pugh and Corcoran reported $E_c$ to be much lower for potential hold experiments performed for 1-5 days as opposed to the traditional methods of measuring $E_c$ over a period of minutes or at the most several hours. They showed the development of a potential-dependent steady-state current where $E_c$ was lowered by as much as 115 mV for long-potentiostatic hold measurements, with a steady dealloying rate of about 1 nm/h with porosity occurring uniformly on the AgAu surface, confirmed by SEM analysis. Their results are shown in Figure 12 below.
Sieradzki, Corderman, et. al.\textsuperscript{31} offered two mechanisms to explain the critical potential. The first was that $E_c$ results from the competing kinetics of active element dissolution and surface diffusion of the more noble element. Hence, the critical potential would represent the balance point between the roughening action of dissolution (potential dependent) and the smoothing action of surface diffusion (potential independent).

The second was that $E_c$ was dependent on the type (e.g. kink, step/ledge or terrace) and number of like-nearest neighbours of the active element. For an alloy with a greater composition of the active element, the dissolution potential would be lower since there would be more high density clusters of the active element, i.e., $E_c$ decreases with increasing mole fraction of active elements. Percolation of atoms with more than $m$ like neighbours is called a high density percolation problem, with threshold written as $p_c(m)$. The relationship between the previously defined parting limit and the high density site percolation threshold (with the rule that atoms with
coordination greater than nine cannot dissolution) was determined\textsuperscript{35} many years later by geometric percolation modeling and KMC simulations.

- From geometric considerations, $p_c(9)$ for AgAu was determined to be $59.97 \pm 0.03\%$
- From KMC, $p_c(9)$ for AgAu was determined to be around $58.4 \pm 0.1\%$, with the difference between geometric and KMC results explained by the local atomic configurations of Ag atoms. A few of these configurations satisfy the percolation requirement but do not sustain dealloying, while a larger number show the opposite behavior.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{terrace ledges kinks.png}
\caption{Schematic diagram to illustrate terrace, ledge and kink sites.}
\end{figure}

Summarily, $E_c$ was traditionally measured in various more or less satisfactory ways, but their scan rates were such that $E_c$ was overestimated, at least in AgAu alloys. Dursun, Pugh and Corcoran’s\textsuperscript{40} potentiostatic hold dealloying curves were the first to show that very slow dealloying could give lower $E_c$, and with Sieradzki and Erlebacher, Corcoran believes he has found a thermodynamic $E_c$ not influenced by surface diffusion (although this can still be argued). The next section presents some of their results. See section 3.2 for results of differing scan rates on the critical potential of AgAu and AgPt alloys.

\section*{1.6 Thermodynamics of dealloying}

In 1993, Sieradzki theorized\textsuperscript{43} a framework for $E_c$ which incorporated both the thermodynamic origin and one based on the balance between dissolution and diffusion, which was an evolution of the thought process from Sieradzki, Corderman et. al\textsuperscript{31} in 1989.

In the 1989 report, two possible explanations of $E_c$ were offered:
1. One explanation related to a competition between dissolution of the more active component leading to surface roughening and the curvature-driven surface diffusion of the more noble component (assumed to be potential independent) resulting in a surface smoothening effect. At low potentials the diffusion of the more noble component covers active dissolution sites, and a surface diffusion-limited current density develops. Above \(E_c\), the dissolution overcomes the diffusion, and a macroscopic surface roughening develops. Viewed in this manner, the roughening transition and the critical potential are kinetically determined.

2. The second explanation of \(E_c\) related to the compositionally determined high density cluster \(p_c(m)\) structure of the more active element. The idea is that the dissolution potential of an atom in an alloy is affected by the identity of its 1\(^{st}\), 2\(^{nd}\), 3\(^{rd}\), etc., nearest neighbors. Alloys richer in the more active element will have larger high density clusters of this atom type, and thus the dissolution potential should be correspondingly lower. Viewed in this manner the critical potential and the roughening transition have a thermodynamic origin.

Subsequently, Sieradzki’s 1993 report developed a formulation of \(E_c\) which combined both of these ideas.

Erlebacher\(^{33}\) also pointed out that the empirical critical potential is a measure of how quickly the alloy reaches steady-state dissolution relative to the rate at which the potential changes. As such, it is “nonintrinsic” and relies on external parameters such as sweep rate. The following section describes the thermodynamics of selective dissolution.

Binary solid solutions are phases which have individual thermodynamic properties and their anodic dissolution (i.e. the oxidation of components) is proportional to the alloy and electrolyte composition. The change in the Gibbs free energy during a dealloying reaction can be written as\(^{41}\):

\[
\Delta G = RT\ln Q = RT\ln N_i = -nF\Delta E
\] (1)
Where

\[ \Delta G = \text{change in Gibbs free energy} \]

\[ R = \text{gas constant} = 8.314472 \frac{J}{\text{mol K}} \]

\[ T = \text{absolute temperature (K)} \]

\[ \ln = \text{natural logarithm} \]

\[ Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ for a reaction written as: } aA + bB \leftrightarrow cC + dD. \]

\[ Q = K \text{ (equilibrium constant) at equilibrium} \]

\[ N_i = \text{mole fraction of the component} \]

\[ n = \text{number of electrons per mole product} \]

\[ F = \text{Faraday constant} = 96,485.3399 \frac{C}{\text{mol}} \]

\[ \Delta E = \text{change in electric potential of the reaction} \]

Rearranging equation (1) leads to equations (2) and (3) below where \( \Delta E_i = \bar{E}_i - E_i^0 \) is the difference between the equilibrium electrode potential of the ith component in the alloy and the corresponding potential of the same component in the individual phase. By definition, since we are theorizing that \( N_i \) is an infinitesimally small component the result of equation (2) will always be positive (i.e. \( N_i < 1 \text{ and } \Delta E_i > 0 \)), meaning that the partial potentials of the alloy components are always more positive than the corresponding potentials of the individual metals. Per Figure 11a, this also shows why the anodic polarization curve of pure A is shifted to more positive potentials when alloyed with element B.

\[ \Delta E_i = -\frac{RF}{nF} \ln N_i \quad (2) \]

Equation (3) shows the potential difference between elements A and B in an alloy. Consequently, because the partial electrochemical properties of alloy components almost always differ, there is always a nonzero thermodynamic probability of the predominant selective dissolution of the more active metal from the alloy. This shows the existence of a difference in the electrochemical potential of each component in the alloy, which is dependent on the difference in their standard electrode potential and the mole fraction in the solid solution.
\[ \Delta E_{A,B} = E_B - E_A = \Delta E^0 - \frac{RT}{nF} \ln \frac{N_B}{N_A} \]  

(3)

In certain cases, we get ‘sub’ potential deposition, which is a phenomenon during which the more noble element of an alloy dissolves at values lower than the standard equilibrium electrode potential of the pure noble element due to curvature effects. In the case of AgAu, selective dissolution of Ag leaves regions of very high positive curvature, \( \kappa \), of Au that can dissolve at a sub-potential given by the Gibbs-Thomson relationship in (4) and (5). This is true for a nanoparticle which will generally dissolve below its normal \( E_0 \). Note here that this is sub-potential dissolution of positive curved regions of noble metal. Another type (which is what we studied in section 3.5) is sub-potential deposition of less-noble metal into negative-curved regions.

\[ \Delta E \approx \frac{\gamma V_{at}}{nq} \kappa = \frac{\gamma V_{at}}{nq} \left( \frac{1}{r} \right) \]  

i.e. \( \Delta E \propto \frac{V_{at}}{r} \)  

(4)

(5)

Where, for a sample Au structure in AgAu:

\( \Delta E = \text{change in equilibrium potential} \)

\( \gamma = \text{solid liquid interfacial surface tension} = \frac{1}{m^2} \)

\( V_{at} = \text{atomic volume of Au} = 10.2 \frac{cm^3}{mol} = \frac{1.02 \times 10^{-5} m^3}{6.022 \times 10^{23} mol^{-1}} = 1.694 m^3 \)

\( \kappa = \text{curvature} = \frac{1}{\text{radius of initial curvature of dealloyed structure}} = \frac{1}{r} = \frac{1}{3 \times 10^{-9} m} \)

\( q = 1.602 \times 10^{-19} C \)

Plugging these values in, we get \( \Delta E = 35 mV \) showing that certain curvature effects could lead to dissolution. In both Au and Pt based systems at potentials where only selective removal of the less noble component occurs, dissolution of both Au and Pt can be thermodynamically
discounted as explained before. During dealloying, when the more active element is selectively
dissolved, it leaves regions of very high positive curvature, \( \kappa \), of the more noble component that
can dissolve at a sub potential (measured with respect to the dissolution potential of pure flat B,
where B is the more noble element in \( A_pB_{1-p} \)) given by equation (4). However, the degree to
which sub potential dissolution actually occurs is determined by the kinetics of the competing
solid-state transport processes of surface and volume diffusion which also act to reduce regions
of high curvature.

Dissolution of the active element creates a morphology with high curvature consisting of atomic-
scale ligaments composed primarily of the more noble atoms. Regions of high curvature are
smoothened by surface diffusion. The percolation model of selective dissolution leads naturally
to the development of a porous structure which has a net zero curvature morphology\(^\text{43}\) (note here
that the positive and negative curvature regions behave differently) characteristic of a two-phase
interpenetrating composite. Intermediate alloy compositions can develop during dealloying can
via surface diffusion mixing of the dealloyed structure.

A very interesting aspect of dealloying is the clustering effect which leads to the ‘intrinsic’
critical potential argument. \( E_c \) (intrinsic) is the critical potential for alloy dissolution in single-
phase systems that depends exclusively on thermodynamic parameters. This is important since it
again represents a change in conventional view from the Sieradzki, Corderman et. al. (1989) and
Sieradzki (1993) reports. Rugolo, Erlebacher and Sieradzki in 2006\(^\text{42}\) suggested that surface-
diffusion and dissolution do not contribute to establishing the intrinsic critical potential of an alloy – i.e. it is solely dependent on the positions of the edges defining the atom clusters within the layer in the percolation backbone. If the potential is large enough (i.e., the critical potential) these clusters are dissolved, resulting in bulk porosity formation.

The 1993 Sieradzki model\textsuperscript{43} (equation) for $E_c$ was based on two effects: thermodynamic (related to dissolving the less noble metal from very small clusters of atoms, thus creating a noble metal surface with very high curvature) and kinetic (related to dissolving these atoms at a certain rate to avoid infilling by surface diffusion of the more noble atoms).

The average cluster size, $\xi$, in 1D percolation (in units of the nearest neighbor spacing) is given by\textsuperscript{29, 43}:

$$\xi = \frac{1+p}{1-p} \quad (6a)$$

Where $p$ is the atom percent of the less noble element in an alloy. The following is a simplified version of the Sieradzki model presented by Newman, for an alloy of AgAu\textsuperscript{44}.

The initial surface of the alloy can be considered to be intersected by numerous clusters of Ag that create tiny pits with highly curved Au surfaces when dissolved. These surfaces have a solid-liquid interfacial free energy $\gamma$. The excess interfacial energy $S$ per unit volume of a hemispherical pit created by the dissolution of a typical cluster (diameter $\xi a$, radius $\xi a/2$) is

$$S = \frac{2\gamma}{\xi a/2} = \frac{4\gamma}{\xi a} \quad (6b)$$

(neglecting the slight difference in $\gamma$ that must exist between the Au-rich pit and the original alloy surface). So, if we multiply $S$ by the molar volume $\Omega$, we obtain the energy per mole. Dividing by Faraday’s constant gives us a shift in the equilibrium electrode potential, $\eta_{th}$, for the Ag that was in the pit compared with ordinary bulk Ag:

$$\eta_{th}(thermodynamic) = \frac{S\Omega}{F} = \frac{4\gamma\Omega}{F\xi a} \quad (6c)$$
This positive shift represents a thermodynamic contribution to the difference between the ordinary Ag equilibrium potential and the critical potential. So, for \( p > p^* \), where \( p^* \) is the parting limit (c. 0.55),

\[
\eta_{th} = \frac{S\Omega}{F} = \frac{4\gamma\Omega (1-p)}{Fa (1+p)} \quad (6d)
\]

This agrees quite well with observation for Au and Pt alloys, provided that the \( E_c \) value for the former is measured extremely slowly (experimentally, we investigate this in section 3.3 on page 61), to give a so-called intrinsic critical potential. However, for easy dealloying it is necessary for the rate of dissolution of the Ag cluster to exceed the rate at which the pit is filled-in by surface diffusion of Au. This requires an additional overpotential \( \eta_k \) that can be written as

\[
\eta_k(kinetic) = b_a \log \frac{i}{i_0} \quad (6e)
\]

with \( i \) being equated to the flux of Au diffusing into the pit at the critical potential (Sieradzki used a linearized kinetic expression rather than this Tafel version). This flux \( j \) is given by a Fickian steady-state diffusion flux of the form

\[
j = \frac{aD_s}{\Omega \xi a} \quad (6f)
\]

where \( \alpha \) is a geometrical coefficient and \( D_s \) the surface diffusivity of Au. So \( \eta_k \) is given by

\[
\eta_k = b_a \log \frac{aF\Omega (1-p)}{\Omega (1+p)a_0} \quad (6g)
\]

and finally the critical potential \( E_c \) is governed by both the thermodynamic and kinetic effects:

\[
E_c = E_o + \eta_{th} + \eta_k = E_o + \frac{4\gamma\Omega (1-p)}{Fa (1+p)} + b_a \log \frac{aF\Omega (1-p)}{\Omega (1+p)a_0} \quad (6h)
\]

A similar equation for \( E_c \) was formulated in 2006\(^{42}\) and is shown below (Equation 7). In an ideal \( A_pB_{1-p} \) binary solid-solution alloy there are length scales defining the size of A and B clusters. In a fcc solid for \( p > 0.198 \), A atoms percolate. i.e., there is near neighbor connectivity of A atoms on the percolation backbone such that each A atom has at least two other A atoms as nearest
neighbours\textsuperscript{29}. The average cluster size of the percolation backbone increases with increasing $p$. However, since these clusters are finite length, they do not percolate through the solid – which supports the argument that below $E_c$ the surface is passivated with the noble metal atoms, but above $E_c$ the solid alloy backbone is attacked\textsuperscript{45} which therefore provides a continuous path for the selective dissolution of the more reactive A-component without the need for diffusive mass transport within the bulk of the solid.

This notion of a pre-existing length scale feature was shown\textsuperscript{42} via an experiment using a series of fixed-composition multilayer samples of AgAu (with a fixed layer thickness ratio of Ag:Au of 3:2). Experimentally, with X-ray scattering confirming the multilayer structure sharpness, the $i$ vs. $V$ behaviour showed that $E_c$ increased with decreasing silver layer width showing that the critical potential was independent of diffusion and dissolution of Au atoms as shown below.

![Figure 15: Current–potential behaviour of AgAu multilayers de-alloyed in 0.1 M HClO$_4$ + 0.01 M Ag$^+$ (reference electrode 0.01 M Ag$^+$/Ag). Critical potentials defined at a current density of 1 mA cm$^{-2}$ increase with decreasing multilayer wavelength. Image from ref [42].]
Theoretically, in this model, $E_c$ is described by the equation below:

$$E_c = \frac{8a E_b}{\xi^2} - k T \ln a_{Ag} \quad (7)$$

$E_c = \text{critical potential}$

$a = \text{nearest-neighbour lattice spacing}$

$E_b = \text{nearest-neighbour bond energy}$

$\xi = \text{average cluster size (or percolation backbone diameter)}$

$k = \text{Boltzmann constant}$

$T = \text{Absolute temperature}$

$a_{Ag} = \text{Atom fraction of Ag in the alloy}$

In previous analyses (represented by 6h) $E_c$ has been partitioned into two terms: a capillary overpotential (thermodynamic term) and a kinetic overpotential (related to the additional energy required for the dissolution process to overcome the tendency of the surface to form a passivating layer via surface diffusion)$^{2,43}$. In equation 7, the kinetic overpotential term is absent because there is no mechanism for a passive Au adatom layer and also there is a lack of the smoothening effect resulting from surface diffusion, implying that Au surface diffusion and Ag dissolution do not contribute towards establishing the intrinsic critical potential. Rugolo, Erlebacher and Sieradzki$^{42}$ elaborate by stating that at potentials near $E_c$, the Au passivation layer does not perfectly cover the underlying AgAu alloy surface. The layer is composed of various ‘artifacts’ like islands, pits or vacancy clusters penetrating the alloy surface. The positions of the edges defining the vacancy clusters within the layer and the edges of the islands continually fluctuate in time and eventually expose Ag clusters that are part of the percolation backbone. When potential approaches $E_c$, these clusters are dissolved, resulting in bulk porosity formation.

There are a couple of aspects of diffusion of noble atoms during dealloying that are interesting and unexpected:

- First, channel diameters in nanoporous metals are wider than the average spacing between atoms in the original alloy. This shows that the more noble (MN) atoms must be diffusing out of the base of pits formed during dealloying to attach to the MN rich ligaments; otherwise, they would passivate the base of the pit and dissolution would stop. The direction of such diffusion opposes both a concentration gradient and a curvature gradient. It is more natural to suspect that the MN atoms would diffuse and flatten the alloy/electrolyte interface, simultaneously passivating it and preventing further
dealloying after only a few monolayers of dissolution, but we know from experimental data that this does not happen.

- The second odd aspect of MN diffusion is that MN diffusivities along the alloy/electrolyte interface must be $\geq 10^{-14}$ cm$^2$/s to be consistent with the observation of nanometer-sized ligaments spaced a few nanometers apart, formed in a few seconds of dissolution.

This is why, in the case of AgAu for example, gold atoms get out of the way of pits. This was also shown by modeling Au adatoms and the electrolyte as a two-species mixture on the surface of the alloy and examining the free energy of the mixture vs. the Au coverage$^{33}$. Gold really does not want to be left as adatoms and subsequently this drives diffusion and agglomeration out of pits and causes capillary action and coarsening to occur on longer time scales.

Schofield, in a 2005 review$^{32}$ has pointed out possible dependence of critical potential $E_c$ on dealloying temperature. She reasons that since dissolution current density and surface diffusion are temperature dependent, by extension, so must critical potential. The two equations in question, written in such a way to elucidate the relationship between $T$ and the other terms, are:

$$T \propto \frac{-\Delta G_{diss}}{(R)(i_{diss})} \quad (8)$$

$$T \propto \frac{-\Delta G_{diff}}{(R)(D_{diff})} \quad (9)$$

Where

- $i_{diss}$ is the dissolution current density
- $\Delta G_{diss}$ is the Gibbs free energy of activation for dissolution
- $D_{diff}$ is the surface diffusion coefficient of the more noble element
- $\Delta G_{diff}$ is the Gibbs free energy of activation for diffusion
- $R = \text{gas constant} = 8.314472 \frac{J}{\text{mol K}}$
- $T = \text{absolute temperature}$
When the temperature increases, dissolution current density, $i_{\text{diss}}$, and surface diffusion coefficient of the more noble atoms, $D_{\text{diff}}$, also increase simultaneously, which indicates the dealloying critical potential might be shifted to a lower value than it would be at room temperature. Theoretically, since this means $E_c$ is lowered by dealloying at higher temperatures. We can observe a higher anodic current during dealloying if we hold the dealloying voltage the same as the one for room temperature.

Given that the preceding sections covered certain basics of dealloying, the following section will list the objectives of this work. We will then examine the experimental details including characterization of the alloys and subsequent voltammetry of AgPt and AgAu.
1.7 **Hypothesis and objectives**

1. A detailed comparison of AgPt and AgAu alloy preparation, dealloying and characterization will be presented, with the objective being to systematically gather data for the AgPt which has up to now not been studied or has only been referenced sparsely in the literature. For comparison, some CuPt and AgAu critical potential values are listed below\(^\text{10}\):

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Polarization (V)</th>
<th>Potential Hold (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(<em>{0.80})Pt(</em>{0.20})</td>
<td>0.605</td>
<td>0.565</td>
</tr>
<tr>
<td>Cu(<em>{0.75})Pt(</em>{0.25})</td>
<td>0.75</td>
<td>0.73</td>
</tr>
<tr>
<td>Cu(<em>{0.71})Pt(</em>{0.29})</td>
<td>0.815</td>
<td>0.8</td>
</tr>
<tr>
<td>Ag(<em>{0.80})Au(</em>{0.20})</td>
<td>0.9</td>
<td>0.81</td>
</tr>
<tr>
<td>Ag(<em>{0.75})Au(</em>{0.25})</td>
<td>1.04</td>
<td>0.94</td>
</tr>
<tr>
<td>Ag(<em>{0.70})Au(</em>{0.30})</td>
<td>1.11</td>
<td>1.01</td>
</tr>
</tbody>
</table>

*Table 1: Comparison of critical potential values determined by extrapolation of alloy polarization data or by long-term potential hold data, vs. SHE.*

For reference, the differences between the two systems (AgAu, CuPt) are as follows:

- The rate of elemental Cu dissolution and the dealloying current of Cu from the Cu–Pt alloy is approximately 1 order of magnitude greater than that of elemental Ag dissolution and the dealloying of Ag from AgAu alloys at a given overpotential
- The effective diffusivity of Pt is at least 3 – 4 orders of magnitude lower than that of Au
- The critical overpotential for CuPt is larger by 110 mV, and
- The critical potential in the CuPt system is not dependent upon the method used to measure it. This is in contrast to the AgAu system where we measure a higher overpotential using polarization data as compared to potential hold data

2. The critical potentials of both alloys will be compared with the objective to test the notion that an intrinsic \(E_c\) exists that is governed purely by thermodynamics of the cluster structure in the alloys, as introduced in section 1.6. In this case AgAu and AgPt should have the same \(E_c\) if measured properly (i.e. slowly, via potentiostatic hold experiments just below and just above \(E_c\) or via very slow scan rates of < 0.01 mV/s). The approach taken was to first measure the ‘apparent’ \(E_c\) by conventional methods of fast potentiodynamic scans followed by a slower scan rate and subsequently by performing potential hold measurements.
3. Porosity, XRD, polarization data as well as capacitance data will be reviewed for AgPt alloys, comparing it to AgAu.

Overall, the following questions and areas will be highlighted:

- Dealloying fundamentals and critical potential
- Structure of dealloyed layers and differences between AgAu and AgPt
- Interfacial energies for AgAu and AgPt
- Surface diffusion differences between AgAu and AgPt
- Examination of the morphology of de-alloyed layers and kinetics of dealloying
- Effect of lattice parameter on dealloying
- Cu replating into nanoporous Pt after dealloying AgPt (ancillary experiment only. From ref [4,52])
1.8 Thesis organization

Now that a preliminary literature review has been conducted and the objectives have been laid out, this thesis will be organized as follows. Section 2 will cover the experimental work showing the methods and materials used for sample preparation, electrochemical and characterization techniques. Section 3 will focus on analysis and discussion focusing on the determination of critical potentials and other promising dealloving conditions for AgPt and AgAu at various scan rates, the comparison of long term current decays at a range of single potentials, followed by a review of characterization methods using SEM and EDX on as-received, annealed and dealloyed AgPt, EIS measurements done on as-annealed and dealloyed AgPt and AgAu samples, and finally a brief look at plating a foreign object (Cu) into nanoporous AgPt. Section 4 will offer some concluding remarks and tie them back to the introduction sections (1.1 - 1.7). Implications and future work are discussed in section 5.
2 EXPERIMENTAL WORK

Experiments were done at room temperature conditions with average temperature range around 20 - 25 °C unless specified otherwise.

AgPt, wherever mentioned, refers to 77Ag-23Pt at%. Two types of AgAu were used: one with 20 at% Au and the other with 23 at% Au.

- Flat, surface mounted samples were used for dealloying and impedance experiments. Sample surface area was approximately equal to 1 – 1.4 cm² measured using a vernier caliper.
- Epoxy mounted on-edge samples were used for routine investigation. Sample surface area was approximately equal to 0.005 cm². Figure 16 shows both types of mounting. The physical forms of the as-received alloys and detailed preparation are described in the following sections.

2.1 Materials and sample preparation

All work in this thesis used AgPt samples from Intech EDM (AHB – 181 #1 MPC 3579M-06) with the following composition: Ag – 64.93 wt%; Pt – 35.07 wt%. Based on the phase diagrams provided for the silver-platinum alloy in APPENDIX A, Ag-35wt%Pt translates into Ag-23at%Pt. The as-received alloys had undergone cold rolling treatment and their final sheet thickness was around 100 µm. The Ag-20at%Au and Ag-23at%Au samples were received as cold-rolled 200 µm sheets from Goodfellow Metals, UK. All references to AgPt and AgAu refer to Ag-23at%Pt and Ag-23at%Au unless otherwise mentioned. We originally started with Ag-20Au for routine investigation but subsequently replaced it with Ag-23Au due to shortage of the Ag-20Au material and also to have the same Au at% composition of 23%.

Suitable strips (with typical size 10 mm x 3 mm as shown in Figure 17) of Ag-23Pt and Ag-23Au were cut using sharp scissors and their edges were smoothened using a file to remove large kinks. The surface was polished using 1200 grit emery paper. They were then annealed and used
for subsequent experiments and analysis (annealing is described in more detail on page 36). Annealed samples were surface or edge mounted into heat and electrolyte-resistant (as claimed by the manufacturer) epoxy resin. The epoxy used was Duralco 4525 Epoxy from Cotronics Corp., which is electrically resistant and cures at room temperature. It is also resistant to hydrochloric, phosphoric, sulfuric and nitric acids, making it quite suitable for the experiments that follow.

Mounted samples were polished again initially using a Smetco double disc polishing machine, starting with the most coarse emery paper (60 grit), subsequently progressing up to the finest (1200 grit) when there was no further change in the ‘scratches’ introduced when polishing. Edge-mounted samples were prepared with the epoxy-mounted sample held orthogonal to the emery paper, and care was taken to ensure the direction of polishing remained consistent for a given sample (i.e. up-down or left-right motion). They were cleaned by sonication for 5-10 minutes at room temperature in acetone using a VWR model 50HT ultrasonic cleaner. All samples were rinsed in de-ionized water and blow-dried with lab air prior to experiments.
A 1.5 L capacity double-walled glass vessel was used for electrochemical experiments. It was typically filled with 150 ml of electrolyte. Water was filled in between the double walls to minimize effects from fluctuations in surrounding temperature. Experiments were performed after de-aerating the solution for approximately 1 h with a porous frit that pumped the solution with high purity N₂ gas (99.998%, O₂ < 3 ppm) to help with uniform dispersion in the electrolyte. A 5 wt% perchloric acid solution (diluted from as-received ACS grade 60 wt% HClO₄) was the electrolyte used for all dealloying and voltammetry experiments, which were performed at room temperature conditions. A platinum wire acted as the counter electrode. A mercury sulfate reference electrode (MSE) was used for both AgPt and AgAu alloys (mercury/mercurous sulfate/sat. K₂SO₄ measured 658 mV vs. SHE⁴⁶).
2.2 Annealing AgPt and Ag-20Au / Ag-23Au

AgPt was annealed in a Micropyretics MHI horizontal tube furnace in air, after carefully reviewing the AgPt phase diagrams in Appendix A. Given that the AgPt phase diagram is a bit tentative with a fairly narrow window of solid solubility, the following temperatures seemed to be the best fit:

- 1035 °C, 7 h in air followed by rapid quenching
- 1035 °C, 73 h in air followed by rapid quenching
- 1050 °C, 7-8 h in air followed by rapid quenching

AgAu (both 20% and 23at% Au) was annealed at 975 °C for 1 h in an Ar/H₂ mix followed by rapid quenching. Quenching was achieved by immersing the AgPt and AgAu samples at the end of their anneal cycles into a mixture of water and ice around 0 °C. It is commonly used to prevent low temperature processes such as phase transformations from occurring by only providing a narrow window of time in which the reaction is both thermodynamically favorable and kinetically accessible for said transformations to occur.
2.3 X-Ray characterization

X-Ray diffraction suggested that the 1050 °C, 7-8 h in air anneal treatment for AgPt was better suited than the 1035 °C, 7 h/73 h treatment. The only risk here is that 1050 °C is so close to the liquidus that there may be some local melting of impurity or segregated areas. The ideal region targeted was the (Ag) phase in the AgPt phase diagram on Figure 52. For the AgPt sample which was annealed at 1035 °C, 7 h in air, it appeared that the peaks were a bit broadened, indicating some residual segregation from casting. However, since the samples were mechanically polished after annealing, it could be possible that broadening occurred due to cold work from polishing.

The treatment which was deemed unsuitable was the 1035 °C, 73 h in air which clearly caused some ordering. The superlattice peaks observed are quite classical (although an extra peak was observed, see Figure 26) but it should not happen according to the phase diagram. While the data are neat in a way, not much else is known to explain this occurrence.

A comparative voltammetry of the differently prepared samples is presented in section 3.1. The 1050 °C samples showed good mechanical properties and did not show any signs of brittleness before dealloying, showing that there was no local melting. Since silver oxidizes approximately less than 180 °C, quenching had to be done quickly to ensure it did not spend a long time in the 100 – 200 °C range. This is only important if as-heat treated samples were used for experiments – i.e. it does not matter if samples were abraded before experiments. The ordering reaction at 23% Pt is likely not much of an issue since samples were quenched.

It was ensured that the furnace used was properly calibrated, keeping in mind the location of the control thermocouple relative to where the sample was placed within. A quartz tube as shown in Figure 17 was used to contain the AgPt and Ag-20Au/Ag-23Au samples inside the furnace.
Figure 17: Clockwise from top: MHI horizontal tube furnace; quartz tubes in which AgPt or AgAu sample strips were annealed; and typical sample strips of Ag23Pt after annealing treatment at 1050 °C for 8 h. Annealing causes the strips to curl inwards along the length of the cut strips.
2.4 Electrochemistry

The Parstat 2263 was used in some very early measurements. It was later replaced by the Gamry Reference 600 for all electrochemical work and the Gamry 600 persisted throughout for all further experiments, for reproducibility. The Parstat 2263 by Princeton Applied Research is a Potentiostat/Galvanostat/FRA that consists of hardware that is capable of ± 10 V scan ranges, 200 mA current capabilities, and EIS measurements up to 1 MHz. Similarly, the Reference 600 is a high performance Potentiostat/Galvanostat/ZRA which is able to measures EIS between 10 Ω and 100,000 Ω at 1 MHz with less than 1 % error, and comes with software to run experiments (in E-Chem Framework) and also perform analysis (with E-Chem Analyst).

A Faraday cage was used in experiments for proper grounding and to reduce noise in low current experiments such as EIS.
Figure 18: Electrochemical double-walled glass vessel showing placement of MSE reference electrode, Pt counter electrode and sample (top), Faraday cage and setup (bottom).
Electrochemical data and characterization results were obtained at room temperature for the following:

- Cyclic polarization data in 5% HClO₄ for the differently annealed AgPt samples
- Comprehensive set of simple voltammetry for AgPt and AgAu: one way scans up to an upper limit and determination of critical potentials for AgPt and AgAu using fast and slow scan rates
- Comparison of long term current decays at a range of single potentials for AgPt and AgAu, below the potential where Pt oxidation starts (~550 mV). The potentials were the same for the two alloys and encompassed potentials below and above E_c. The current decays were run for ~1000 s at lower potentials and shorter times above E_c.
- SEM and EDX characterization was done for as-received, as-annealed and as-dealloyed samples
- Impedance spectra were at OCP obtained for AgPt and AgAu after dealloying to the same charge density to compare porosity and pore size effects
- Replating experiment: AgPt was dealloyed in HClO₄, then the potential was scanned backward to replate a foreign ion (Cu, added via CuO) into pores (exact procedure is in section 3.5 on page 77)
- Determination of Ag left behind after dealloying and whether this depended on potential, time and electrolyte: EDX linescans were done to confirm this since this is an important parameter for potential applications
2.5 SEM and EDX characterization on as-received, annealed and dealloyed AgPt

SEM and EDX examinations were done on as-received AgPt, AgPt annealed at 1050 °C for 8 h in air and AgPt dealloyed at 0.40 V (vs. MSE) for 6 h for a total accumulated charge of 11.95 C (or 7.7 C/cm²). Preliminary XRD results are shown for AgPt annealed at 1050 °C/7 h in air and 1035 °C/73 h in air.

Figure 19: SEM images of AgPt: (a) As-received [scale bar 50µm], (b) Thermal annealed at 1050 °C/8 h in air [scale bar 50 µm].

Figure 1, Figure 2 and Figure 3 on pages 3, 4 and 5 show examples of the free surface porosity formed during dealloying. One reason for choosing AgPt in this work is the high melting point of Pt and its low surface diffusivity which creates a very fine nanoporosity on the order of 2-3 nm (other than the straightforward reason to compare AgPt and AgAu under identical conditions). There is evidence to support local small-scale shrinkage and coarsening after dealloying, but the bulk dealloyed layer volume remains unchanged from the starting material. Average EDX analysis indicates that the starting 77Ag-23Pt material changes composition after dealloying to about 12Ag-88Pt (at. %) after dealloying at 0.4 V for 6 h, as shown by the data in Figure 23 on page 45. Note that dealloying does not alter the crystal structure (as shown via XRD) or the orientation of individual grains.
Secondary electron imaging and backscattered electron imaging reveal some additional useful information on the grain structure and composition of annealed AgPt samples. Secondary electrons are emitted from the atoms occupying the top of the sample surface. The contrast from the image is determined by the sample morphology and a high resolution image is obtainable due to the diameter of the primary electron beam. Backscattered electron images are formed by primary electrons reflected in the specimen interaction volume by elastic scattering interactions with specimen atoms. Heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image. A BSE image will indicate bright areas for Pt rich regions and dark areas for Ag rich regions (Pt Z=78, Ag Z=47) and is useful for distinguishing different chemical phases. Figure 21 below shows BSE images of AgPt annealed in air and in H₂/Ar. Average grain size is around 20 μm for the air annealed treatment and around 10 μm for the H₂/Ar annealed treatment. Figure 21 may show Pt rich phases in the alloy. This would not affect E_c measurements but would affect mechanical properties of the alloys.
Figure 21: BSE images of AgPt annealed at 1050 °C for 8 h in air (left), and AgPt annealed at 1035 °C for 8 h in H₂/Ar. Scale bars 50 µm.

Figure 22: Secondary image (left) and BSE image (right) of AgPt dealloyed at 0.4 V vs. MSE for 6 h. Scale bars 50 µm.
Figure 23 shows the secondary and BSE image after dealloying at a suitable voltage until porosity is formed. It shows spontaneous intergranular fracture due to tensile stress developed during dealloying. It is evident from Figure 23b that the specimen appears suitably homogeneous showing that only Pt-rich regions remain. One of the reasons for doing EDX was to determine if the as-annealed alloy had Pt-rich regions which facilitated dealloying, which we can also confirm to be true by SEM based on Figure 21. The complete EDX results are also shown in Appendix D (page 96) we can see the Ag versus Pt atomic % composition of as-received (81Ag-19Pt), as-annealed (78Ag-22Pt) and dealloyed (12Ag-88Pt) samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag L</td>
<td>6.78</td>
<td>11.63</td>
</tr>
<tr>
<td>Pt M</td>
<td>93.22</td>
<td>88.37</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

*Figure 23: EDX results of dealloyed AgPt. The composition changes from 77Ag-23Pt to 12Ag-88Pt (at. %) upon dealloying.*

The figure below shows a plot of the variation of AgPt lattice parameter with composition. It can be estimated to be around 4.04 Å for an alloy with 23 at% Pt. PXRD patterns indicate the actual lattice parameter to be 4.04 Å exactly, based on Figure 25.
XRD results of annealed AgPt are shown below. Figure 25 shows the XRD pattern of AgPt annealed at 1050 °C/7 h in air and Figure 27 shows the XRD pattern of AgPt annealed at 1035°C/73 h in air. The phase constitution of the AgPt alloy are single phase fcc but the peaks after the shorter heat treatment appear to be a bit broad, perhaps indicating some segregation. The XRD in general is encouraging and it is interesting that the lattice parameter change from short (a = 4.039 Å) to long heat treatment (a = 4.012 Å) is quite small. Ag has a lattice constant of $a_{\text{Ag}} = 4.090$ Å, Pt has a lattice constant $a_{\text{Pt}} = 3.920$ Å, Au has a lattice constant $a_{\text{Au}} = 4.080$ Å and Cu has a lattice constant $a_{\text{Cu}} = 3.610$ Å. The AgPt system is unique in that Ag has a bigger lattice constant than Pt and it is possible that this material has a low induced stress after dealloying because of this.
Figure 25: Powder XRD (Cu Kα anode) of AgPt annealed at 1050 °C/7 h in air. The structure is cubic, fcc with lattice parameter $a = 4.04$ Å. The peaks are marked with their d-spaces. There is no superlattice peak. The black curve (on the bottom) indicates the peak after subtracting background noise. The red and blue bars indicate expected 2θ values of pure Ag and pure Pt, respectively.

Calculated lattice parameter: $a = 4.0351(7)$ Å
Figure 26: Powder XRD (Cu Kα anode) of AgPt as-annealed at 1035 °C/73 h in air showing an extra (100) superlattice peak.

Figure 27: Powder XRD (Cu Kα anode) of dealloyed AgPt annealed 1035 °C/73 h in air. The structure is cubic, fcc with lattice parameter $a = 4.012$ Å. The peaks are marked with their d-spaces. There is no superlattice peak.
Dealloying shifts the AgPt peaks towards that of pure Pt. The table below lists some of the expected peak positions for AgPt and Pt.

<table>
<thead>
<tr>
<th>Position</th>
<th>AgPt 2θ angle</th>
<th>Pt 2θ angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>38.51</td>
<td>39.78</td>
</tr>
<tr>
<td>(200)</td>
<td>44.77</td>
<td>46.27</td>
</tr>
<tr>
<td>(220)</td>
<td>65.17</td>
<td>67.52</td>
</tr>
</tbody>
</table>

Table 2: Expected XRD 2 theta values for AgPt and Pt.

X-rays penetrate into a sample. The depth of penetration depends on the mass absorption coefficient of the sample and the incident angle of the X-ray beam. This produces errors because not all X-rays are diffracting from the same location. Such errors are present due to peak asymmetry and are greatest for organic and low absorbing (low atomic number) samples, but can be reduced by using thin samples. For AgPt, the depth of penetration is shown below, calculated from NIST attenuation coefficients.

Figure 28: Depth of penetration of Ag and Pt.
3 ELECTROCHEMICAL RESULTS AND DISCUSSION

The following section describes systematic experiments aimed at documenting the voltammetry of AgPt and AgAu.

3.1 Cyclic polarization data in 5% HClO₄ for the differently annealed AgPt samples

Since there was no previous work at characterizing the polarization of AgPt, our first attempts were to first establish a baseline of the behaviour of AgPt in an oxidizing environment. Of primary importance were the shape of the polarization curve, the range of potentials at which we could expect a sharp increase in current and whether there were any prominent features specific to AgPt. Once this basic information was found, we could proceed with adjusting experiment variables. In order to determine the effect of anneal times on the AgPt samples, systematic cyclic polarization was done in 5% HClO₄, for anneal times of 7 h and 73 h at 1035 °C. The current densities vs. potential graphs below show several runs. The solution was deaerated for 1 hour and these edge-on samples were polished to a 0.3 µm finish.
Figure 29: Cyclic polarization data of AgPt annealed for 7 h at 1035 °C (and 1050 °C) in air for an edge-on sample. Several runs were performed to ensure reproducibility.

Figure 30: Cyclic polarization data of AgPt annealed for 73 h at 1035 °C in air for an edge-on sample.
The scans were done from -0.6 V to +1.2 V and back to -0.6 V vs. MSE, at 5 mV/s, for each of the differently annealed samples. Figure 29 shows the 73 h annealed AgPt polarization curve, Figure 30 shows the 7 h annealed AgPt polarization curve, and Figure 31 shows a combined curve overlay on the same graph. The 7 h annealing treatment shows a sharp increase in current density in the 270 – 400 mV region which is indicative of the onset of bulk porosity formation. There is also a ‘double current wave’ feature showing small current spikes at 250 mV and 425 mV which could be interpreted as a double critical potential. It is possible this is real but we think a more likely explanation is that the alloy is not homogeneous. It could be possible that the segregation left over from the alloy manufacturing process is too great to be annealed out in 73 h, meaning these double waves would disappear when annealing is done for longer times. It may also be possible that different regions of the sheet are different and that certain sections of the sheet (for both edge-on and flat samples) are better to obtain polarization data.

![Image overlay of polarization data of AgPt 7 h and 73 h anneal treatment.](image)

The current density of the 7 h annealed sample is higher than the longer annealed sample above 0.40 V. Figure 29 also shows us that AgPt annealed at 1050 °C for 7 h displays very similar
characteristics to the 1035 °C 7 h annealed sample. The notable feature of these plots is that the 7 h annealed sample displays a noticeable increase in current density (broad peak) around 270 mV to 400 mV whereas the 73 h sample shows this (albeit a much sharper increase with the peak not being as broad) just under 400 mV.

It appears that the long anneal treatment which causes ordering is prone to give lower dealloying rates and less sharp critical potentials. This is consistent with the results reported by Parks Jr., Fritz and Pickering\(^{27}\) where from Figure 7 we note that the disordered alloys have a lower critical potential and a much sharper increase in current at \(E_c\). The very high current densities and high OCP on the reverse scan are indicative of the high capacitance and/or partial oxidation of Pt on the dealloyed AgPt structure.
3.2 Determination of critical potentials for AgPt and AgAu using scans from OCP to around 800 mV vs. MSE

In the previous section, we saw the effect of annealing treatment on $E_c$. The critical potential value or region is an important result for dealloying. This section presents the measured values of $E_c$ for Ag-23Pt and Ag-23Au in 5% HClO$_4$, but we’re not calling these measurements the intrinsic critical potential yet – those will be covered via potentiostatic hold experiments in section 3.3. Given that $E_c$ is dependent on scan rate, the latter was varied by a factor of 10 to determine the resulting $E_c$. Runs were repeated several times in fresh solution for each scan rate and the sections below present the fast scan rate first (3.0 mV/s) followed by the slower scan rate (0.3 mV/s).

3.0 mV/s scan rate:
Different methods produce different results for measuring the critical potential of an alloy. As we measure $E_c$ using the potentiodynamic scan method in this section, we look at the value of the potential at which current density increases significantly. We can refer to $E_c$ measured via this method to be the apparent or derived critical potential because another method exists (section 3.3) that reportedly gives us a more accurate value of $E_c$ which we can refer to as the intrinsic critical potential.

AgPt mounted on-edge in epoxy was scanned from -0.6 V to 1.0 V vs. MSE in 5% HClO$_4$ using a 3.0 mV/s scan rate. Figure 32 and Figure 33 show potentiodynamic scans using a scan rate of 3.0 mV/s. In this set of experiments, the critical potentials of AgPt and Ag-23Au were found to be 350 mV and 390 mV vs. MSE respectively.
Figure 32: Ag-23Pt potentiodynamic scan in 5% HClO$_4$ at 3.0 mV/s scan rate. $E_c$ occurs around 350 mV vs. MSE.

Figure 33: Ag-23Au potentiodynamic scan in 5% HClO$_4$ at 3 mV/s scan rate. $E_c$ occurs around 390 mV vs. MSE.

0.3 mV/s scan rate:

AgPt mounted on-edge in epoxy was scanned from -0.6 V to 1.0 V vs. MSE in 5% HClO$_4$ using a 0.3 mV/s scan rate, similar to the 3.0 mV/s scan conditions. The first significant increase in current density occurs at 310 mV vs. MSE.
On-edge samples could have interface fractures and other deformities that could produce messy data. To avoid this, AgPt was dealloyed at 1050 °C for 8 h in air and fresh flat samples with areas 1.34, 1.05 and 1.41 cm² were used with scan rates of 0.2, 1.0 and 5.0 mV/s to observe if sample surface area played any role in dealloying. The 0.2 mV/s scan rate produced the most visual increase in current density. $E_c$ is lower at the lower scan rate. From Figure 36, $E_c$ is at 280 mV (at 0.2 mV/s scan rate), 310 mV (at 1.0 mV/s scan rate) and 330 mV (at 5.0 mV/s scan rate). This is evidence and an early indication that conventional fast scan measurement methods overestimate the intrinsic $E_c$ for a given alloy.
Figure 35b: Second derivative plot of current density versus potential for AgPt. The zero crossing value at $E_c$ is at 293 mV.

Figure 35 shows a second derivative plot of Run #3 from Figure 34, showing a mathematical approach to determining critical potential from potentiodynamic scans, as opposed to determining it subjectively based on the plot. In a second derivative plot, the value at which zero is crossed on the x-axis indicates the “inflection” point on the potiodynamic curve and will give the critical potential. Here, we note that it is 293 mV which is a closer approximation to $E_c$ compared to 310 mV.
Similarly, from Figure 38, Ag-23Au was scanned from -0.3 V to 0.8 V vs. MSE in 5% HClO₄ using a 0.3 mV/s scan rate. The first significant increase in current density occurs around 360 mV vs. MSE, indicating the onset of bulk dealloying. Results from Pugh, Dursun and Corcoran\(^\text{10}\) are listed in Table 1 on page 30 (vs. SHE). Interpolating their results to our Ag-23Au, we find that \(E_c\) should be around 0.97 V vs. SHE (or 0.31 V vs. MSE) which seems to be close to our 360 mV vs. MSE. Of course, some differences could still exist due to the acid concentration, manufacture method and annealing temperature.
Figure 37: AgAu critical potential vs. SHE versus alloy composition. The 20% Au, 25% Au and 30% Au were actual experiments done in ref [8]. The 23% Au was interpolated assuming a linear fit with equations as shown. Two types of measurements were performed: one via polarization using potentiodynamic scans and the other via potential hold experiments which are described in detail in section 3.3.

Between the fast and slow scan rates, the slow scan rates resulted in lowering the apparent $E_c$ by 40 mV for AgPt (from 350 mV to 310 mV) and 30 mV for Ag-23Au (from 390 mV to 360 mV) from the faster scan rate. By extension of this same argument, we can also see that in AgPt, this apparent critical potential was further lowered from 310 mV to 280 mV when the scan rate was...
reduced from 0.3 mV/s to 0.2 mV/s. This ‘lowering’ of the apparent $E_c$ indicates that there is a true intrinsic potential at a low enough scan rate that affects dealloying.

As noted in Figure 32 through Figure 38, there is some ambiguity when determining the critical potential in defining the onset of the rapidly increasing current. Here, the critical potential was derived by the intersection between the extrapolation of the slope of the rapidly increasing current and the slope in the ‘passivation-like’ flat region. In the literature, another common method is to pick a predefined current density (usually 1 mA/cm$^2$)\textsuperscript{38, 48} and measure the value at which the potential reaches this threshold. Table 3 on page 65 lists critical potential values of Ag-20Au as reported in the literature, derived from various methods. Recent literature\textsuperscript{33,40,42,48} suggests that this method of ‘extrapolation by intersection’ tends to overestimate $E_c$ because the flat region current is too high. To counter this, a common experimental approach is to hold the potential over a long period of time (order of several hours to days) at regions below, above and close to $E_c$ and to plot the resulting log ($i$) vs. log (t) data. As shown previously in Figure 12 expected results indicate that below $E_c$, the plot shows a rapidly decaying current following power law behavior. Above $E_c$, the plot shows a constant mean dealloying current with time and sometimes a steadily increasing current. Close to $E_c$, the plot transitions from a power law decay into a steady-state current. This type of measurement commonly referred to as a potential hold experiment, will be elaborated on in the next section.
3.3 Comparison of long term current decays at a range of single potentials for AgPt and AgAu

So in order to find the intrinsic value of $E_c$, the following series of experiments was developed. Potential was held for 20 minutes for AgPt and Ag-23Au. For AgPt, the potential was held at 15 mV intervals over a suitable range (-85 mV to +400 mV, though not all data are shown). For Ag-23Au, the potential was also held at 15 mV intervals over a suitable range (200 mV to 460 mV, though not all data are shown). Log current density vs. log time results are presented in Figure 39 and Figure 40. Each potential hold experiment was a completely new experiment on a new sample and not a progressive stepping of the potential on the same sample.

![Figure 39: Potential was held for AgPt for 20 min (or 1 h) at the potentials listed (all vs. MSE). The best estimate of critical potential is 275 mV.](image)

The AgPt steady state $E_c$ measurements in Figure 39 indicate that 390 mV is above the critical potential since the current remains uniformly constant over time. At 275 mV, there is a slight decay but the overall current is still potential dependent, which is a good indicator of the
potential being very close to $E_c$. Over the 250 – 260 mV range, there is a much stronger decay with current being potential independent (overlapping current decays) from which we can interpret this to be the range below the critical potential. It is also obvious that as potential decreases, the time taken to reach steady-state current increases. Indicative of the reproducibility of the current for a given potential are the curves at 290 mV and 300 mV, where there is some degree of overlap in their current decays for a short time.
Figure 40: Potential was held for Ag-23Au for 20 min (or 1 h) at the potentials listed (all vs. MSE). The top figure shows a range over 320 – 455 mV and the bottom figure shows a range over 215 – 320 mV. The critical potential appears to be close to 290 mV.

Figure 40: Potential was held for Ag-23Au for 20 min (or 1 h) at the potentials listed (all vs. MSE). The top figure shows a range over 320 – 455 mV and the bottom figure shows a range over 215 – 320 mV. The critical potential appears to be close to 290 mV.
In Ag-23Au, the intrinsic critical potential is around 290 mV (the first instance of a slight current decay curve followed by a constant flat current region over time). Interpolating for 23%Au from Pugh, Dursun and Corcoran\(^\text{10}\) as shown in Figure 37, we expect \(E_c\) to be at 0.88 V vs. SHE (or 0.22 V vs. MSE).

While the data in Figure 39 and Figure 40 could be improved by increasing the time to several hours or days, we can still extract useful information by plotting the final current density for each potential hold. This, in effect, gives the value of a steady-state critical potential. The final current densities vs. potential for AgPt and Ag-23Au are shown below. Note that each data point is a separate potential hold experiment. These plots show that \(E_c\) (ss) for AgPt is 275 mV vs. MSE and \(E_c\) (ss) for Ag-23Au is likely around 290 mV vs. MSE. The pattern observed here (shown in Table 3) is that the apparent critical potential is overestimated for conventional \(E_c\) measurements and is reduced by almost 30 – 40 mV when using the potential hold method. Another finding we observed is that AgPt hardly depends on the method while AgAu shows a stronger dependence on the method used to measure \(E_c\). We can interpret this because the delta in \(E_c\) is 35 mV for AgPt (from 310 mV using conventional slow rate potentiodynamic scans to 275 mV using potential hold) but is much larger at 70 mV for Ag-23Au (from 360 mV using conventional slow rate potentiodynamic scans to 290 mV using potential hold).

Figure 41 is quite clear and shows the potential hold experiments plotted on the same figure. It shows that both alloys are very similar and suggests \(E_c\) values indicated might be a little too high.
Figure 41: Plot of log \( i \) (final) vs. potential. Each data point on this plot is a separate potential hold experiment from Figure 40, for AgPt and Ag-23Au.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( E_c ) (extrapolation)</th>
<th>( E_c ) (fixed current)</th>
<th>( E_c ) (ss potential hold)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-23Pt @ 0.2 and 0.3 mV/s</td>
<td>310 mV</td>
<td>590 mV</td>
<td>275 mV</td>
</tr>
<tr>
<td>Ag-23Pt @ 3 mV/s</td>
<td>350 mV</td>
<td>410 mV</td>
<td></td>
</tr>
<tr>
<td>Ag-20Au (vs. SHE) @ 1 mV/s (MSE is 0.658 V vs. SHE at RT)</td>
<td>0.90 V vs. SHE (= 0.242 V vs. MSE) from ref 48</td>
<td>1.10 V vs. SHE (= 0.442 V vs. MSE) from ref 48</td>
<td>0.8 V vs. SHE (= 0.142 V vs. MSE) from ref 48</td>
</tr>
<tr>
<td>Ag-23Au @ 0.3 mV/s</td>
<td>360 mV</td>
<td>460 mV</td>
<td>290 mV</td>
</tr>
<tr>
<td>Ag-23Au @ 3 mV/s</td>
<td>390 mV</td>
<td>440 mV</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Critical potentials derived from various methods. Extrapolation was done by the determining the intersection of the rapid current rise to the plateau. Column 3 (fixed current) was determined by measuring the potential necessary for the current to reach a value of 1.0 mA/cm\(^2\). Column 4 (steady state potential hold) gives the critical potential values as determined by the potential hold data from ref 48. All potentials vs. MSE.
Figure 42 and Figure 43 are representative of the current decays typically seen in such alloys. They were obtained by dealloying new samples at each potential for 1 h in fresh HClO₄. It is interesting to note the unusual increase in current with time for AgPt, whereas Ag-23Au shows the typical decay curve behaviour.

### 3.3.1 Dealloying curve of AgPt

![AgPt current decay curves at the given potentials. All potentials are referenced to MSE.](image)
3.3.2 Dealloying curve of Ag-23Au

At low applied potentials where the kinetics of dissolution are slower, there is no “steady-state” achievable. However, with a large enough applied potential which provides a high driving force, dealloying kinetics are able to achieve this pseudo steady-state for Ag dissolution. For applied potentials greater than $E_c$, there is definite porosity formation. For potentials below $E_c$, the surface is passivated.\textsuperscript{33}

However, at high overpotentials the dissolution rate would dominate and no hindrance to dealloying would occur, i.e., the system would approach the pseudo steady-state currents measured in the potential hold experiments. In this region, the Butler-Volmer equation simplifies to $E - E_o = b \log(i/i_o)$ with $b$ being positive for an anodic reaction and negative for a cathodic reaction. The ‘$i$’s are absolute values.
3.4 **Electrochemical Impedance Spectroscopy**

Electrochemical impedance spectroscopy (EIS) measurements were done on as-annealed and dealloyed AgPt and Ag-23Au samples. EIS is a simple and non-destructive method of studying dealloyed layers since it can provide information on total surface area, shape, size and distribution of porosity without actually changing the morphology or integrity of the sample being measured. Using the same Gamry Reference 600 instrument, AC electrochemical impedance spectra were measured at various conditions, including before and after the de-alloying, to compare the capacitance changes in both alloys and to further estimate the porosity of the resulting nanoporous de-alloyed layers.

Typically, EIS data are presented in Bode plots, which show log |Z| (impedance) and the phase angle versus log $f$ (frequency). Such plots allow the possibility to detect regions dominated by resistive behaviour where the Bode plot slope is zero and regions dominated by capacitive behaviour in which a slope of -1 is observed in an ideal case. In a Nyquist plot, the imaginary part of impedance is plotted on the y-axis versus the real part of impedance on the x-axis. Each point on a Nyquist plot is the impedance at a single frequency. Low frequency data are on the right side of the plot and higher frequencies are on the left. In general, the measured impedance spectra are depressed semicircles in the complex plane, and they do not show the “semicircle centered on the real axis” feature that is typically observed in systems that can be represented by a simple resistance-capacitance equivalent circuit. Typically, this deviation results from inhomogeneities or porosity present in the samples. In EIS data impedance usually falls as frequency rises. Presented together, Bode and Nyquist impedance plots give a more complete picture of dealloying.

This section shows the difference in the Bode and Nyquist plots for AgPt and AgAu, samples of which were dealloyed to the same charge density via chronocoulometry. The experiment typically starts at a potential (Initial E) at which there is no electrolysis with subsequent instantaneous stepping of potential to a value that leads to oxidation or reduction of some species in solution. Since sample surface areas were known and potential was constant, only dealloying time needed to be controlled. In the experiment, dealloying was stopped (automatically) when 10
mC of charge was reached for AgPt or 5.2 mC of charge was reached for AgAu. For the dealloying times and charge densities listed, calculations showed that the depth of dealloying was around 0.3µm for the 0.5 V dealloying. The procedure has some inherent error due to the way the software was scripted, which resulted in some error (shown in the % difference column in Table 4) instead of the charge densities being exactly the same for both samples.

<table>
<thead>
<tr>
<th>Potential vs. MSE</th>
<th>Dealloying time: (charge density) Ag23Pt</th>
<th>Dealloying time: (charge density) Ag23Au</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 V</td>
<td>550 s (15.98 mC/cm²)</td>
<td>1000 s (15.41 mC/cm²)</td>
<td>4%</td>
</tr>
<tr>
<td>0.2 V</td>
<td>650 s (31.39 mC/cm²)</td>
<td>600 s (34.59 mC/cm²)</td>
<td>9%</td>
</tr>
<tr>
<td>0.3 V</td>
<td>585 s (30.45 mC/cm²)</td>
<td>400 s (28.83 mC/cm²)</td>
<td>6%</td>
</tr>
<tr>
<td>0.425 V</td>
<td>85 s (40.43 mC/cm²)</td>
<td>120 s (43.97 mC/cm²)</td>
<td>8%</td>
</tr>
<tr>
<td>0.5 V</td>
<td>125 s (275.6 mC/cm²)</td>
<td>50 s (273.3 mC/cm²)</td>
<td>1%</td>
</tr>
</tbody>
</table>

Table 4: Comparison of AgPt and AgAu dealloyed to the same charge density (shallow dealloying) to depth around 0.3 µm for the 0.5 V dealloying.
Figure 44: Top to bottom: Bode impedance plot and Nyquist impedance plots of Ag-23Pt after dealloying above critical potential at 0.425 V (85 s) and 0.5 V (100 s) vs. MSE, along with as-annealed curve for reference. The last Nyquist plot is a magnified view showing end frequencies.
Figure 45: Top to bottom: Bode impedance plot and Nyquist impedance plots of Ag-23Au after dealloying at 0.1 V (1000 s), 0.425 V (120 s) and 0.5 V (50 s) along with as-annealed curve for reference. The last Nyquist plot is a magnified view showing end frequencies.
EIS measurements were done after dealloying at potentials 100, 200, 300, 425 and 500 mV vs. MSE for the times and charge densities listed in Table 4. The electrolyte was 5% HClO₄. Impedance data were obtained between the initial frequency (100 kHz) and the final frequency (100 mHz) for all alternating current electrochemical experiments of as-annealed and dealloyed samples of AgPt and Ag-23Au. Since E_c (fixed current) was 410 mV for AgPt and 440 mV for AgAu, 425 mV was chosen as the potential at which AgPt would theoretically be dealloyed but not Ag-23Au (however, if the critical potentials are taken to be the intrinsic values of 275 mV for AgPt and 290 mV for Ag-23Au, then we can expect dealloying to occur for both samples at 425 mV). For 425 mV and 500 mV we notice a greater departure from a classical capacitive response indicative of either deeper porosity of similar size or smaller porosity of a similar depth.

Using the charge densities listed in Table 4 for the dealloying performed at 0.5 V vs. MSE, we have a charge density of 0.276 C/cm² for AgPt and 0.273 C/cm² for Ag-23Au. Then, using Faraday’s second law, the density of silver (10.5 g/cm³) and its atomic weight (107.9 g/mol) with Faraday constant (96,500 C/mol), the depth of the de-alloyed layers can be obtained by multiplying these charge densities (C/cm²) with a factor of 1.1 x 10⁻⁴ (cm³/C). We calculate the depth of the dealloyed layers to be 0.3 μm assuming all silver was dissolved (which is likely not the case). This seems to be a reasonable result given the short dealloying times used (125 s for AgPt and 50 s for AgAu).

Next, using the Bode impedance plots shown above for 0.5 V, we can calculate the capacitance of the dealloyed layer via the equations below. Capacitance measurements show up any increase in surface area indicative of porosity, providing confirmation of any assignations of E_c.

\[
\frac{C_{dl}}{C_0} \approx \frac{1}{(2\pi f)\text{Z}_{mod}}
\]

(10)

\[
\frac{C_{dl}}{C_0} = \frac{A}{A_0} = \frac{0.46L}{r}
\]

(11)

The capacitance is estimated from the Bode plots where the gradient is approximately equal to (-1). If C₀ is the capacitance of the original flat surface alloy (i.e. no dealloying done), then the ratio of C_{dl}/C₀ obtained for AgPt was 28. The same ratio obtained for Ag-23Au was 54. Equation
(11) shows the relationship between the capacitance and area ($A_0$ being the area of the sample before dealloying). Here, $r$ is the pore radius and $L$ is the depth of the dealloyed layers. Equation (11) was derived assuming the de-alloyed layer is made up of parallel rods in the thickness direction, with an overall space filling fraction of 0.23 (since our sample is 23% MN element; when all gold or platinum (77%) was dissolved the remaining MN element would occupy the space of dealloyed layers). If the rods lie on a square lattice of side $h$, then the number of rods per unit area ($N$) is $1/h^2$ and $\pi r^2/h^2 = 0.23$, i.e. $h^2 = 4.35\pi r^2$. The internal surface area $A$ of the layer (per unit nominal area) is $2\pi r LN$, i.e. $2\pi rL/h^2$ so that $A = 0.46L/r$. From this we can estimate pore size to approximately be 10 nm for AgPt which is consistent with results obtained by Erlebacher. Other things being equal, we expected AgPt to have higher capacitance (i.e. smaller pores) compared to AgAu, but the timescale used in dealloying both alloys was very small. However, based on the Bode impedance plots in Figure 44 and Figure 45, we obtained a $C_{dl}/C_0$ ratio of 100 using data points around $\omega = 1$ Hz for dealloying potentials 0.425 V and 0.5 V compared to the as-annealed samples, for both AgPt and AgAu. The capacitance increase is approximately equal for both samples (capacitance of around 2.5 mF/cm$^2$). The pore size of Au is not less than that of Pt but is similar, which is inconsistent with Corcoran et. al. It is still surprising that they are similar at two different potentials. This could be due to higher mobility of Pt in AgPt than CuPt or could be due to the short dealloying times, e.g. with incomplete Ag dissolution or non-uniform dealloying, or perhaps to do with dealloying being wholly within the Beilby layer.

It can perhaps be speculated that the rates of removal of Ag (keeping in mind that the samples were dealloyed to the same charge density) were different between AgPt and Ag-23Au. Dealloyed Ag-23Au has previously resulted in ligaments and pore sizes around 5 nm. For nanoporous Pt, dealloying Cu-25Pt has previously resulted in porosity with diameter of 3.4 nm which was confirmed using FESEM and SANS analysis and is currently the smallest porosity resulting from a dealloying process to date.

However, the Nyquist plots on Figure 44 and Figure 45 at 425 mV seem to indicate that porosity was present in both samples. This is interpreted from the spectra, where the real impedance component at very high frequency ($f > 100$ kHz) was found to be almost constant from
experiment to experiment, and from sample to sample. At low frequencies \((f \rightarrow 100 \text{ mHz})\) we observe a scatter in the data especially for dealloying potentials above 0.3 V. We can also plot the difference between the real part of impedances at extremely low and high frequencies \((\Delta Z = Z_{\text{real}(f\rightarrow 0)} - Z_{\text{real}(f\rightarrow \infty)})\) which is the electrochemical polarization resistance\(^{51}\) (which gives us the corrosion rate). Porosity can be obtained from log \(Z_{\text{img}}\) versus frequency plots. This leads to the conclusion that the fixed current method of determining critical potential was probably the least reliable, since we see porosity at potentials below 425 mV. Extrapolating critical potential as shown in Figure 34 and Figure 38 gives a better approximation to the true critical potential with slower scan rates providing more accurate measurements. The most reliable method of determining critical potential appears to be to perform a series of potential hold experiments in the immediate vicinity of the critical potential in order to accurately determine the transition from a purely current decay to a steady state current behavior over long times\(^{48}\). Alloys held at or above the critical potential display a (slight current decay followed by a) constant dealloying current while alloys held below the critical potential display rapidly decaying currents, as shown in section 3.3 on page 61.

As an aside, APPENDIX C shows how the thesis work evolved to include porosity investigation in AgPt and Ag-23Au to obtain spectra used in estimating sample capacitance (charge density divided by potential based on Table 4). APPENDIX C does not involve the potential step method, rather is shows the process of dealloying to a specific charge density and then performing EIS measurements.
3.5 Cu replating in nanoporous AgPt

In previous work conducted\textsuperscript{52}, Cu-30Pt was dealloyed in H\textsubscript{2}SO\textsubscript{4} containing copper (II) sulfate, then the potential was scanned back to replat Cu into the pores formed. It was postulated that small amounts of bulk Cu were getting plated into regions of high negative curvature within the dealloyed material but XRD done on such samples did not show any evidence of bulk Cu. In a few ways, this was an unsatisfactory experiment mainly because the Cu nanoparticles that were thought to be replated into the pores above the normal Cu/Cu\textsuperscript{2+} equilibrium potential (which occurs around -328 mV vs. MSE\textsuperscript{52}, i.e. 0 mV vs. Cu) are bound to be air oxidized, so diffraction would not show anything, and also that there is Cu in the alloy as well as plated out from the solution. This set of experiments was aimed at dealloying AgPt, then doing voltammetry in a solution containing Cu (II). With AgPt, Cu is not present in the alloy (as it was in CuPt). Alternatively, by plating Ag from solution instead, we can get over air stability issues (but this was not in our scope).

The following experiment was done to study the electrodeposition of copper into nanoporous Pt (Ag-depleted AgPt alloy).

Dealloying was done at 0.55 V for 30 minutes. Cyclic voltammetry scans were then performed from +350 mV to -400 mV (vs. MSE) for 4 cycles at a scan rate of 5 mV/s. The electrolyte used was a solution containing 0.25 M HClO\textsubscript{4} + 0.05 M Cu (II). The Cu (II) was added by mixing 0.6 g of black CuO powder into 0.25 M HClO\textsubscript{4} and stirring for around 30 minutes until a homogeneous blue solution was obtained. No deaeration was done. Figure 46 shows several runs for a typical edge-on sample of AgPt dealloyed at 0.55 V for 30 min which are indicative of the reproducibility of dealloying.
To systematically determine the effect of Cu$^{2+}$ on dealloyed AgPt layers, the following steps were performed (all potentials vs. MSE) as show in Figure 47.

- The first run was conducted in fresh 0.25 M HClO$_4$ with no Cu$^{2+}$, to establish a baseline. The reduction peak at -280 mV is suspected to be AgCl reduction from Cl impurity in the acid. This happens on the first negative scan but would not happen on subsequent ones.

- Subsequently, scans done with Cu (II) in solution yielded a new anodic (oxidation) peak at -65 mV with the cathodic (reduction) peak shifting slightly to a more positive value at around -250 mV, using a scan rate of 5 mV/s.

- The experiment was repeated at a much slower scan rate of 0.1 mV/s after dealloying at 0.31 V for 22 h.
Figure 47: Potential scans performed on AgPt dealloyed at 0.55 V for 30 minutes. Electrolyte was 0.25 M HClO₄. Scan rate was 5 mV/s. Two runs confirm the presence of an anodic peak at -65 mV and a cathodic peak at -250 mV. Starting potential was +350 mV and scan direction was right to left as indicated by the arrow on the figure.

Each run had 4 back-and-forth scans over the same potential range (+350 mV to -400 mV). Figure 48 shows scan #2 and Figure 49 shows scans #3 and #4 for two distinct experiment sets (runs). With the relatively fast scan rate of 5 mV/s, there is plenty of time for dissolved Ag formed during dealloying to escape from the alloy surface into the bulk electrolyte. The reduction peak at -250 mV indicates the large porous surface area, and would have a charge on the order of 1 C/cm². Subsequent baseline scans remove the reduction peak at -280 mV in Figure 48 and Figure 49. The current at ca. -100 mV vs. MSE can be used to estimate the capacitance. The double-layer capacitance of the de-alloyed structure can be found using $i = C \frac{dV}{dt}$. Estimating $i$ from the plot to be around 1.5 mA/cm², we obtain $C = 0.3$ F/cm².
Figure 48: Potential scans performed on AgPt dealloyed at 0.55 V for 30 minutes. Electrolyte was 0.25 M HClO₄ + 0.05 M Cu (II). Scan rate was 5 mV/s. Continuation of the scans on AgPt from Figure 47.

Figure 49: Potential scans performed on AgPt dealloyed at 0.55 V for 30 minutes. Electrolyte was 0.25M HClO₄ + 0.05M Cu (II). Scan rate was 5mV/s. Continuation of the scans on AgPt from Figure 47 and Figure 48.
This series of continuous potential backscans and forward scans produce a few interesting observations. The first anodic peak shifts slightly to the left from -300 mV to -320 mV as the cycles progress. This peak is the first stripping peak, and shows the uninteresting oxidation of the bulk copper deposited around -328 mV vs. MSE (i.e. the Cu/Cu$^{2+}$ equilibrium potential). Progression of cycles from an experiment standpoint indicate continual deposition into (cathodic) and stripping of (anodic) Cu from porous Pt. The second peak at -65 mV is the potential at which curvature driven electrodeposition (CDD) is thought to occur. Complete pore filling is not possible since a dealloyed material has net zero curvature (see Figure 14a, CDD can only occur at regions with negative curvature, i.e. $\kappa < 0$). In equation 6a on page 35, we noted that the thermodynamic shift in potential for a cluster (‘blob’) exposed at the alloy surface compared with a flat surface was $\eta_{th} (thermodynamic) = \frac{5\Omega}{F} = \frac{4\gamma\Omega}{F\xi a}$.

To determine the effect of slow scan rate, AgPt was dealloyed in HClO$_4$, then the potential was scanned from +350 mV to -400 mV (vs. MSE) for 4 cycles, similar to above, but this time with a scan rate of 0.1 mV/s. Dealloying was done at 310 mV for 22 h in 0.25 M HClO$_4$ for a total charge of 10 mC (or charge density 1.3 C/cm$^2$).

![Figure 50: Dealloying of AgPt was done at 310 mV for 22 h in 0.25 M HClO$_4$ for a total charge of 10 mC (or charge density 1.3 C/cm$^2$). The green curve on the Y2 axis is the applied potential, showing a constant 310 mV was applied for the duration.](image)
Slow scan rates during potentiodynamic back scans allow the Cu\textsuperscript{2+} ions in solution sufficient time for diffusing and migrating through the diffusion layers, to further penetrate into the nanoporous channel concave walls. While this may be true, the main effect is that CDD requires time for reasons that are not completely known. One simple one is that the other (capacitive) background currents need to be as close to zero as possible to see it, but also the process itself seems to be slow, perhaps requiring some kind of surface reconstruction or surface diffusion to occur.

![Cyclic Voltammetry](image)

**Figure 51:** Potential scans performed on AgPt dealloyed at 0.31 V for 22 h. Electrolyte was 0.35 M HClO\textsubscript{4} + 0.05 M Cu (II). Scan rate 0.1 mV/s. Scan direction was right to left, starting at +0.35 V.

Once dealloying was completed, the AgPt sample was placed in a solution containing 0.35 M HClO\textsubscript{4} + 0.05M Cu (II). Figure 51 shows the backscan starting from +0.35 V vs. MSE. The charge under the curve during dealloying of Ag from AgPt is 1.3 C/cm\textsuperscript{2} and that of the first part
of the backscan from 350 mV to about 30 mV (just below the PtO reduction peak) is approximately 0.4 C/cm². The above experiment set was Cu plating into dealloyed layers of AgPt (if, however, the electrolyte used was silver based such as AgClO₄, we can compare the overall coloumometric balance between dealloyed silver and replated silver, which is another interesting experiment but not in scope of this work). The charge under the conventional first anodic copper stripping peak at -340 mV is approximately 0.24 C/cm². Lee et. al² have previously reported charges around 32 C/cm² and 6.1 C/cm² for dealloying of Cu from CuPt and replating of Cu on the forward scan.

Based on the charge passed during dealloying (1.3 C/cm² plus 0.4 C/cm²) and the subsequent anodic stripping peak charge (0.24 C/cm²), we can confirm that about 15% of the porous voids resulting from dealloying have been filled by Cu (compared to 20% observed in the Cu plating of Cu-30Pt by Lee et. al.). The broad peaks found at -320 mV and -65 mV also indicate that surface curvature affects the extent to which Cu nanoparticles become embedded into the pores.
The following points can be highlighted from this work:

1. We successfully made AgPt solid solution and compared its dealloying behaviour with AgAu of the same composition. The critical potential of Ag-23Pt has been found to lie in the range 275-293 mV vs. MSE. Steady state potential hold experiments on Ag-23Pt show that \( E_c \) is around 275 mV MSE. The critical potential of Ag-23Au lies in the range 290 mV-350 mV. Steady state potential hold experiments on Ag-23Au show that \( E_c \) is around 290 mV MSE (consistent with 0.22 V vs. MSE obtained by Pugh, Dusrun and Corcoran\(^8\)). Critical potential depends on alloy composition and tends to approach its intrinsic value at slow enough scan rates. We also found that \( E_c \) for AgPt was method-independent while AgAu shows a stronger dependence on the method used to measure \( E_c \). Subsequent experiments should make more use of edge-on sample potentiodynamic data compared to flat samples since they look more reliable.

2. The potential hold experiments in section 3.3 indicate that dissolution-diffusion doesn’t contribute as much to the intrinsic critical potential as clustering-thermodynamics does. The surface mobility of gold is quite high and the pore size tends towards 5 or 10 nm in the initial stages of dealloying, and continues to coarsen with time. Pt-based alloys have a much lower pore size. The quantity in equation (5) on page 32 is on the order of tens of mV for an Au based alloy and hundreds of mV for a Pt based alloy. This quantity gives the subpotential (or curvature driven deposition) metric – the potential from the equilibrium potential at which CDD can occur. This is consistent with the first conclusion and we can interpret that it does not matter what MN element is used – i.e. \( E_c \) didn’t much depend on whether the noble metal is Au or Pt.

3. The potential hold experiments seem to indicate that \( E_c \), based on equation (6h) on page 35 is governed by a purely thermodynamic effect, assuming it is measured slowly enough. This was tested this using a pair of alloys that could be dealloyed in the same electrolyte and should have the same \( E_c \). 275 mV for Ag-23Pt and 290 mV for Ag-23Au seem to be close enough to warrant further scrutiny with a revised approach using longer
time scales (on the order of days). This difference could be attributed to some non-ideality in the AgPt solid solution, or to the experiment approach itself. AgPt versus AgAu were interesting for a first pass at determining comparing $E_c$, but one pair of alloys is not quite robust enough.

4. There is a noticeable difference in the critical potential measured via potentiodynamic scans as seen in Figure 31. For the same annealing temperature of 1035 °C, the resulting $E_c$ was around 270 mV for 7 h and just less than 400 mV for 73 h anneal times. However, this seemed to be a perceived difference which disappeared when the experiment approach was changed from potentiodynamic scans to potentiostatic holds. Figure 41 is quite clear and shows the potential hold experiments plotted on the same figure. It shows that both alloys are very similar and suggests $E_c$ values indicated might be a little too high.

5. If surface diffusion is not involved in setting $E_c$ then the critical potentials of AgAu and AgPt (or CuPt) should be similar. The counter argument here, however, is that CuPt is a less ideal solid solution which spinodally transforms at low temperature. Even the thermodynamic tendency to do that means that the atoms will move around differently during dealloying – e.g. there may be a preference for like to unlike clustering (CuPt preferred over CuCu or PtPt) that will possibly retard dealloying. The majority of our work was conducted in the same electrolyte (5 wt% HClO$_4$) to eliminate acid concentration affecting $E_c$. It is possible that concentration and type of electrolyte will also affect $E_c$.

6. Some possibilities for the different AgPt and AgAu kinetics for different annealing temperatures could be because AgPt is a solid solution and is not randomly clustered. Interfacial energies are also different compared to AgAu and surface diffusion is very different in some way. AgPt has a finer nanoporous structure since Pt has low surface diffusion. The lattice parameters discussed in section 2.5 also indicate the large change in lattice constant between CuPt ($\Delta=0.31$ Å) compared to AgPt ($\Delta=0.17$ Å).
7. SEM secondary imaging and backscattered imaging of AgPt annealed in air and in H$_2$/Ar indicate average grain size is around 20 µm for the air annealed treatment and around 10 µm for the H$_2$/Ar annealed treatment. Average EDX analysis indicates that the starting 77Ag-23Pt material changes composition to about 12Ag-88Pt (at.%) after dealloying at 0.4 V for 6 h.

8. Impedance measurements indicate the onset of porosity around the critical potential regions for both alloys. The EIS measurements were done on annealed and dealloyed samples of AgPt and AgAu. We estimated pore size to approximately be 10 nm for AgPt and 3 nm for AgAu which is consistent with results obtained by Erlebacher$^2$. We expected AgPt to have higher capacitance (i.e. smaller pores) compared to AgAu, but the timescale used in dealloying both alloys was very small.

9. Cu replating into nanoporous Pt after dealloying AgPt was examined. It is a potentially new method of creating nanocomposite materials. Backscans in 5% HClO$_4$ from above the critical potential display the expected cathodic deposition peak and the anodic stripping peak on the forward scan at -320 mV and -65 mV vs. MSE, as shown in Figure 49. This peak at -65 mV is distinct and broad, suggesting Cu is likely present in different pores (varying curvature) requiring different overpotentials for dissolution.

10. XRD information revealed some interesting details such as ordering in AgPt. Disordered samples do not show the superlattice (110) peak due to destructive interference, however, we observed this peak in Figure 26.

11. Finally, we can speculate as to the usefulness of dealloyed AgPt and AgAu for applications requiring high surface area conducting material with tough corrosion resistant properties such as in biomedical sensors or even in reducing the quantities used in coinage metals (such as Au, Ag, and Cu) to make porous composites.
The focus of this work was to produce preliminary characterization of AgPt from a mechanical and electrochemical perspective and to demonstrate its feasibility as a useful binary alloy system for generating nanoporous Pt. The formation mechanism of nanoporous Pt and its importance in catalyst materials, membranes and sensors with relevant biomechanical properties should be considered for future studies.

Systematic XRD studies on dealloyed AgPt should be performed to complement section 2.5 along with further characterization using transmission electron microscopy to resolve the small nanometer sized pore sizes formed in nanoporous Pt, since it appears that the SEM images produced in this work – while useful – are unable to determine this visually. This can also be extended to the Cu pore filling experiment to determine optimum conditions for Cu atoms to fill Pt nanopores.

A natural extension is further investigation of $E_c$ determined at time scales longer than a few hours. This could add to the body of knowledge on the dealloying mechanisms of AgPt and AgAu and perhaps provide a definite answer to whether dealloying follows a kinetic (dissolution-diffusion) or a more thermodynamic (clustering) process in such alloys.

One possible study could focus on dealloyed AgPt capacitance for dealloying at longer times and further elimination of possible annealing artifacts. We have previously seen CuPt + Cu pore filling and tried AgPt + Cu pore filling. Interesting composite nanomaterials can be produced by dealloying suitable alloys and replating them with metals atoms. Appropriate potentials and hold times could be determined with possible application to fuel cells and sensors. This series of experiments could also easily be extended to ternary AgAuPt alloys with perhaps better mechanics but also smaller pore size.
6 APPENDIX A: AgPt phase diagrams

6.1 AgPt Phase diagram – 1

The following is a compilation of AgPt Phase diagrams investigated during this research. The equilibrium condensed phases of the Ag-Pt system above 965°C are a liquid, (L), and an fcc solid solution, with a large degree of immiscibility. The existence of intermetallic phases β’, γ and γ’ at lower temperatures has been reported, along with α’, α”, β. In the phase diagram below, the phase boundaries shown by the full lines have been established mainly on the basis of a thermodynamic modeling. The dashed boundaries associated with intermetallics are reproduced from earlier work, but the intermetallic at about 90 at.% Pt has been disregarded.

Figure 52: AgPt phase diagram, from reference [53].
### Table 5: AgPt and various phases $\alpha'$, $\alpha''$, $\beta$, $\beta'$, $\gamma$ and $\gamma'$ by composition of %Pt.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition wt% Pt</th>
<th>Pearson symbol</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ag)</td>
<td>0 to 55.3</td>
<td>$cF4$</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td>(Pt)</td>
<td>86.4 to 100</td>
<td>$cF4$</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td>$\alpha'$</td>
<td>26 to 47</td>
<td>$cF4$</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td>$\alpha''$</td>
<td>26 to 43</td>
<td>$cP4$</td>
<td>$Pm\bar{3}m$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>61 to 67</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$\beta'$</td>
<td>57 to 60</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>80 to 89</td>
<td>$cP4$</td>
<td>$Pm\bar{3}m$</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>83 to 85</td>
<td>$cF^*$</td>
<td>...</td>
</tr>
</tbody>
</table>

6.2 AgPt Phase diagram – 2

![Figure 53: Another AgPt phase diagram, from http://www.platinummetalsreview.com/jmpgm/data/datasheet.do?record=7.](http://www.platinummetalsreview.com/jmpgm/data/datasheet.do?record=7)
A complete revision of the binary AgPt system was published in 1996 using data from differential thermal analysis (DTA), X-ray diffraction and electron microprobe analysis (EMPA) on long-time annealed specimens. EMPA is a technique for determining the elemental composition of solid samples. The instrument can display and resolve small features that appear on the surface of a sample, so the method is efficient at identifying the composition of small inclusions embedded in a matrix.

Long annealing times (200 days at 300°C, 150 days at 500°C and 100 days at 800°C) confirmed reproducible results. A new composition, $\text{Ag}_{15}\text{Pt}_{17}$ was also observed and confirmed by the lattice parameter variation shown in Figure 24.
6.4 AgPt Phase diagram – 4

Figure 55: AgPt phase diagram wt% Pt, from reference [55].

Figure 56: AgPt phase diagram at% Pt, from reference [56].
APPENDIX B: AgAu phase diagram

7.1 AgAu Phase diagram – 1

Phase diagram for AgAu is a simple lens type. It shows that for temperatures above 900°C, the FCC phase shows complete solid solubility.

Figure 57: Typical AgAu phase diagram.
In order to investigate the porosity in the 300 – 350 mV range, AgPt and Ag-23Au alloys were dealloyed at 310, 330 and 350 mV for the following times so that they reached the same charge density before EIS measurements.

<table>
<thead>
<tr>
<th>Potential vs. MSE (mV)</th>
<th>AgPt time (to dealloy to 10 mC)</th>
<th>Ag-23Au time (to dealloy to 5.2 mC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>26.2 h</td>
<td>17.8 h *</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*strange result, lower potential dealloyed faster</td>
</tr>
<tr>
<td>330</td>
<td>10 h</td>
<td>38.3 h</td>
</tr>
<tr>
<td>350</td>
<td>6 h</td>
<td>22.7 h</td>
</tr>
</tbody>
</table>

Table 6: Dealloying times for AgPt and AgAu in the 300-350 mV vs. MSE range.

Figure 58: Bode impedance plots for AgPt after dealloying at 310, 330 and 350 mV.
AgPt and Ag-23Au chronocoulometry experiments: AgPt was dealloying to a specific charge of 10 mC and Ag-23Au was dealloyed to a specific charge of 5.2 mC with the charge densities being equivalent for both samples.
Figure 61: Dealloying Ag-23Au to 5.2 mC at the potentials indicated: 310, 330, 350 mV.
APPENDIX D: EDX measurements on AgPt

EDX results are shown for as-received, annealed and dealloyed samples of AgPt. EDX measurements cannot give such precise (accurate to 2 decimals) compositions as shown below - these are a result of the EDW software measuring to its' internal degree of accuracy.

- As-received AgPt.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag L</td>
<td>69.92</td>
<td>80.79</td>
</tr>
<tr>
<td>Pt M</td>
<td>30.08</td>
<td>19.21</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
EDX results:

- AgPt annealed at 1050 °C/ 8 h in air. EDX results confirm composition as 78Ag-22Pt at%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag L</td>
<td>65.74</td>
<td><strong>77.63</strong></td>
</tr>
<tr>
<td>Pt M</td>
<td>34.26</td>
<td><strong>22.37</strong></td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
EDX Results:

- AgPt dealloyed at 0.4V MSE for 6hrs in 5% HClO₄. EDX results show final composition as 12Ag-88Pt at %.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag L</td>
<td>6.78</td>
<td>11.63</td>
</tr>
<tr>
<td>Pt M</td>
<td>93.22</td>
<td>88.37</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES