NANOPOROUS PLATINUM

by

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ABSTRACT

Dealloying is a corrosion process in which one or more elements are selectively removed from an alloy leading to a 3-dimensional porous structure of the more noble element(s). These porous structures have been known to cause stress corrosion cracking in noble metal alloy systems but more recent interest in using the corrosion process to produce porous metals has developed. Applications for these structures range from high surface area electrodes for biomedical sensors to use as skeletal structures for fundamental studies (e.g. low temperature heat exchangers or sensitivity of surface diffusivity to chemical environment). In this work we will review our current understanding of alloy corrosion including our most recent results demonstrating a more accurate method for calculating alloy critical potential based on potential hold experiments. The critical potentials calculated through the potential hold method were $-0.030\text{V}_{\text{MSE}}$, $0.110\text{V}_{\text{MSE}}$, and $0.175\text{V}_{\text{MSE}}$ for Cu$_{80}$Pt$_{20}$, Cu$_{75}$Pt$_{25}$ Cu$_{71}$Pt$_{29}$ respectively. We will present the use of porous metals for making surface diffusivity measurements in the Pt systems as a function of chemical environment. A review of the use of small angle neutron scattering to make accurate measurements of pore size is presented and the sensitivity of pore size to electrolyte, electrolyte composition, applied potential and temperature will be explained. The production of porous Pt with pore sizes ranging from 2-200nm is demonstrated.
To my wife;

Christina Elizabeth Pugh
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Chapter 1. Demonstration of the Formation of Nanoporous Platinum by Dealloying

1.1 Introduction

In this dissertation we study various subjects, beginning with the development of a novel material as nanoporous platinum to the use of such structure to make surface diffusivity measurements. It was of the opinion of the author to make each subject however relevant, a separate chapter. In chapter 1 we will demonstrate our ability to produce nanoporous platinum by selective dissolution. In chapter 2 we will use current theories for calculating the critical potential and compare them to the steady state method. In chapter 3 we will calculate surface diffusivities of Pt in different electrolytes, electrolytes containing halides and in air with temperature. In chapter 4 we will discuss the possible length scale ranges we can obtain and how they correlate to current theories.

Selective dissolution of one or more elements from an alloy is achieved through a corrosion process known as dealloying. Consider a binary alloy, $A_pB_{1-p}$, where the reactivities of $A$ and $B$ are significantly different relative to a specific corrosive environment and element $A$ is the more reactive. Under the appropriate driving force (applied voltage or presence of oxidizing species), we can selectively remove $A$ from the alloy. The alloy will now evolve in one of two directions depending on the driving force for dissolution. At moderate driving force, the alloy surface will enrich in component B resulting in a protective B-rich layer thus hindering further dissolution. However, at slightly higher driving force, a structural instability occurs resulting in the formation of porosity. This porosity allows for the ingress of the corrosive environment and a continuation of the process. We are unaware of any investigations that define the limit of the depth of porosity that can be created but it has been demonstrated that depths of 2 mm are easily achievable[1]. The mechanism of the structural instability that leads to porosity formation has been the focus of many recent investigations[2, 3].
Dealloying has been observed in numerous systems including Cu-Au [4, 5, 6, 7, 8], Zn-Cu[4, 9, 10, 11] Mg-Cd [12, 13], Al-Cu[9], Ag-Au [1, 14, 15, 16, 17, 18, 19, 20, 21], Mn-Cu[9, 22] Pd-Cu[23], Ni-Cu[9], and even during the reduction of titanium dioxide in molten calcium chloride[24, 25]. Beyond its potential for the creation of new porous materials, a better understanding of dealloying processes is relevant to stress corrosion cracking of some alloy alloy-environment systems (see for example [26, 27, 28, 29, 30, 31]), the accelerated corrosion in AA2024-T3 [32, 33], corrosion of austenitic stainless steel in acidified chloride containing electrolyte [27, 34] and the production of Raney metal catalysts [35, 36].

The morphology of typical dealloyed structures consists of a highly tortuous completely interconnected porosity with a pore diameter as small as 3 nm. The structure can be coarsened to larger length scales (up to micrometers) at elevated temperatures [1] and has shown to coarsen at room temperature (to size scales as large as a few 100 nm in the case of Au) [16,18-21, 37] as a function of the applied voltage [16,20] and electrolyte composition [15].

1.2 Motivation

From an applications viewpoint, the question remains, “How universal is this behavior?” That is, can we design new porous materials based on our current understanding of the dealloying process gained in most part by such model systems as Ag-Au. This work is a step in this direction by demonstrating the ability to produce nanoporous Pt through the selective dissolution of Cu from a Cu75Pt25 alloy. There is interest in developing nanoporous Pt from an application standpoint and a fundamental point of view.

1.2.1 Application

First there is the applications point of view which is motivated by our interest in developing alternative processing routes for the creation of high surface area electrodes for biomedical applications. Of particular interest is its direct application to cardiac pacing leads. The addition of a porous layer to the cardiac pacing tip and electrode sensors could have multiple benefits, from increasing the longevity of the battery in the system generator, to optimizing the
impedance response of the electrode. For more detailed information on its relevance to cardiac pacing technology please see Appendix A.

Applications for porous Au have been explored in the area of low temperature heat exchangers [38] and its use in fundamental studies to determine the superfluid density and heat capacity of $^4$He [39]. One can also envision that these open porous structures with interconnecting pores could be used as filters for separating micro/nanoparticles or species suspended in a solution. The high surface area to volume ratio makes of these novel materials make them ideal for catalysts and sensor electrodes.

1.2.2 Fundamental

The fundamental approach for creating nanoporous platinum is also of great interest. Pt has a very high melting point 1772.0°C and hence, a very low surface diffusivity at room temperature of order $10^{-23} \text{cm}^2/\text{s}$ as compared for example to the model Au system which has a melting point of 1064.5°C and a surface diffusivity of order $10^{-16} \text{cm}^2/\text{s}$. The difference in metal/metal ion potentials for the Cu-Pt system is in the range of 800mV while for the Ag-Au system it is approximately 690mV. The Cu-Pt system is one of high strain; the lattice mismatch is 8% compared to that of the Ag-Au system, which is 0.2%. These properties make the Cu-Pt system very attractive as a comparison to the Ag-Au system, allowing us to verify the universality of existing theories only proven with Ag-Au. These differences will be discussed further in the following chapter.

In general dealloying in Pt-based systems has been virtually unexplored. Simmonds et al. [40] observed selective removal of Al from sputter deposited Pt-Al thin films immersed in 4M NaOH at 300K as evidenced through compositional analysis indicating an enrichment of Pt after exposure to NaOH. The presence of porosity was not confirmed. The Pt-Al system was not chosen in our investigation because the presence of multiple intermetallic phases complicates fundamental studies on the dealloying process. Pickering et al. [41] investigated the de-alloying of $Pt_{0.1}Co_{0.9}$ exposed to HCl gas at elevated temperatures (900-1300) K and confirmed the
presence of porosity. Owing to the elevated temperatures required for the dealloying in this system only microporous platinum was demonstrated.

1.3 Experimental

The alloy samples were prepared at AMES Laboratory by arc melting the Cu (99.999% pure) and Pt (99.99% pure) on a water-cooled copper hearth plate in a reduced pressure atmosphere of argon. The alloy was then heat-treated and drop-quenched into an oil bath at 1000°C to avoid the formation of ordered phases. After quenching, the alloy was then cold rolled to a thickness of 200µm. The rolled foil was then annealed at 1000°C for 1.5 hours and quenched by removing it from the inert atmosphere furnace and allowing it to cool in a stream of blowing air.

Prior to use in the electrochemical cell, the foils were cut into 2 x 3 cm samples and masked with Teflon tape to a known exposed area. The electrolyte consisted of reagent grade 1M sulfuric acid, two platinum counter electrodes parallel to the alloy’s exposed area were used along with a saturated calomel electrode (SCE) as a reference. A Luggin probe was used to avoid contamination of chlorides into the solution. A model 263A potentiostat from Princeton Applied Research was used for all experiments. Typically, the potential was scanned at a rate of 1mV/s from open circuit to the desired dealloying potential. The samples were then rinsed in deionized water prepared with a Barnstead Nanopure system with a specific resistivity of 18.2 MΩ/cm.

Small angle neutron scattering (SANS) experiments were conducted at the National Institute of Standards and Technology 20MW reactor in Gaithersburg, MD. The samples were placed in an evacuated chamber in transmission geometry to avoid H2 scattering. The measurements were performed using a 30m long SANS instrument (typically NG3). The wavelength of the incident neutrons was 6Å. The measurement range for the scattering vector \( Q \) was \((0.009-0.174) \ \AA^{-1}\) where:

\[
|Q| = \frac{4\pi}{\lambda_{\text{neutrons}}} \sin \Theta \tag{1.1}
\]
Field emission scanning electron microscopy was performed with a LEO 1550 to compare with the results obtained from the SANS data.

### 1.3.1 Alloy Selection Considerations

Based on our experience with the system Ag-Au and the literature for other dealloying systems, we believe we can identify two general requirements for alloy systems to undergo porosity formation during selective dissolution. First, the alloy, \( A_{p}B_{1-p} \), should exist as a single phase solid solution at a value of \( p \) of at least 20 atomic percent but more typically in range of 60 – 80 atomic percent. The minimum value of \( p \) is dependent upon the relative rates of dissolution of A and surface diffusivity of B [2], e.g. for Zn-Cu where there is relatively large difference in the metal/metal-ion equilibrium potentials the value \( p \) is approximately 18 a/o [42] while for Ag-Au where the equilibrium potential for Ag is relatively close to the oxidation potential for Au the value \( p \) is much higher at approximately 60 a/o [43]. If multiple phases exist in the alloy, porosity formation of any individual phase would follow the same requirement and hence typically only the A-rich phase would dealloy. In this case, dealloying would be isolated to only surface grains unless a mechanism existed for the penetration of the electrolyte throughout the alloy, for example the A-rich grains form a percolating path through the alloy. The dealloying in multiple phase alloys from this perspective has not been investigated to date. The second condition for porosity formation is that an electrochemical environment must be found in which the dissolution rate of A is significantly greater than the dissolution rate of B (ideally B undergoes no dissolution). One easy scenario to accomplish this condition is to select two elements that have significantly different corrosion potentials and then drive the alloy system with a corrosion potential significantly greater than the potential of A but less than that for B. This is the approach taken in this paper.
Considering the above criteria, we chose Cu$_{0.75}$Pt$_{0.25}$ as our model system. The Pt-Cu system exists as a single-phase solid solution for all compositions at elevated temperatures Figure 1.1, and the dissolution of Cu is easily driven in acid electrolytes at potentials where Pt is highly stable.

### 1.3.2 Electrochemical Results

The electrochemical behavior of Cu$_{0.75}$Pt$_{0.25}$ in 1 M H$_2$SO$_4$ is shown in Figure 1.2. The inset in Figure 1.2 shows the same data on a linear scale over a narrow range of potential. The value of the current density gives the total electrochemical reaction rate occurring at a given potential. For values of potential in the range of 0.4 V to 1.0 V secondary electrochemical reactions on Pt occur with values less than 1 -2 μA cm$^{-2}$. From 1.0 V to approximately 1.2 V the onset of Pt oxidation and oxygen evolution increases the current density to approximately 10 μA cm$^{-2}$ which is still significantly less than the dealloying currents observed in Figure 1.2. If we then make the approximation that the anodic current is due solely to the Cu dissolution reaction, we can convert the current density into a Cu dissolution rate through Faraday’s law. Under this
assumption, a current density of 100 $\mu$A cm$^{-2}$ corresponds to a Cu dissolution rate of $3 \times 10^{14}$ atoms cm$^{-2}$ sec$^{-1}$ or a porosity formation rate of approximately 180 nm hour$^{-1}$.

The rapid increase in the dissolution rate observed in the inset of Figure 1.2 at a potential of approximately 0.6 V SCE is indicative of the onset of dealloying and is referred to in the literature as the dealloying critical potential [29]. If we hold the potential of the alloy below this value, the current will decay as the surface enriches in Pt; within several minutes the current density approaches nA cm$^{-2}$ values. Above this potential, the dealloying current increases with time during a potential hold and maintains dealloying currents in the mA cm$^{-2}$ range. All samples held above the critical potential result in the formation of porosity as confirmed by field emission scanning electron microscopy (FESEM) and small angle neutron scattering (SANS). These results are discussed below.

Figure 1.2: Alloy Polarization Curve for Cu$_{75}$ Pt$_{25}$ alloy in aerated 1M H$_2$SO$_4$, scan rate 1mV/s. Inset shows current density on a linear scale near the critical potential.
1.3.3 Morphological Characterization

Figure 1.3 (a) is a FESEM image of nanoporous platinum created by the dealloying of \( \text{Cu}_{0.75}\text{Pt}_{0.25} \) at 1.2V SCE in 1 M \( \text{H}_2\text{SO}_4 \) for 18 hours. The quality of the image is poor since we are at the limit of resolution of the FESEM but the presence of porosity is evident. From the image, we can estimate the pore diameter to be 3.5 – 4.0 nm. To provide confirmation of the bicontinuous nature of the porosity, a dealloyed sample identical to that shown in Figure 1.3 (a) was encapsulated in evacuated quartz tubing (\( 10^{-6} \) torr) and heat treated for 30 minutes at 500°C.

![Figure 1.3](image)

**Figure 1.3:** Porous Pt created by selectively dissolving Cu from \( \text{Cu}_{0.75}\text{Pt}_{0.25} \) at 1.2V SCE in 1 M \( \text{H}_2\text{SO}_4 \) for 18 hours (a) as dealloyed, and (b) coarsened at 500°C for 30 minutes.

The heat treatment coarsened the porosity to length scales easily observable in the FESEM as shown in Figure 1.3 (b). The 30 minute heat treatment resulted in porosity on the order of 100 nm in diameter. Porosity of varying length scales can be created through similar heat treatment procedures as a function of time and temperature [44]. Porosity on the size scale of many microns has been demonstrated in our laboratory and by others [1] for dealloyed Au structures. In order to better quantify the room temperature porosity, we performed neutron scattering measurements at the NIST Center for Neutron Research in Gaithersburg, MD as discussed below.

Previously we demonstrated that small angle neutron scattering (SANS) is ideal for characterizing the morphology of nanoporous metals [19-21] in the 1 – 200 nm range and with
the more recent development of ultra-small angle neutron scattering (USANS) porosity can be characterized as large as 10 \( \mu \text{m} \) [45]. The method is briefly reviewed here. SANS from nanoporous metals closely resembles that of the scattering from microemulsions [46] and spinodally decomposed materials [47] all of which display a bicontinuous morphology. In the case of microemulsions, we have continuous water and oil phases while for dealloyed structures we have continuous phases of metal and void. Interestingly, the scattering from such structures results in a peak in the scattering intensity data. Figure 1.4 demonstrates this for the scattering from porous Pt produced by dealloying \( \text{Pt}_{0.75}\text{Cu}_{0.25} \) at 1.2 V SCE in 1 M H\(_2\)SO\(_4\) for 2.4 hours. The inset shows the same data on a linear scale. The solid line shows the fit to the data, which will be discussed below. The presence of a peak indicates that the morphology contains a well defined average length scale and was first explained by Berk et al. [48]. If we take a simple approach and associate this length scale as being the sum of the pore and ligament length, we can approximate this length as \( 2\pi/Q_p \) where \( Q_p \) is the position of the peak in Figure 1.4. This gives a value of 7 nm. If we take the pore size to be approximately half of this value we expect porosity on the order of 3.5 nm. We now discuss a more rigorous analysis of the scattering data.

![Figure 1.4](image)

**Figure 1.4:** Small angle neutron scattering data for dealloyed Pt (squares) and fit (solid line) to data using the Berk model. The Inset shows the data and fit on linear
The scattering from bicontinuous morphologies was treated by Berk [46,47] and Chen [49, 50]. In this paper, we follow the analysis of Berk et al. since it allows for the generation of real space images. In the Berk analysis, the bicontinuous morphology is mathematically modeled as a three dimensional continuous contour of a stochastic standing wave following the development by Cahn [51] for describing the morphology of spinodally decomposed systems. This standing wave $S_N(r)$ is generated by summing a large number $N$ of plane waves with random amplitudes $A$, wavevector directions $\hat{k}_n$, and phase constants $\phi_n$, and is given by:

$$S_N(r) = \frac{1}{\left(N\langle A^2 \rangle \right)^{1/2}} \sum_{n=1}^{N} A_n \cos \left( \frac{2\pi}{\lambda} \hat{k}_n \cdot \bar{r} + \phi_n \right)$$

The only adjustable value in this equation is the wavelength, $\lambda$. Note this $\lambda$ is the well-defined length scale intrinsic to the morphology that results in the scattering peak. For a single value of $\lambda$, the scattering results in a Bragg-like peak at a Q value of $2\pi/\lambda$ although the real space structure still consists of a random bicontinuous morphology. By adding dispersion into the values chosen for $\lambda$, the scattering peak broadens and resembles that measured experimentally. The normalization in $S_N(r)$ is chosen such that $0 \leq S_N(r) \leq 1$. If we now choose a value, $\alpha$, such that $0 \leq \alpha \leq 1$ and assign all positions, $\bar{r}$, in real space which have a value of $S_N(r) > \alpha$ as metal and all positions with a value of $S_N(r) < \alpha$ as void we generate a real space 3-dimensional bicontinuous structure as shown in Figure 1.5. The scattering from such a structure can then be calculated and compared to the experimental data. The value for $\lambda$ and dispersion is adjusted until a good fit is found. The result is a fit to the data and a real space representation of the structure that can then be analyzed directly for determining pore size distribution, metal ligament size distribution and surface area.
The fit using this model to our data is shown by the solid line in Figure 1.4. This fit had a $k_{\text{mean}} = 2 \pi / \lambda = 0.11617 \ \text{Å}^{-1}$ and the dispersion about this mean followed a log normal distribution with a $\sigma = 0.360$. The 3-dimensional real space structure corresponding to this fit is shown in Figure 1.5. A 2-dimensional slice through the corresponding real space structure is shown in Figure 1.6. An average pore size of 3.4 nm was obtained from this figure by making chord length measurements on the image. This represents the smallest ligament sizes that we have obtained in a dealloyed structure. Under approximately the same set of conditions Ag/Au alloys display pore sizes in the range of 8 - 20 nm depending upon the dealloying potential [52], this increase in pore size is due mainly to the greater values of surface diffusivity expected for Au as compared to Pt.

Figure 1.5: Simulation of porous Pt calculated from the fit to the SANS data of Figure 1.3. (a) Three dimensional slice of size 56 nm x 56 nm x 7 nm and (b) magnified view of the structure 14 nm x 14 nm x 7 nm. Note that the pixel spacing used in the calculation of this image which results in the fine scale structure observed was chosen as 0.28 nm (the atomic radius of a Pt atom).
1.4 Conclusions

The production of nanoporous platinum through the selective dissolution at room temperature of Cu from Pt$_{0.25}$Cu$_{0.75}$ has been demonstrated. Both FESEM and SANS analysis confirm the presence of porosity with a diameter of approximately 3.4 nm. This is the smallest porosity reported from a dealloying process to date. We attribute the small size to the extremely small values of surface diffusivity expected for Pt at room temperature and solution chemistry used effectively eliminating room temperature coarsening processes. We have also demonstrated that larger length scales can be achieved through coarsening at elevated temperatures. The ease of production of porous platinum may make this method of processing attractive for applications as high surface area biomedical electrodes or as catalyst materials.

We found through experimental determination that the Cu-Pt alloys free-corrode in aerated solutions. This free corrosion is due to the oxygen reduction driving the system. The reduction of oxygen on the counter generates negative currents by convention and has the effect of reducing the total anodic current recorded by the potentiostats, hence shifting the open circuit to positive potentials. The presence of oxygen does not have any effect on the dealloying process since we are applying an overpotential larger than that generated by the oxygen reduction. However from this point on we will use N$_2$ deaerated solutions for conducting our electrochemical studies and a saturated mercury sulfate electrode (MSE) as a reference to avoid the presence of chlorides, which alters the surface diffusivity of Pt.
Chapter 2: Electrochemical Characterization of Dealloying

2.1 Introduction

Dealloying is a corrosion process in which one or more elements are selectively dissolved from an alloy leaving behind a porous residue of the more noble elements. The remaining porous material is an isotropic bicontinuous metal-void structure as shown in Figure 2.1.

Dealloying was observed in an attempt to establish a mechanism for stress corrosion cracking of α-brass under an ammonia solution [53]. Initial observations indicated that the cracks were initially created as a result of local embrittlement of the material. Such a model demanded that the embrittlement zone should have its mechanical properties modified in a way as to allow the crack to propagate and reach critical velocity. At the time, there was not a satisfactory explanation for this type of phenomenon. The cause of the local embrittlement was the same that produced stress corrosion cracking in Cu-Au alloys when immersed in a ferric chloride solution. Robertson and Backish [54] 1956 provided evidence that the embrittlement was due to the selective removal of copper from the gold alloy leaving behind a “gold sponge”. Later research proved that stress corrosion cracking of Cu-Zn and Cu-Al alloys in cuprous ammonia solutions could only occur when the composition of the less noble element in the alloy was enough to sustain selective dissolution [55], rendering the material brittle. To date the exact mechanism of the brittle nature of the porous material is not known. The question still remains as to whether the nanoligaments of metal are inherently brittle or whether the size scale porosity and its distribution result in the embrittlement of the macroscopic structure [1].

Beyond its direct relevance to stress corrosion cracking, interest in the dealloying phenomenon extends to the accelerated corrosion of AA2024-T3 [32], and the production
of catalysts such as Raney® Nickel [36]. *Very little attention has been focused on using the selective dissolution process to produce useful materials such as tailored nanoporous platinum for high surface area electrode applications.*

Let us consider the situation for an alloy system of composition $p, A_pB_{1-p}$ with perfect solid solubility across its composition range. For dealloying to take place, the alloying elements $A_pB_{1-p}$ must have different metal/metal-ion equilibrium potentials and the more reactive element must exist in the alloy at a certain critical composition. The Nernst equation (2.1) describes the equilibrium metal/metal-ion electrode potential for elemental metals, $E_{\text{metal}}$, as a function of the ion concentration in solution, where $E^0$ is the standard potential for the half cell reaction, $R$ is the gas constant, $T$ is absolute temperature, $n$ is the number of electrons transferred, $F$ is Faraday’s constant, $c$ is the

![Figure 2.1: Field Emission Image of Nanoporous Platinum from Cu_{75} Pt_{25} coarsened at 650 C for 30 minutes.](image)
concentration of the oxidizing and reducing ions in solution and \( \nu \) is the stoichiometric coefficient. In our case, \( E_{\text{metal, B}} >> E_{\text{metal, A}} \). The \( E_{\text{alloy, ApB1-p}} \) cannot be determined a priori as there is no way of obtaining or estimating the activity of the elemental metals in the alloy at compositions of interest; in any case, we do know that \( E_{\text{metal, B}} > E_{\text{alloy, ApB1-p}} > E_{\text{metal, A}} \).

\[
E_{\text{metal}} = E^0 + \frac{RT}{nF} \ln \frac{c_0^{\nu}}{c_R^{\nu}} \tag{2.1}
\]

**Figure 2.2** is a schematic illustration of the current behavior of a binary alloy undergoing selective dissolution as well as the corresponding dissolution of the pure elemental metals that form such alloy. It is evident from the curves that the pure metals and the alloy have distinct behavior. When the pure metals are subject to an increasing external potential the current, \( i \), increases exponentially as given by the Butler-Volmer equation for large overpotentials, \( \eta \), equation (2.2)

\[
i = i_0 e^{-\frac{\alpha F \eta}{RT}} \tag{2.2}
\]

where, \( i_0 \) is the exchange current density, \( \alpha \) is the transfer coefficient that can range from zero to unity, ideal behavior \( \alpha = 0.5 \), \( F \) is Faraday’s constant, \( R \) is the ideal gas constant and \( T \) is the absolute temperature.

However, when the same potential scan is applied on the binary alloy, the current is passivated until a critical potential [29] is reached and the current increases drastically. It is important to recognize that the critical potential is not very well defined; the dashed lines represent the ambiguity of such a transition. The position of this transition is dependent upon the potential scan rate, alloy surface, composition and electrolyte.
composition. Note that this critical potential presents an increased stability for $A$ dissolution.

At potentials below the critical potential, the alloy remains in the passivation regime and the surface remains microscopically flat and enriched in the more noble element. Above the critical potential there is selective dissolution of the less noble element leading to the formation of an isotropic, bicontinuous structure with a well-defined length scale. The critical potential defines the onset of selective dissolution and a morphological transition in the surface of the alloy.

There are several common experimental features associated with dealloying systems that will be of use in this work and are summarized here.

i) The electrochemical behavior of dealloying systems, when the difference in standard potentials of the pure metals that form the alloy is great enough, consists of a dealloying critical potential that defines the onset of selective dissolution and the morphological transition in the surface of the alloy that leads to the bicontinuous morphologies shown in Figure 2.1. The critical potential is dependent upon scan rate, electrolyte composition [1], presence of halides [14], temperature, and alloy composition [2, 14].

ii) The dealloyed structure is bicontinuous, displays a well-defined average ligament size and the morphology qualitatively resembles that of a spinodally decomposed system [21]. The pore morphology does not resemble that of negative dendrite-like morphologies characteristic of aggregation processes [56].

iii) The average pore size is a function of a coarsening process. The pore size increases as $t^{0.25}$, consistent with surface diffusion coarsening [20].

iv) There is a composition threshold below which dealloying will not occur. This critical composition is often referred to as the “parting limit for
dealloying” and is the smallest atomic percent of the less noble element in the alloy at which dealloying occurs. This parting limit has been linked to the site percolation threshold of the fcc lattice in the percolation model described below.

v) For complete selective dissolution to take place in a binary system the alloying elements must have significantly different equilibrium ion-metal potentials, e.g. in the Au and Pt alloy systems. In binary alloys where this does not occur both elements may undergo dissolution albeit at different rates, e.g. the Cu-Zn system.

**Figure 2.2:** Schematic illustration of the current potential behavior for elemental metals $A$ and $B$ and dissolution of the alloy $A_pB_{1-p}$. The critical corresponds to the knee in the curve.
2.1.1 Mechanisms

Dealloying has been an area of heated debates in the last decade regarding the mechanism that allows selective dissolution to maintain over more than a few atomic layers that leads to the 3-dimensional porous structure. Four possible mechanisms have been offered for the formation of porous metals:

1) Ionization redeposition mechanism
2) Surface diffusion mechanism
3) Volume diffusion mechanism
4) Percolation model

1) The ionization redeposition mechanism was one of the first proposed for explaining the dezincification of brass under the influence of seawater. The first step is the dissolving of brass as a whole; both copper and zinc are anodically attacked and ionized in solution. The second step is the redeposition of copper. This redeposition can only take place if there is some mechanism holding the dissolved copper in solution in contact with the brass. The redeposition can be accomplished via two ways: one by the presence of a membrane, the other by the saturation of copper in solution [11]. However, rotating disc-ring electrode experiments do not support such a mechanism [57]. Furthermore, this mechanism does not explain the dealloying of a wide range of systems such as the Ag-Au system in which the dissolution of the more noble element can be thermodynamically discounted. In systems such as the Zn-Cu, dissolution of the less reactive element can occur at potentials below $E^{0}_{Cu/Cu} + 2$ especially from high curvature regions due to the Gibbs-Thompson effect, but it is not the underlying mechanism controlling the porosity formation. Forty and Edeleanu [53] modified this mechanism and added that the leaching process may not be merely superficial and that zinc could be removed from internal lattice sites by a dislocation piping mechanism, a similar idea to the percolation model for selective dissolution.

2) The surface diffusion model or the surface disordering-reordering model [58, 29] proposes that only the less-noble element is dissolved by the acid, leaving the noble component as a disordered distribution of adatoms on the surface of the alloy. The
more noble element does not dissolve but may be partially ionized and solvated to account for the extremely high diffusivities of the gold adatoms \((10^{-10} - 10^{-12})\text{cm}^2/\text{s}\). The model restricts the dissolution of the less noble element to the surface of the alloy, and it ignores the possibility that diffusion of the less noble metal occurring from underlying layers of the alloy to contribute to the dissolution at the surface. The second step in the sequence involves diffusion of the residual noble metal adatoms over the surface and nucleation of islands. The islands then grow with further aggregation of surface adatoms from the surrounding disordered surface. The surface of the alloy now uncovered by the growth of the islands exposes more of the dissolving element, and these regions undergo dissolution. Growing neighboring islands approach each other so that channels are created between them. Further growth of the islands causes these channels to shrink with time. Pits are formed as a result of the incomplete coalescence of islands in the final stage of channel closure. As time continues the pits shrink at a decreasing rate. This model predicts that for selective dissolution to continue indefinitely a critical composition of the less noble element must exist above 50\text{at.\%}. In this case, the channels and pits shrink at an ever decreasing rate, tunnels are developed when these pits shrink below a critical radius. The most common argument against this model is the mechanism that sustains the creation of the 3-dimensional porosity. The model predicts an enrichment of the surface with the more noble element and a continual shrinking of the channels, pits and tunnels, making it difficult to sustain the increasing dealloying currents observed experimentally. This prediction is also in conflict with small angle neutron scattering experiments [20], which revealed a continual increase of the overall pore diameter due to a surface diffusion coarsening process.

3) **The volume diffusion model** was introduced in 1967 by Pickering and Wagner [57], considers the ionization of the less noble metal and movement of both metals in the atomic state by volume diffusion. Let us consider an alloy \(A_pB_{1-p}\) subject to anodic polarization and only atoms of the less noble element \(A\) enter the solution as ions. As \(A\) atoms are ionized from a kink position they reveal \(B\) atoms which become adsorbed atoms, moving and allowing a new atom \(A\) to be at a kink position for
subsequent dissolution. The adsorbed B atoms tend to move back to the kink positions at the end of the step. A atoms from the lattice layer also ionize and enter the solution creating surface vacancies. These surface vacancies can be filled by adatoms, or by atoms from the lattice layer underneath the surface creating vacancies and divacancies in the interior of the alloy. Excess vacancies may diffuse to greater distances from the surface allowing movement of A atoms from the bulk of the alloy to the surface and backward diffusion of B atoms according to the gradient of the \( A_pB_{1-p} \) alloy. However, this mechanism via diffusion of vacancies is not sufficiently rapid to account for the experimental currents observed in the dealloying process of binary alloys. In [2] the authors calculate a limiting current density of \( 10^{-4} \) A/cm\(^2\) using a volume diffusion for divacancies of \( 10^{-12} \) cm\(^2\)/s (volume diffusion of monovacancies is seven orders of magnitude lower), and a divacancy mole fraction of 10\(^{-2}\); this upper bound current is 10 to a 100 times lower than the experimentally observed. Not only does this current fall short of the experimental values, the divacancy mole fraction used is 100 times larger than the equilibrium mole fraction of monovacancies at the melting point of similar metals. Further, the model does not provide any basis for explaining experimentally observed compositional dependencies for the dealloying current, critical composition thresholds and prediction of the critical potential.

4) Critical compositions exist in some binary systems e.g. Zn (18±2 at.%) in Zn-Cu alloys, and Al (14±2 at.%) in Al-Cu alloys below which dealloying does not occur [55]. The existence of sharp-dealloying thresholds is not consistent with any of the previous views on selective dissolution. However, these experimentally observed critical compositions are very close to the percolation threshold of the f.c.c. lattice (19.8 %) [59]. These observations lead Sieradzki [18] to the development of the percolation model for selective dissolution which adds to the surface diffusion model the importance of atomic placement in a randomly packed alloy. In order for the A atoms to be selectively dissolved from more than just the surface which is exposed to solution, a continuous connected cluster of A atoms must exist in the bulk of the alloy. This percolating cluster of A atoms provides a continuous active pathway for
the dissolution process. This dissolution provides a channel for the electrolyte to enter the bulk of the alloy and continue with the dealloying process. The dissolved structure consists primarily of B atoms and random clusters of A atoms. The initial pore spacing \( \xi \) is determined in a stochastic manner by the initial composition of the alloy equation (2.3). Because of the very high surface to volume ratio of these ligaments and the high energy curvature regions, surface diffusion of B atoms leads to coarsening of the initial structure, this has been confirmed by electrochemical impedance spectroscopy [16] (EIS) studies and small angle neutron scattering [20]. This coarsening process begins to occur at the dealloying front and enlarges the pores allowing further electrolyte into the alloy. Sieradzki [17] analyzed the critical potential for selective dissolution in terms of a kinetic roughening transition. This transition results from a competition between curvature-dependant dissolution (surface roughening) and surface diffusion (smoothening). At potentials below the critical, surface diffusion takes over the competing process and diffusing B atoms cover and passivate the surface. This analysis also gives explanation to those critical compositions that do not fall close to the site percolation threshold. More recently, an expression for the critical potential equation (2.4) was derived [2] which considers both compositional and morphological fluctuations on the alloy surface at the incipient point of either stability (passivity) or instability (bulk dealloying):

\[
\eta(p)_{\text{crit}} = \frac{2}{\xi_a} \delta + \frac{2k_B T}{nq} \sinh^{-1} \left( \frac{\pi^2 \gamma \Omega D_S N_S}{nq \delta J_0} \frac{1}{\xi_a^2} \right) \quad (2.3)
\]

where \( \xi_a \) and \( d \) are given by

\[
\xi_a = \frac{(1 + p)a}{1 - p} \quad \delta = \beta - \frac{\gamma \Omega}{nq}
\]
and where $\beta$ is the variation in equilibrium potential of the alloy surface owing to compositional fluctuations, $\gamma$ is the solid/liquid interfacial energy, $\Omega$ is the atomic volume, $n$ is the number of electrons transferred per atom, $q$ is the charge of the electron, $\xi_a$ is the compositional cluster length scale which we can take as the percolation cluster size, $p$ is the fraction of dissolving species A, $a$ is the near neighbor distance in the lattice, $k_B$ is the Boltzmann constant, $T$ is the temperature, $D_s$ is the surface diffusivity, $N_S$ is the atom density on the surface, and $J_0$ is the exchange current density. The authors defined the critical potential as the value of the potential at which current densities reach a value of 1mA/cm$^2$. However, the fitting parameters $\delta$, $J_0$, and $D_s$ need to be carefully scrutinized. The values reported for $D_s$ in the Au system are 4 orders of magnitude larger than those calculated experimentally.

2.1.2 Steady State Measurements

One of the most important characteristics of dealloying is the presence of the critical potential. The critical potential as previously described is thought to mark the transition from alloy passivity (planar stability) to rapid dealloying (porosity formation). The dealloying process has most recently been treated as a kinetically controlled morphological transition [2]. In the past this transition has been experimentally calculated with the aid of a typical electrochemical dissolution experiment. The potential is ramped at a fixed rate and the current is measured simultaneously, a typical anodic dissolution curves can be seen in Figure 2.3. There are two ways to calculate the critical potential from this curve. The more consistent manner is to identify a critical anodic dissolution current as the threshold and identify the potential that corresponds to this current as the critical potential. Sieradzki chose this current to be 1mA/cm$^2$. We will refer to this value as $E_{\text{Scrit}}$ to distinguish it from other measurements. The other method is to locate the onset of the rapidly rising current through extrapolation of the baseline current of the passivation region [29]. We will refer to this value as $E_{\text{pcrit}}$. The low current region below $E_{\text{pcrit}}$ during an anodic polarization scan has been generally
described as potential independent in the literature [29]. It has been typically accepted that a potential hold below but in the vicinity of Epcrit would result in a potential independent current transient [5], which follows a power law decay \( i \propto t^n \) with \(-0.5 \leq n \leq -1\) [23, 57, 60]. Typically these current transients were monitored only over a period of minutes or at the most several hours.

Both of the methods described above for calculating the critical potential are a function of scan rate, as we increase the scan rate the critical potential shifts to more noble potentials. We now present a new method for the experimental determination of the critical potential; this new method consists of doing a series of potentiostatic holds for long periods of time to study the current behavior. Potential holds above or at the critical will result in steady state currents indicative of the continuous dissolution of the less noble element. Potentials below the critical will lead to decaying currents and the subsequent passivation of the surface.

We have previously proven [61] in the Ag-Au system that the critical potential as determined through potential holds is actually 115mV below the one determined through alloy polarization techniques. Interestingly enough Jonah et al [62] has found the same conclusion through atomistic simulation of the same ideal system. In this paper we extend the steady state method to the Pt-Cu system. Not only is this system interesting due to its potential application as biomedical sensors. The high melting point low surface diffusion of Pt, lattice parameter mismatch, the large difference in electrochemical potential between Pt and Cu, and the need for dearated electrolytes, make this system very attractive as a contrast to the ideal AgAu system.

### 2.2 Experimental

The alloy samples were prepared at AMES Lab by arc melting the Cu (99.999% pure) and Pt (99.99% pure) at the correct stochiometry on a water-cooled copper hearth plate in a reduced pressure atmosphere of argon. The alloy was then heat-treated and
drop-quenched into an oil bath at 1000°C to avoid the formation of ordered phases. After quenching, the alloy is then cold rolled to a thickness of 200µm. The rolled foil was then annealed at 1000°C for 1.5 hours and quenched by removing it from the inert atmosphere furnace and allowing it to cool in a stream of blowing air. The composition of the alloys was confirmed through wavelength dispersive spectroscopy (WDS) utilizing a Cameca SX-50 electron microprobe operating at 15kV and 20nA. The x-ray intensities were calculated using the PAP general method which uses a modified version of the φ(ρz) polynomial used in the standard ZAF correction scheme.

The samples are then polished and cut to a total surface area near 1cm². A small hole was punctured in the alloy and threaded with Pt wire (99.99% pure) for electrical contact and subsequent immersion in the electrolyte.

An electrolyte of 1M H₂SO₄ was prepared from reagent grade chemicals and deionized water prepared with a Barnstead Nanopure system with a specific resistivity of 18.2MΩ/cm. The solutions were deaerated for 30 minutes with N₂ gas prior and throughout the experiments, all experiments were performed at room temperature. The electrochemical cell consisted of a 250ml-4-neck flask. A Pt foil was used as a counter electrode and a saturated mercury sulfate electrode (MSE) was used as a reference. The potentiostats used to conduct the experiments were a 263A and 273 Princeton Applied Research under control of CorrWare by Scribner and Associates. Micrographs of the samples were obtained using a LEO 1550 Field Emission Scanning Electron Microscope (FESEM) with a typical accelerating voltage of 5.00kV and working distance of 4mm.
2.3 Results and Discussion

Figure 2.3 is an anodic polarization curved performed in N₂ dearated \textit{1M H₂SO₄} at a scan rate of 1mV/s for the CuₚPt₁₋ₚ (alloys, where p=(0.8, 0.75, and 0.71) and 10mV/s for Cu, all potentials are vs. MSE, (0.642V vs. NHE).

![Anodic polarization graph in dearated 1M H₂SO₄, vsMSE, scan rate 1mV/s for alloys, Cu 10mV/s](image)

Figure 2.3 Anodic polarization graph in dearated 1M H₂SO₄, vsMSE, scan rate 1mV/s for alloys, Cu 10mV/s

It is interesting to note that all curves have the same open circuit as pure Cu. One would think prior to the experiments that the alloys with increasing noble component would have higher open circuit measurements. This suggests that we have a layer of pure Cu across the whole surface. However it is important to note that after the first scan this Cu layer is dissolved and the open circuit does shift to noble potentials as can be seen from the curves in Figure 2.4.
After the first scan, the Cu over layer is dissolved leaving the Cu atoms in the lattice. We will make use of the first scan since the critical potential is measured in reference to the dissolution of the less noble elemental metal, Cu. From Figure 2.3 we can see the well-defined passivation region, especially for the Cu$_{80}$Pt$_{20}$ and Cu$_{75}$Pt$_{25}$ and the subsequent transition to the active regime. From these curves and using the anodic polarization techniques we will determine $E_{\text{Scrit}}$ and $E_{\text{Pcrit}}$.

Figures 2.5 show a magnification of the region in interest for our three alloys.
From this figure we determined the critical potential values and summarized them in Table 1. It is clear from our results that the $E_{Scrit}$ method of using a critical current of 1mA/cm$^2$ is to be discarded, however, the extrapolating anodic polarization method gives reasonable results.

![Anodic Polarization Scan, 1mV/s](image)

**Figure 2.5.** Anodic Polarization curves for Cu$_{1-p}$Pt$_p$ alloys, where $p$=(0.2, 0.25, and 0.29), showing the passive and active regions.

From this figure we determined the critical potential values and summarized them in Table 1. It is clear from our results that the $E_{Scrit}$ method of using a critical current of 1mA/cm$^2$ is to be discarded, however, the extrapolating anodic polarization method gives reasonable results.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$E_{Pcrit}$ vs. MSE</th>
<th>$E_{Scrit}$ vs. MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{80}$Pt$</em>{20}$</td>
<td>-0.030V</td>
<td>0.058V</td>
</tr>
<tr>
<td>Cu$<em>{75}$Pt$</em>{25}$</td>
<td>0.122V</td>
<td>0.185V</td>
</tr>
<tr>
<td>Cu$<em>{71}$Pt$</em>{29}$</td>
<td>0.170V</td>
<td>-----------</td>
</tr>
</tbody>
</table>

**Table2.1.** Summary of critical potentials calculated through the anodic polarization techniques
2.3.1 Ag-Au System

We have reported that current transients held as much as 115mV below \(E_{\text{pcrit}}\) for significant periods of time eventually show potential dependent steady state currents that lead to porosity formation. **Figure 2.6(a,b)** is a reproduction of the graphs to be published in [61] and explained more fully in [63].

![Figure 2.6](image)

**Figure 2.6.** a) Anodic polarization scans of Ag\textsubscript{75}Au\textsubscript{25} in aerated 1M HClO\textsubscript{4}, scan rate 1mV/s. b) Current behavior for potential hold vs. NHE

Region A corresponds to the identified region of the critical potential as determined by the hold data, Region B corresponds to the region of critical potential determined by extrapolation of the polarization data, these regions are separated by 115mV. It is also important to observe the potential independent current region from which the steady state currents depart.

The potential independent current observed in the Ag-Au system is due primarily to the rapid surface diffusion of the Au approx. \(1 \times 10^{-14} \text{cm}^2/\text{sec}\). During the anodic polarization ramp the alloy is perturbed and the Ag atoms want to dissolve. However at lower potentials the driving force to dissolve Ag atoms is smaller than the reordering of the Au atoms covering new Ag sites, this lowers the dissolution current reaching a potential independent current. The kinetics of the polarization scan are too fast and the driving potential is too small for the alloy to reach steady state potential dependent currents, and the currents are a function of the Au reordering. After a period of time, the
entropy of the system is lowered as the Au atoms aggregate into clusters or islands and
the new released Au adatoms are driven to aggregate into clusters leaving the Ag sites
open for dissolution, and the creation of porosity. The authors have shown that this
“incubation time” is a function of potential and is shorter for increasing potentials until
the driving force for Ag dissolution is so strong that it controls the dealloying process.
The potential at which the initial currents in the AgAu system become potential
dependant correspond to their $E_{Pcrit}$.

2.3.2 Cu-Pt System

Figures 2.7-2.9 show the current behavior of the three Cu-Pt alloys when the
potential is held at different magnitudes for a period of 24hours.

![Figure 2.7](image.png)

Figure 2.7. Current behavior at fixed potentials for Cu$_{80}$Pt$_{20}$ alloys in dearated
1M$\text{H}_2\text{SO}_4$, all potentials are vs.MSE
Figure 2.8. Current behavior at fixed potentials for Cu$_{75}$Pt$_{25}$ alloys in dearated 1M$\text{H}_2\text{SO}_4$, all potentials are vs.MSE

Figure 2.9. Current behavior at fixed potentials for Cu$_{71}$Pt$_{29}$ alloys in dearated 1M$\text{H}_2\text{SO}_4$, all potentials are vs.MSE
We have found that due to the nature of the Cu-Pt system, the low surface diffusion of Pt 1x10^{-18} cm^2/sec and the reactivity of Cu in 1M H_2SO_4, the current independent region is not present. The Pt atoms are practically “frozen” and the “true” potential required to pull the Cu out of the alloy represents the thermodynamic potential i.e. surface diffusion of Pt is not hindering the dissolution as it does in the Au base system. Figures 2.7-2.9 show that after the potential step all current transients are a function of applied potential and the initial currents at the beginning of the hold increase as the potential step is increased. Following this thought, the critical potential calculated through the steady state method should be in the vicinity of those extrapolated from the alloy polarization curves.

Figures 2.7-2.9-15 show that at potentials below the critical potential (-0.075Vmse, -0.064Vmse for Cu_{0.80}Pt_{0.20}, 0.088Vmse and 0.105Vmse for Cu_{0.75}Pt_{0.25}, and 0.150Vmse and 0.165Vmse for Cu_{0.71}Pt_{0.29} ) the current densities decay reaching 1x10^{-8} A/cm^2 after approximately 60000 seconds for the Cu_{0.75}Pt_{0.25} and Cu_{0.71}Pt_{0.29}. Current densities at the critical potential are steady and fluctuate in the 5x10^{-5}A/cm^2 for Cu_{0.75}Pt_{0.25} to 5x10^{-4}A/cm^2 for Cu_{0.80}Pt_{0.20}. Currents 30-50mV above the critical potential increase reach a peak and decay to a steady state. We believe that this peak is related to the depletion of the Cu rich grain boundaries.

If we are to take a closer look at the behavior of the currents we can identify three distinct behaviors, decaying currents, steady currents, and rising currents.

*Decaying currents* correspond to those below the critical potential. Below the critical potential, Cu remains stable in the lattice, Cu rich zones such as grain boundaries become unstable and dissolve. As these zones are depleted Figure 2.10 the surface remains passive and is responsible for the low currents. As explained above, the higher energy and enrichment of Cu along the grain boundaries causes preferential segregation at these sites, pitting is also noticeable at these potentials, Figure 2.11, but we do not see bicontinuous porosity.
Figure 2.10. Cu₃₅Pt₂₀ dealloyed at −0.050V vs. MSE, t=24 hours. Heat treated at 250°C for 30minutes.

Figure 2.11. Cu₇₅Pt₂₅ dealloyed at 0.088V vs. MSE, t=24 hours. Heat treated at 250°C for 30minutes.
The concentration fluctuations can be considerable in some cases and the
dissolution of Cu will actually uncover the grains as can be seen in Figure 2.12.

In [62] the author finds the creation of pits of order 14nm due to fluctuations in
the alloy composition through atomistic simulation of the Ag-Au system just above the
critical potential, the pits eventually lead to the formation of porosity. The pits observed
in our system do not evolve to form porosity.

Steady currents occur for potentials less than 30mV above the critical potential.
At these potentials the most Cu rich grains are attacked Figure 2.13, porosity initiates at
these sites moving into these large grains keeping the dissolution of the less noble
element alive. Figures 2.14-2.16 show the morphology of the steady state currents, these
images represent the lowest potential at which porosity was found, corresponding to the
critical potential $E_{\text{crit}}$. The dissolution will slowly but steadily continue until the Cu sites
are depleted. This steady state current behavior is observed in the Ag-Au system at

Figure 2.12. Cu$_{71}$Pt$_{29}$ dealloyed at 0.160V vs. MSE, t=24 hours. Heat treated at
250°C for 30minutes.
potentials at and above the critical. We found porosity at the first sign of steady state current after the last current decay in all three compositions; these are summarized in Table 2.2.

Figure 2.13. Cu$_{80}$Pt$_{20}$ dealloyed at –0.030V vs. MSE, t=24 hours. Heat treated at 250°C for 30 minutes.

Figure 2.14. Cu$_{71}$Pt$_{29}$ dealloyed at 0.170V vs. MSE, t=24 hours. Heat treated at 250°C for 30 minutes.
Figure 2.14. Cu₇₁Pt₂₉ dealloyed at 0.170V vs. MSE, t=24 hours. Heat treated at 250°C for 30 minutes.

Figure 2.15. Cu₇₅Pt₂₅ dealloyed at 0.110V vs. MSE, t=24 hours. Heat treated at 250°C for 30 minutes.

Figure 2.16. Cu₈₀Pt₂₀ dealloyed at –0.030V vs. MSE, t=24 hours. Heat treated at 250°C for 30 minutes.
Increasing currents are seen at potentials 30-50mV above $E_{\text{crit}}$. This increasing behavior is not observed in the AgAu systems. We believe it is due to the high driving dissolution of Cu that initiates at the most rich Cu grain boundaries going into the lesser rich ones Figure 2.17, allowing the electrolyte to continue into the alloy and begin to selectively dissolve the individual grains inside the bulk. The current begins to decay once the grain boundaries are depleted and the dissolution reaches steady state as in the previous case.

Table 2.2  Summary of critical potentials calculated through alloy extrapolation and steady state method

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$E_{\text{Crit}}$ vs. MSE</th>
<th>Steady State vs. MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{80}$Pt$</em>{20}$</td>
<td>-0.030V</td>
<td>-0.030V</td>
</tr>
<tr>
<td>Cu$<em>{75}$Pt$</em>{25}$</td>
<td>0.120V</td>
<td>0.110V</td>
</tr>
<tr>
<td>Cu$<em>{71}$Pt$</em>{29}$</td>
<td>0.170V</td>
<td>0.175V</td>
</tr>
</tbody>
</table>

Increasing currents are seen at potentials 30-50mV above $E_{\text{crit}}$. This increasing behavior is not observed in the AgAu systems. We believe it is due to the high driving dissolution of Cu that initiates at the most rich Cu grain boundaries going into the lesser rich ones Figure 2.17, allowing the electrolyte to continue into the alloy and begin to selectively dissolve the individual grains inside the bulk. The current begins to decay once the grain boundaries are depleted and the dissolution reaches steady state as in the previous case.

Figure 2.17. Cu$_{80}$Pt$_{20}$ dealloyed at 0.050V vs. MSE, t=24 hours. Heat treated at 250°C for 30 minutes.
Figure 2.18 shows a sample dealloyed at $0.6V_{\text{MSE}}$ in 1M $\text{H}_2\text{SO}_4$, the sample was then mounted in a polymer resin and sliced through a cross section with a diamond blade. The mounted sample was then coated with Au particles for viewing with the FESEM.

Figure 2.18 shows the creation of large pathways where the dissolution of Cu rich regions has occurred. These pathways allow the ingress of the electrolyte into the bulk increasing the dissolving surface area and hence, increasing the currents. This effect can be seen in more detail in the following schematic illustration Figure 2.19.
If we are to take a closer look at the increasing current regions in Figures 2.7-2.9 we notice that current does not continue to increase with potential when we are above \( E_{\text{crit}} \). Actually, for all three alloys as we continue to scan to more noble potentials the magnitude of the currents decrease. This behavior has a very simple explanation as evidence in the anodic polarization graphs of Figure 2.3. Once we have surpassed the critical potential and continue to increase in potential there is a change of slope in the anodic curve and we reach a second “nose”; this “nose” is associated with the slight passivation of Cu that limits the dissolution current. This type of behavior is not uncommon; Tromans et al. [64] found the same transition from active to limiting current behavior occurring with rising potentials for Cu dissolution in 1M H\(_2\)SO\(_4\). This behavior is associated with the formation of hydrated sulfate films CuSO\(_4\) \( \cdot \) 5H\(_2\)O, that inhibits the dissolution of Cu. It is important to note that this hydrated film is not stable or strong enough to passivate the dissolution of Cu as would a copper oxide but is enough to perturb the trend.

![Alloy Surface Exposed to Electrolyte](image)

**Figure 2.19** Schematic illustration of the dissolution behavior of Cu-Pt alloys at high potentials
2.4 Conclusions

In this section we have shown the ability to experimentally measure the critical potential through the potential hold method. We have demonstrated that the first steady state current observed at long times after the decaying currents corresponds to the formation of bicontinuous porosity as demonstrated through heat-treated FESEM images. This method has lead us to identify three distinct regions that display distinct morphologies, decaying currents (below $E_{\text{crit}}$) with pitting and grain boundary dissolution, and steady state-rising currents (above $E_{\text{crit}}$) with porosity formation.

The results from the anodic polarization data and the steady state current method as can be seen in Table 2.2 are approximately the same if we consider a reasonable 10mV error for the Cu-Pt system. We believe the close proximity of these results is due to the low surface diffusivities of Pt, which opposes little or no competition to the dissolution of Cu once the potential is high enough to pull the Cu out of the lattice, hence, the extinction of the incubation time. These findings do not support the idea that the critical potential is due to the competition between surface smoothening and induction of curvature form the percolation model.

The idea that the transition from planar stability to roughening of the surface is solely due to the energy required to pull the Cu out of the lattice is not unreasonable. Cu displays underpotential deposition (UPD) on Pt, that is it deposits at potentials above that of bulk deposition, in the region where bulk Cu would be undergoing dissolution. Figure 2.20 is a cyclic voltamagram (CV) for Pt in dearated 1M H$_2$SO$_4$ with the addition of 2 10$^{-4}$ M CuSO$_4$. The scan was performed at 20mV/s and the figure represents the last of ten cycles.

Peak 1 and 2 at 0.050V and –0.08V correspond to the stripping and the deposition of a Cu monolayer on the Pt electrode. What is important to note from this curve and supports our theory on the abrupt critical transition is that the potential required to strip a monolayer of Cu from a Pt surface is nearly 0.470V above the Cu dissolution potential.
for the elemental metal in the same solution, that occurs at a potential of –0.420V vs. MSE.

We have also demonstrated the lack of a potential independent current region for the Cu-Pt system. This result is also an effect of the low surface diffusivity of Pt, but is surely accentuated by the rich Cu grain boundaries and Cu concentration fluctuations. As we increase the potential we increase the accessibility to dissolve smaller grains and smaller Cu rich regions, giving rise to the current. This behavior explains why it takes so long 60000s to reach passivation currents in the 10⁻⁸A area, we first have to exhaust the Cu rich areas before we are able to passivate the surface. It would be interesting to study a Cu-Pt single crystal; with the lack of grain boundaries and composition fluctuations we predict that there will be some sort of potential independent current region.

Figure 2.20. Cyclic Voltamgram showing the underpotential deposition of Cu on a Pt electrode in deaerated 1M H₂SO₄ with the addition of 2 \(10^{-4}\) M CuSO₄, scan rate 20mV/s, the last of ten cycles.
Chapter 3. Surface Diffusivities of Pt

3.1 Introduction

What control do we have over the bicontinuous structure, that is can we predict the final pore size by controlling the surface diffusivity of the Pt adatoms? The surface diffusivities can be modified by varying applied potential, electrolyte, presence of contaminants, and temperature.

Surface diffusion plays in important role in many electrochemical processes such as electrocrystallization of metals, electrocatalyst, nucleation and growth of epitaxial films, and electromigration through thin films. Surface diffusion may also determine the activity and lifetime of electrodes taking part in electrosynthetic processes and is involved in metal electrodissolution-electrodeposition, but most importantly, it is a fundamental event controlling the dealloying mechanism. Thus, the measurement of the kinetics of surface diffusion can produce experimental data useful in predicting the lifetime of high surface area metal electrodes or corrosion rates of alloys in aggressive environments.

The noble element ligaments of bicontinuous structures created through selective dissolution are surface diffusion dominated. In situ coarsening studies conducted by Corcoran et. al.[20] with Au alloys displays a \( t^{0.25} \) kinetics at long times, as opposed to a \( t^{0.33} \) dependence if it were to be volume diffusion dominated. This is also in agreement with the literature for the relaxation of surface metal electrodes in contact with electrolytes [65, 66,67, 68]. The surface mobility of metal adatoms is a function of the possible ions in the electrolyte. These ions are able to absorb on the metal surface modifying the interactions of the adatoms with the neighboring sites. Temperature and potential has also been found to play a role in the change of mobility. The influence of potential has been explained as the consequence of an accumulation of charge on the electrode surface, which modifies the enthalpy of formation of the surface moving
entities and to the formation of absorbed bonds between neighboring sites due to electron transfer reactions.

The evaluation of surface diffusion coefficients from particle coalescence processes is widely used in solid-state physics. This method involves studying the time dependence of crystals or coalescing nuclei by microscopy [69], optical diffraction [70], ion scattering [71], scanning tunneling microscopy coupled with a scanning electron microscope [72], and through the use of the theory first developed by Mullins [73] based on the effect of the curvature of a surface on the chemical potential of the surface atoms given by the classical Gibbs-Thomson equation. Mullins theory was later extended by several authors [74-75] as a method to determine the surface heterodiffusion coefficient based on the observation of the transfer of macroscopic quantities of a substance A along a substrate B. Considering A and B the same phase, we can describe the coarsening process of dealloyed Pt as:

$$r^4 - r_0^4 = \frac{2\gamma a^4 D_s t}{kT} \tag{3.1}$$

Where $r$ is the average ligament size at time $t$, $r_0$ is the initial pore size, $\gamma$ is the surface energy, $a$ is the atomic radius of the metal, $D_s$ is now the surface diffusivity, $k$ is the Boltzmann constant, and $T$ is the absolute temperature.

In this chapter we will review the above equation to reaffirm its validity. As mentioned above, the equation is widely used but a precise derivation of such is not found in the literature. We will present a simple method for deriving equation (3.1) and will discuss the assumptions made regarding its application to the coarsening of bicontinuous structures. Finally we will calculate experimental surface diffusivity results using equation (3.1) with the aid of ligament data obtained through SANS, and compare them to the existing literature results.

There are some general assumptions made for both derivations:
- The relaxation of the surface is calculated under the assumptions that all surface properties are independent of orientation.
- For the sake of simplicity of the derivation we will assume that the coarsening nuclei (ligaments for our porous structures) are spherical. This assumption is not too far fetched since we are comparing radii to a one-dimensional parameter, ligament width, obtained from the SANS data.

### 3.1.1 Geguzin et al. [75] derivation.

Let’s consider a solid particle of substance A of a hemispherical shape placed on a substrate B. The time dependence of such a particle may change because of material transfer due to the surface diffusion mechanism. Regardless of the type of gradient governing the driving force to equilibrium, the equation for the steady state diffusion along the surface may be written as [76]

\[
\frac{\partial \xi}{\partial t} = D_a \nabla^2 \xi + q - \frac{\xi}{\tau} = 0 \tag{3.2}
\]

Where, $\xi = a^2 n_a$ is the adatom concentration, $a$ is the lattice parameter of A, and $n_a$ is the number of adatoms of A on the unit surface, $q$ is the relative number of particles incident upon a unit surface per unit time, $\tau$ is the mean “life” time of an adatom A in the absorbed state. The solution of the above equation is given by

\[
D_a \nabla^2 \xi = \frac{\partial \xi}{\partial t} = 0 \tag{3.3}
\]

If we consider this hemispherical particle to belong to an ensemble of similar particles of various radii, we can define the concentration at infinity as
\[ \xi \bigg|_{r \to \infty} = \overline{\xi} \]  

(3.4)

Where \( \overline{\xi} \) is determined by the ensemble in a self-congruent way. At the surface of the particle the following conditions are met.

\[ \xi \bigg|_{r = R} = \xi_{\infty} + \frac{\alpha^s}{R} \]  

(3.5)

\[ \alpha^s = \left( \frac{2a^2 \gamma}{kT} \right) \xi_{\infty} \]  

(3.6)

where \( \gamma \) is the surface tension of A, \( k \) is Boltzmann’s constant and \( T \) is absolute temperature. This last expression is derived from the Gibbs-Thompson equation and will be shown further in more detail. Equation (3.2) solved for boundary conditions (3.3-3.5) results in the following expression

\[ \left( \frac{dR}{dt} \right) = \frac{D_a}{R} \frac{a}{\omega} \left( \Delta^s - \frac{2a^2 \gamma}{kTR} \right) \]  

(3.7)

where \( \omega = \left( D_a \tau \right)^{1/2} \). At \( t \to \infty \), with \( \Delta^s \to 0 \) the law of mass conservation of the ensemble of particles involved in the self consistent mass transport may be written as

\[ \frac{2\pi}{3} \int_0^\infty f(R)R^3 dR = Q_0 = \text{const} \]  

(3.8)

Here \( f(R) \) is the size distribution normalized by the unit surface, \( Q_0 \) is the total volume of the particles per \( 1\text{cm}^2 \) of the substrate surface. Assuming the A and B are the same material and same phase, and following the calculations of \( R(t), f(R,t), \Delta^s(t) \)
derived in the same manner as the same as in the paper by Lifshitz and Slezov [77] we present only the results at, \( t \to \infty \).

\[
\overline{R^4} = \left( \frac{4}{3} \right)^3 \frac{D_o \alpha^2 at}{\frac{1}{4} \ln(2\omega R)}
\]  

(3.9)

The final equation is given assuming that the factor \((\frac{1}{3})^{\frac{1}{4}} \frac{1}{4} \ln(2\omega R)\) may be within the experimental accuracy replaced by a unit and considered time independent, and that \(D_o=D_s\) finally obtaining

\[
D_s = \frac{kT}{2a^4 \gamma} \frac{\Delta R^4}{\Delta t}
\]  

(3.1)

As shown, the derivation of the final expression of the surface diffusivity as a function of the fourth order of the average of the coalescing particles is not trivial, and the way the constants are calculated is reason for concern. We now present a more simplistic manner for reaching the same expression based on Fick’s second Law, and the change in chemical potential of surface adatoms due to curvature. The initial setup of this derivation is the same as that presented in [74].

### 3.1.2 Modified Derivation

Let us consider a system formed of a substrate with coalescing particles of the same metal. As we vary the surface diffusivity through temperature, applied potential, presence of contaminants, a considerable redistribution of the nuclei occurs driven by the necessity of the system diminish its interfacial energy, which is directly proportional to surface area. Since we will have a distribution of these nuclei-particles, we can say that there will be average radii for all the particles. We can also say that there will be a
critical radius, particles with radii grater than the critical will tend to grow larger at the expense of those that are smaller than the critical which will tend to dissolve, therefore reducing the total surface to volume ratio of the nuclei and the number of these. As the redistribution proceeds, the adatom population will diminish reaching a concentration as that of a flat surface at long times.

We will suppose a unit of such a substrate at a constant temperature $T$, containing a distribution of nucleus sizes with an average adatom concentration $\bar{c}$, which will diminish as time progresses. The nucleus has the shape of a 3-dimensional spherical cap as shown in Figure 3.1, the cap has an isotropic interfacial energy, and we will also neglect the line tension at the base.

![Figure 3.1 Model of a coalescing particle on a substrate, represents a 3-dimensional spherical cap](image)

\[
\begin{align*}
\text{Volume} &= \frac{1}{3} \pi r^3 \alpha_1(\theta) \\
\text{Surface} &= 4 \pi r^2 \alpha_2(\theta) \\
\text{Periphery} &= 2 \pi r \sin \theta
\end{align*}
\]

\[
\alpha_1(\theta) = \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \\
\alpha_2(\theta) = \frac{1 - \cos \theta}{2}
\]

The mechanism of particle growth as we have already pointed out is dominated by the surface diffusion of adatoms and its eventual transfer at the interface of the nucleus. The rate of this process will be determined by the slowest step (surface diffusion or interface transfer).
Considering surface diffusion first we can write Fick’s second law in polar coordinates, for quasi-steady state as

\[
\frac{1}{R} \frac{d}{dR} \left[ R D_a \frac{dC(R)}{dR} \right] = 0 \tag{3.10}
\]

where \( C(R) \) is the local concentration of adatoms as a function of \( R \), which is the distance from the origin of the nuclei to any point in the system, and \( D_a \) is the coefficient of the surface adatoms. The surface diffusivity is proportional to the coefficient of surface adatoms the lattice parameter squared and the concentration at long times, that of the flat surface \( D_s = D_a C_0 a^2 \). The solution to Fick’s Law can be written as follows.

\[
C(R) = K_1 \log R + K_2 \tag{3.11}
\]

Setting the following concentration boundary conditions, \( C(r \sin \theta) = C' \) at the edge of the nucleus, and \( C(r' \sin \theta) = \overline{C} \), \( r' \) is a constant distance away from the nucleus where the concentration of adatoms reaches the average value. Introducing them into equation (3.11), resulting in \( K_2 = 0 \), and solving for \( K_1 \) we can write the concentration as

\[
C(R) = \frac{\overline{C} - C'}{\log l} \log R \tag{3.12}
\]

The surface adatoms are only able to attach to the nucleus by the perimeter of such, therefore the number of adatoms attaching per second can be written as
For the mechanism of interface transfer, the probability of atom addition or dissolution is proportional to the surface area and the local adatom concentration.

\[
J_s = 2\pi r \sin \theta \left[ D_a \frac{dC(R)}{dR} \right]_{R=r \sin \theta} \quad \Rightarrow \quad J_s = \frac{2\pi D_a}{\log l} \left( \bar{C} - C' \right)
\]

(3.13)

The term \(C_0\) comes from assuming a hypothetical equilibrium concentration, that of the flat surface. The net flux of adatoms by interface transfer as

\[
\begin{align*}
\text{# of adatoms added per unit time} & = 4\pi r^2 \alpha_2(\theta)C' \\
\text{# of adatoms detached per unit time} & = 4\pi r^2 \alpha_2(\theta)C_0
\end{align*}
\]

(3.14-15)

These two mechanisms, surface diffusion and interface transfer must give equal rates at steady state \(J_{\text{steady state}} = J_i = J_s\). Utilizing this last equality we can eliminate the unknown, \(C'\) and obtain the steady state flux \(J\) as

\[
J = \frac{2\pi D_a}{\log l} \frac{4\pi r^2 \alpha_2(\theta)}{\log l + 4\pi r^2 \alpha_2(\theta)} \left( \bar{C} - C_0 \right)
\]

(3.17)

As previously explained, the process at which the larger particles grow at the expense of the smaller ones is an effort by the system to reduce the surface potential \(\gamma A\),
consequently, the volume fraction of material in the system remains essentially constant so that we may write

$$\sum_{\text{All Particles Sizes}} \left( \frac{\text{Rate of atom loss}}{\text{Particle}} \right) = 0 \quad \text{(3.18)}$$

If we take the volume of nuclei to be $V$ and $V_m$ as the volume per atom in a particle, then the rate of atom loss per nuclei is $(dV/dt)(1/V_m)$, we can also rewrite this equality as $(dR/dt)(dV/dR)(1/V_m)$, for a hemispherical cap, $dV/dR=4\pi r^2 \alpha_1(\theta)$. We can now write the expression for the rate of change of a single particle due to coarsening by

$$J = 4\pi r \alpha_1(\theta) \frac{1}{V_m} \frac{dR}{dt} \quad \text{(3.19)}$$

equating (3.19) and (3.17) we obtain

$$\frac{dR}{dt} = \frac{V_m}{4\pi r^2 \alpha_1(\theta)} \frac{2\pi D_a}{\log l} 4\pi r^2 \alpha_2(\theta) \left( \frac{C}{C_0} \right) \quad \text{(3.20)}$$

The rate of atom loss or growth from a particle is controlled by either the rate of transfer across the particle-substrate interface (between particles) or by surface diffusion of adatoms from the particle to the substrate (at the particle). This equation is quite general and can be considerably simplified for two limiting cases.

1- Surface diffusion is much faster than interface transfer $\frac{2\pi D_a}{\log l} \gg 4\pi r^2 \alpha_2(\theta)$

2- Interface transfer is much faster than surface diffusion $4\pi r^3 \alpha_2(\theta) \gg \frac{2\pi D_a}{\log l}$
Our system is Case 2 in which surface diffusion is the rate determining step, we can then rewrite expression (3.20) for the coarsening of a spherical particle where $\alpha_i(\theta)=1$ as

$$\frac{dR}{dt} = \frac{V_m D_m}{4\pi^2 \log l} (\bar{C} - C')$$  \hspace{1cm} (3.21)$$

The effect of curvature of a surface on the chemical potential of the surface atoms is given by the classical Gibbs-Thompson formula when $\gamma$ is independent of orientation

$$\mu = V_m \gamma (K_1 + K_2)$$  \hspace{1cm} (3.22)$$

where $K_1$ and $K_2$ are the principle curvatures of the nuclei, since we are assuming a spherical particle and $K=1/R$ we can rewrite the Gibbs Thompson equation for a sphere as

$$\mu = \frac{2\gamma V_m}{R}$$  \hspace{1cm} (3.23)$$

The corresponding change in chemical potential when an adatom is added to the particle changing its concentration can be expressed as

$$\mu = kT \ln \frac{\bar{C}}{C_0}$$  \hspace{1cm} (3.24)$$

at long times we can say the concentration of the particle approximates equilibrium, that of a hypothetical flat surface, then $|\bar{C} - C_0|/C_0 << 1 \Rightarrow \ln \frac{\bar{C}}{C_0} \cong \frac{\bar{C} - C_0}{C_0}$ by making the chemical potentials (3.23) and (3.24) equal we can solve for the change in concentration
\[
(\bar{C} - C_0) = C_0 \frac{2\gamma V_m}{kT} \frac{1}{R}
\]  \hspace{1cm} (3.25)

introducing this last expression into equation (3.21), and introducing \( D_s = D_o a^2 C_o \) and solving for \( \frac{dR}{dt} \) we obtain.

\[
\frac{dR}{dt} = \frac{a^4 \gamma D_s}{4kT \log l} \frac{1}{R^3}
\]  \hspace{1cm} (3.26)

For expression (3.26) to become (3.1) \( \log l \) has to be 1/2. This constant will be a function of the distribution and concentration of each system.

\[
\Delta R^3 = \frac{2\gamma a^4 D_s}{kT} \Delta t
\]  \hspace{1cm} (3.1)

The final expression derived in the literature was not obtained in a very strict manner; however we do believe that the assumptions made in this last derivation are lighter than those encountered in the literature. Hence we are concerned with the validity of such widely used expression. We are primarily concerned with the constant of proportionality, and agree that it will be a function of the shape of the particle as well as the constant distance \( rl \) at which we recover the average concentration away from the nuclei. For a more rigorous derivation we will need to turn to atomistic simulation, and an attempt to do so is in the process. However, we will now use the final equation to estimate surface diffusivities in different environments from the chord length measurements obtained from 2-dimensional simulated images from our SANS data.
3.2 Experimental

The alloy samples were prepared at AMES Laboratory by arc melting the Cu (99.999% pure) and Pt (99.99% pure) on a water-cooled copper hearth plate in a reduced pressure atmosphere of argon. The alloy was then heat-treated and drop-quenched into an oil bath at 1000°C to avoid the formation of ordered phases. After quenching, the alloy is then cold rolled to a thickness of 200µm. The rolled foil was then annealed at 1000°C for 1.5 hours and quenched by removing it from the inert atmosphere furnace and allowing it to cool in a stream of blowing air.

Prior to dealloying in the electrochemical cell, the foils were cut into 2 x 3 cm samples and masked with Teflon tape to a known exposed area. The electrolytes used in these experiments were prepared with reagent grade chemicals and deionized water prepared with a Barnstead Nanopure system with a specific resistivity of 18.2 MΩ/cm. Two platinum counter electrodes parallel to the alloy’s exposed area were used along with a saturated mercury sulfate electrode (MSE) as a reference. Model 263A and 273 Potentiostat from Princeton Applied Research under the control of CorrWare were used for all experiments. Typically, the potential was scanned at a rate of 1mV/s from open circuit to the desired dealloying potential, and held at that potential for the desired time.

After the samples were dealloyed temperature coarsened samples were placed in a preheated 1500 Thermolyne furnace for the desired time and temperature. The samples were removed from the furnace and allowed to cool at room temperature.

Potential coarsening experiments were performed in new solutions to avoid the plating of Cu ions created from the dealloying process on the electrode. The halide solutions were prepared from reagent grade salts and reagent grade chemicals.

Small angle neutron scattering (SANS) and ultra small angle neutron scattering (USANS) experiments were conducted at the National Institute of Standards and Technology 20MW reactor in Gaithersburg, MD. The samples were placed in an
evacuated chamber in transmission geometry. The SANS measurements were performed using a 30m long instrument (typically NG3).

### 3.3 Results and Discussion

We know that the coarsening of dealloyed structures is surface diffusion dominated, we also know the relationship between the change in ligament size and the surface diffusivity as given by equation (3.2). We have shown in previous chapters the ability to make accurate pore size measurements from the SANS data. Utilizing these tools we can alter the ligament size of our structures and calculate the surface diffusivity of the coarsening process. We will now study the effect of electrolyte, electrolyte composition, halides, applied potential and temperature on the Pt surface diffusivities. We will also compare our results with the existing literature when possible.

The experimental setup and the method in which we calculate pore sizes is identical to that in 1.3. We are however now concerned with the ligament width data extracted from simulated images as Figure 1.6. The ligament chord data was fitted to a Lorentzian Distribution to obtain the average ligament width using ORIGIN software.

#### 3.3.1 Reproducibility

Before we begin, it is important to check the reproducibility of the experimental setup. To do so we dealloyed two samples under the same conditions, these samples were Cu$_{80}$Pt$_{20}$ dealloyed in 0.5M H$_2$SO$_4$ at 0.5V vs. MSE for a period of 20 hours, the samples numbers are 041902-a, and 042302-a, and Cu$_{80}$Pt$_{30}$ dealloyed in 0.5M H$_2$SO$_4$ at 0.2V vs. MSE for a period of 20 hours, the samples numbers are 042202-a, and 050602-b for information on the dealloying currents SANS data fit and ligament data for these samples see Appendix E. The ligament sizes are reproduced in Table 3.1.
These results demonstrate that the experimental setup gives reproducible results. The maximum difference in ligament width for both experiments is for the alloys held at $E=0.2V_{MSE}$, and that difference is of $\Delta l = 0.02 \text{ Å}$.

<table>
<thead>
<tr>
<th></th>
<th>Ligament Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cu_{80}Pt_{20}$, $0.5M H_2SO_4$, $E=0.5V_{MSE}$, $t=20h$</td>
<td></td>
</tr>
<tr>
<td>0419023-a</td>
<td>1.28</td>
</tr>
<tr>
<td>042202-a</td>
<td>1.27</td>
</tr>
<tr>
<td>$Cu_{80}Pt_{20}$, $0.5M H_2SO_4$, $E=0.2V_{MSE}$, $t=20h$</td>
<td></td>
</tr>
<tr>
<td>042202-a</td>
<td>1.32</td>
</tr>
<tr>
<td>050602-b</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Table 3.1 Reproducibility of the experimental setup

3.3.2 Potential Hold

For this set of experiments we want to reproduce surface diffusivity values obtained by using equation (3.2) applied to the relaxation of columnar structured Pt electrodes for various potentials in $0.5M H_2SO_4$ \[78\].

The alloys used were of $Cu_{71}Pt_{29}$ composition, dealloyed in $1M HClO_4$ at $0.7V$ for a period of approximately 56 hours. The alloys were then rinsed to remove any Cu ions on the electrode and immersed in $0.5M H_2SO_4$ at the voltages shown in Table 3.2 for a period of 7200s. The surface diffusivity measurements were made with respect to a control sample. For details on these experiments see Appendix C.
Table 3.3 presents surface diffusivity values for the same coarsening potentials for the relaxation of columnar structured type Pt electrodes, reproduced from[67]

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Potential V vs. MSE</th>
<th>Surface diffusion $10^{-18} \text{cm}^{2}/\text{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M H$_2$SO$_4$</td>
<td>-0.572</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>-0.490</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td>-0.430</td>
<td>10.34</td>
</tr>
<tr>
<td></td>
<td>-0.200</td>
<td>5.60</td>
</tr>
<tr>
<td></td>
<td>0.000</td>
<td>2.41</td>
</tr>
<tr>
<td>1M HClO$_4$</td>
<td>-0.550</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>-0.390</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>0.000</td>
<td>0.47</td>
</tr>
</tbody>
</table>

The surface diffusivities obtained in this experiment are very reasonable when compared to those in the literature. What is very interesting is that asides from the sample coarsened at $E=-0.490 V$ the trend seems to be the same. The lowest surface diffusivity obtained is that for $E=-0.572 V$ and the others behave in the similar manner. The surface diffusivities calculated in the literature may have more error since their
structures are not stable at room temperature and degrade with time. On the other hand our structures are very stable at room temperature. To prove this statement we have conducted SANS experiments the same dealloyed sample one year apart. The results are summarized in Table 3.4. The sample was dealloyed at \( E = 0.6V_{MSE} \) in 1M H\(_2\)SO\(_4\) for 2h, the sample number is J6.

![Table 3.4 Ligament size from dealloyed sample coarsened at room temperature for one year](image)

<table>
<thead>
<tr>
<th>Cu(<em>{75})Pt(</em>{25})</th>
<th>Ligament Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J6 2001</td>
<td>1.73</td>
</tr>
<tr>
<td>J6 2002</td>
<td>1.73</td>
</tr>
</tbody>
</table>

The data represents the stability of the structure over a period of a year, the experimental values are the same inside our margin of error.

### 3.3.3 Halide Coarsening

In [14] we presented the results of delloying studies of Ag\(_{0.7}\)Au\(_{0.3}\) and Ag\(_{0.65}\)Au\(_{0.35}\) alloys in 0.1 M HClO\(_4\) with the addition of 0.1 M KI, 0.1 M KBr, or 0.1 M KCl. The size scale of the porosity produced during the dealloying of Ag\(_{0.65}\)Au\(_{0.35}\) in the above electrolytes was found to increase with the addition of halides. Without the addition of halides, a pore size of approximately 8 nm is produced while 17 nm, 16 nm and 67 nm is measured in the KCl, KBr and KI containing electrolytes respectively.

The addition of halides has the effect of modifying the surface diffusivity of Au from \( 2 \times 10^{-16} \text{ cm}^2/\text{s} \) in 0.1M HClO\(_4\) to \( 8 \times 10^{-13} \text{ cm}^2/\text{s} \) in 0.1M HClO\(_4\) +0.1M KI. We have developed a set of experiments to study the change in the surface diffusivity of Pt with the addition of halides; we will use the same solutions as in the case of Au for comparison purposes.

For these experiments we dealloyed Cu\(_{80}\)Pt\(_{20}\) in 1M HClO\(_4\), at potential \( E = 0.6V_{MSE} \) for \( t = 20 \text{ hours} \). Post dealloying the samples were placed in 0.1M HClO\(_4\) with the
addition of $0.1M \text{KI}$, $0.1M \text{KBr}$, and $0.1M \text{KCl}$ and held at $E = -0.430 \text{V}_{\text{MSE}}$ for $t=20\text{hours}$. This potential was chosen because it is well below the critical potential and according to the Table 3.3 the corresponding surface diffusivities are in the $10^{-19}\text{cm}^2/\text{s}$. The results are compiled in Table 3.5. For the control we used the ligament radius of the Cu$_{80}$Pt$_{20}$ that gave us the $r_0$ for the percolating cluster, sample 061402-a.

Table 3.5 Summary of the effect of the of halides on ligament size and surface diffusivities

<table>
<thead>
<tr>
<th>Cu$<em>{80}$Pt$</em>{20}$</th>
<th>0.1M HClO$_4$</th>
<th>Ligament Size(nm)</th>
<th>Surface Diffusivities $10^{-20}\text{cm}^2/\text{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>061402-a</td>
<td>--------------</td>
<td>1.16</td>
<td>--------</td>
</tr>
<tr>
<td>051302-b</td>
<td>0.1M KI</td>
<td>1.66</td>
<td>4.49</td>
</tr>
<tr>
<td>051402-b</td>
<td>0.1M KBr</td>
<td>1.48</td>
<td>2.32</td>
</tr>
<tr>
<td>052002-b</td>
<td>0.1M KCl</td>
<td>1.88</td>
<td>8.29</td>
</tr>
</tbody>
</table>

From the data we see that the addition of halides does in fact alter the surface diffusivity of the Pt adatoms. The greatest change came with the addition of 0.1M KCl to the coarsening solution of 0.1M HClO$_4$. However the effect of the halides on the Pt diffusivity is not as drastic as that obtained with Au.

The increase in the surface diffusivity of Pt with the addition of Cl$^-$ can be explained by the following. It is well known that the absorption of chloride ions on metals results in weaker metal-metal bond [79]. The formation of Cl-Pt structure should then enhance the surface mobility of Pt adatoms as the higher surface diffusivities reveal.

3.3.4 Effect of Electrolyte.

It is obvious from Table 3.3 that different electrolytes have the effect of altering the surface diffusivity of the metal adatoms. To measure this effect we dealloyed samples at the same potential, for the same amount of time but in different electrolytes.
We chose to study the effect of $0.5M \text{ H}_2\text{SO}_4$ and $1M \text{ HClO}_4$ for purposes of comparison with the existing literature. For this set of experiments we chose to dealloy $\text{Cu}_{80}\text{Pt}_{20}$ in the indicated solutions for two different potential holds $E=(0.2, 0.5)V_{MSE}$ for a period of time of 20 hours. As a control in the calculation of surface diffusivities we used the ligament radius of the $\text{Cu}_{80}\text{Pt}_{20}$ that gave us the $r_0$ for the percolating cluster, sample 061402-a. The results are summarized in Table 3.6.

Table 3.6 Summary of the effect of the of electrolyte on ligament size and surface diffusivities

<table>
<thead>
<tr>
<th>$\text{Cu}<em>{80}\text{Pt}</em>{20}$</th>
<th>Potential, Electrolyte</th>
<th>Ligament Size (nm)</th>
<th>Surface Diffusivities $10^{-20}\text{ cm}^2/\text{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>061402-a</td>
<td>-----------------------</td>
<td>1.16</td>
<td>-----------------------</td>
</tr>
<tr>
<td>042402-b</td>
<td>0.2V, 1M HClO$_4$</td>
<td>1.62</td>
<td>3.94</td>
</tr>
<tr>
<td>042502-a</td>
<td>0.5V, 1M HClO$_4$</td>
<td>1.82</td>
<td>7.12</td>
</tr>
<tr>
<td>042202-a</td>
<td>0.2V, 1M H$_2$SO$_4$</td>
<td>1.32</td>
<td>0.95</td>
</tr>
<tr>
<td>041902-a</td>
<td>0.5V, 1M H$_2$SO$_4$</td>
<td>1.28</td>
<td>0.67</td>
</tr>
</tbody>
</table>

The message conveyed from Table 3.3 is that the bisulfate ions have the effect of increasing the mobility of the Pt adatoms over that of the perchlorate ions. In [15] it states that the perchlorate ions do not have any specific absorption on the Pt atoms. In [67] the authors support [15] and say that presence of chloride contaminates can be neglected because the surface diffusivities are small and the chloride ions have the effect of increasing the mobility as we have already demonstrated. However our results show the opposite effect, an increase in surface diffusivity, the only explanation for this behavior is chloride contamination. The reagent grade chemical used for making the solution contains a maximum level of impurities of chloride of 0.001%, this could be the source of our impurities.
3.3.5 Effect of Electrolyte Composition

We can change the surface diffusivity of the metal atoms by varying the electrolyte. What has yet to be determined is the change in surface in diffusivity due to a variation in electrolyte composition. To study this effect we will dealloy Cu$_{80}$Pt$_{20}$ at the same potential $E=0.5 V_{MSE}$ for the same period of time=$18h$ and different electrolyte concentrations $X M H_2SO_4$ where $X=0.0$, $0.5$, $1.0$. The calculation of surface diffusivities will be with respect to the previous control. Results are summarized in the following Table 3.7.

<table>
<thead>
<tr>
<th>Cu$<em>{75}$Pt$</em>{25}$</th>
<th>Electrolyte</th>
<th>Ligament Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>031902-c</td>
<td>0.1M H$_2$SO$_4$</td>
<td>0.82</td>
</tr>
<tr>
<td>0539002-a</td>
<td>0.5M H$_2$SO$_4$</td>
<td>0.78</td>
</tr>
<tr>
<td>032402-a</td>
<td>1.0M H$_2$SO$_4$</td>
<td>0.76</td>
</tr>
</tbody>
</table>

As we increase the concentration we find a slight decrease in the ligament size. This suggest that at these potentials the bisulfate ions hinder the mobility of the Pt adatoms. It is well known that Cu passivates at high sulfuric concentrations. We could be forming an oxide that hinders diffusion.

3.3.6 Temperature Coarsening

We have shown in the previous chapter that larger length scales can be obtainable through high temperature coarsening. In this section we will study the effect of lower temperatures. We do not expect the behavior to be any different than that of higher temperatures, but the lower temperatures will allow us to measure surface diffusivities using the SANS data.

We are going to explore two temperatures, 250°C and 500°C. All the samples are Cu$_{80}$Pt$_{20}$, they have all been dealloyed in 0.5M H$_2$SO$_4$ at an applied potential of 0.5V$_{MSE}$,
and the only differentiating variable is the hold time, 5 hours and 3 hours for 250C and 500C respectively. The surface diffusivity measurements were made with respect to a control sample that was dealloyed in the same manner but not heat-treated; the results are summarized in Tables 3.8, 3.9.

Table 3.8 Summary of temperature coarsening at 250C for Cu₈₀Pt₂₀

<table>
<thead>
<tr>
<th>Cu₈₀Pt₂₀</th>
<th>Time at T=250C</th>
<th>Ligament Size (nm)</th>
<th>Surface Diffusivities 10⁻²⁰ cm²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>042402-a</td>
<td>---------------</td>
<td>1.42</td>
<td>------</td>
</tr>
<tr>
<td>042902-a</td>
<td>30m</td>
<td>1.46</td>
<td>29.5</td>
</tr>
<tr>
<td>050602-a</td>
<td>5h</td>
<td>1.54</td>
<td>9.7</td>
</tr>
<tr>
<td>050802-a</td>
<td>15h</td>
<td>1.54</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table 3.9 Summary of temperature coarsening at 500C for Cu₈₀Pt₂₀

<table>
<thead>
<tr>
<th>Cu₈₀Pt₂₀</th>
<th>Time at T=500C</th>
<th>Ligament Size (nm)</th>
<th>Surface Diffusivities 10⁻¹⁸ cm²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>051302-a</td>
<td>---------------</td>
<td>1.32</td>
<td>------</td>
</tr>
<tr>
<td>051402-a</td>
<td>5m</td>
<td>1.44</td>
<td>6.3</td>
</tr>
<tr>
<td>051502-a</td>
<td>15m</td>
<td>1.62</td>
<td>6.4</td>
</tr>
<tr>
<td>051602-a</td>
<td>30m</td>
<td>1.78</td>
<td>5.9</td>
</tr>
</tbody>
</table>

The results obtained are difficult to verify with the literature due to the lack of data of Pt diffusivities at low temperatures and non-evacuated atmosphere. It is important to note that the surface diffusivities are higher at lower times. The pores coarsen quicker when they are smaller due to higher curvature.
What we can do is try to calculate the activation energy from Table 3.7. The surface diffusivity as a function of temperature can be expressed as an equation (3.27).

\[
D_s = D_0 \exp \left( -\frac{Q_d}{RT} \right)
\]  

(3.27)

From the average values of the surface diffusivities of Table 3.7, and the aid of the above equation we can calculate the activation energy \(Q_d\) from Figure 3.2.

By using the fit we can calculate the surface diffusivities at room temperature from our system at 298K we obtain \(D_s = 3.23 \times 10^{-23} \text{cm}^2/\text{s}\), which is approximately what we expect from our room temperature coarsening experiments over a year.
3.4 Conclusions

In this chapter we have produced a new method to derive the well-used equation (3.2) from Fick’s second law and the change in chemical potential of the surface due to curvature. The equation needs to be placed under further scrutiny through atomistic simulation to be tested.

We have used equation (3.2) to calculate surface diffusivities as a function of applied potential, halides, electrolyte, electrolyte composition and temperature. The surface diffusivities calculated through the potential coarsening experiments agree very well with that found in the literature. We have also confirmed the reproducibility of our experimental setup as well as the stability of the porous Pt structure at room temperature.

The addition of halides also modified the surface diffusivities with the addition of KCl having the most effect, by increasing the diffusivities less than one order of magnitude. We believe this is due to the absorption of the chloride ions on the surface weakening the metal-metal bond and increasing the metal adatom mobility.

We found that the structures coarsened in 1M HClO$_4$ increased the surface diffusivity over the ones coarsened in 0.5M H$_2$SO$_4$. This behavior contradicts the literature. We believe this is due to the presence of chloride ions in the solution. These impurities arrive from the reagent chemical used and possible impurities in the water. Electrolyte composition had the effect of decreasing mobility as we increased in molarity.

The temperature coarsening experiments gave reproducible results; the diffusivities did however decrease as the time of the heat treatment was prolonged. We believe this is due to the higher curvature and adatom concentrations at earlier times; this effect should be implicit in the equation, reason to place it under further scrutiny. From our temperature coarsening data we calculated the activation energy and diffusivity coefficient; from these we calculated a surface diffusivity at room temperature of $D_s = 2.5 \times 10^{-23}$ cm$^2$/s. If we insert this value into equation (3.1) and calculate the change in
radius over a period of a year, we obtain a change of 0.01% confirming the results obtained in Table 3.4.
Chapter 4. Tailoring Porosity

4.1 Introduction

Over what range can pore sizes be tailored in porous Pt? Following the percolation model proposed by Sieradzki et al. [17, 18] and recently reanalyzed by the same authors [2], we argue that the surface diffusivity of the remaining element, Pt in our case, dominates the resultant size scale porosity created during dealloying. We expect the dealloying rate to have very little effect on the final ligament size. The dealloying rate has the only effect of establishing the initial pore size, \( r_0 \), with the further constraint that it must be equal to the preexisting compositional length scale in the alloy given by the percolation cluster size of the atoms of the less noble element, \( \xi_{\text{Perc}} = \xi_a \), equation (4.1).

\[
\xi_a = \frac{(1 + p)a}{1 - p} \quad (4.1)
\]

where \( \xi_a \) is the compositional cluster length scale which we can take as the percolation cluster size, \( p \) is the fraction of dissolving species, Cu, \( a \) is the near neighbor distance for the Cu lattice. If these percolation concepts are correct, we should be able to approach \( r_0 \) to \( \xi_{\text{Perc}} \) for an alloy where the noble component has a high melting point, i.e. low value of surface diffusivity at room temperature. For Ag\(_{0.70}\)Au\(_{0.30}\) \( r_0 \) is equal to 1.6nm, and the smallest size scale observed so far for porous Au is 8nm [14]. Can we determine \( \xi_{\text{Perc}} \) in the percolation model for the Cu\(_x\)Pt\(_{1-x}\) system?

From the percolation model; the percolating cluster size should be the smallest pore size achievable. But what is the largest size scale supported by the porous Pt structure? We know that size scales in the micron region are observable in the Au system.
4.2 Experimental

The alloy samples were prepared at AMES Laboratory by arc melting the Cu (99.999% pure) and Pt (99.99% pure) on a water-cooled copper hearth plate in a reduced pressure atmosphere of argon. The alloy was then heat-treated and drop-quenched into an oil bath at 1000°C to avoid the formation of ordered phases. After quenching, the alloy is then cold rolled to a thickness of 200µm. The rolled foil was then annealed at 1000°C for 1.5 hours and quenched by removing it from the inert atmosphere furnace and allowing it to cool in a stream of blowing air.

Prior to use in the electrochemical cell, the foils were cut into 2 x 3 cm samples and masked with Teflon tape to a known exposed area. The electrolyte consisted of reagent grade 1M Sulfuric Acid, two platinum counter electrodes parallel to the alloy’s exposed area were used along with a saturated mercury sulfate electrode (MSE) as a reference. A model 263A Potentiostat from Princeton Applied Research was used for all experiments. Typically, the potential was scanned at a rate of 1mV/s from open circuit to the desired dealloying potential. The samples were then rinsed in deionized water prepared with a Barnstead Nanopure system with a specific resistivity of 18.2 MΩ/cm.

After the samples were dealloyed some were placed in a preheated 1500 Thermolyne furnace for the desired time and temperature. The samples were removed from the furnace and allowed to cool at room temperature.

Small angle neutron scattering (SANS) and ultra small angle neutron scattering (USANS) experiments were conducted at the National Institute of Standards and Technology 20MW reactor in Gaithersburg, MD. The samples were placed in an evacuated chamber in transmission geometry. The SANS measurements were performed using a 30m long instrument (typically NG3).
4.3 Results and Discussion

4.3.1. Determination of the minimum pore size.

When dealloying takes place there is a creation of vacancies and roughness develops. In an ideal random solid solution, the disordered high-density regions determine the curvature or the size scale of the vacancies or clusters of the less noble atoms set by the composition of the alloy. These clusters form due to fluctuations in the simple stochastic packing. The high-density cluster size that we want to describe is actually the average cluster size in one-dimensional percolation given by (4.1). This can be more visually seen in Figure 4.1. The circle represents a region of high-density reactive element created by the random packing of the alloy. If the more noble element is “frozen in” due to low surface diffusivities then that high density region should approximate the final pore size.

![Figure 4.1](image)

**Figure 4.1** Schematic image showing the stochastic random packing of an alloy. At low surface diffusivities the cluster of the high-density regions should approximate the final pore size.

As explained above dealloying rate has the only effect of establishing the initial pore size, \( r_0 \). After the creation of \( r_0 \) surface diffusion takes over the coarsening process
to reduce the overall energy of the system and the pores develop. Surface diffusion is a function of the electrolyte, electrolyte contaminates, as halides, applied potential and temperature. The effect these variables except for temperature have on the surface diffusivity is not well known; this will be the task for the next chapter. This assumed it is very difficult to set the appropriate conditions for obtaining the smallest diffusivities in the Pt system. What we can do is look through our extensive data set and find the samples that scattered with the smallest pore size; we will compare these results to the percolating cluster size.

The method used to calculate the average pore size is the same as that explained in section 1.3. We selected three alloys, one from each composition that scattered with the highest $Q_p$, smallest pore size. We then used the level wave model to simulate the 2-dimensional images, from which we made random chord length measurements, for a schematic interpretation see Figure 4.2(a). Figure 4.2(b) is a histogram of the number of chords versus the length of the chords. The maximum represents the dominant chord length, in this case we measured the distance between voids. Figures 4.3-5 displays the void data as a function of counts for each of the samples, the maximum corresponds to the dominant pore size in the structure.

Figure 4.2 (a) Schematic illustration of the random chord length measurements made on the 2-dimensional image created from the Level Wave Model (b) histogram of the number of chords versus the length of such chords from the random chord lengths of (a).
Figure 4.3 Void data corresponding to Cu$_{80}$Pt$_{20}$ with a $Q_p=0.19323$

Figure 4.4 Void data corresponding to Cu$_{75}$Pt$_{25}$ with a $Q_p=0.17733$

Figure 4.5 Void data corresponding to Cu$_{71}$Pt$_{29}$ with a $Q_p=0.177028$
The samples that scattered with the highest $Q_p$, smallest pore size, were the following. For Cu$_{80}$Pt$_{20}$ it was run 061402-a, dealloyed at 0.4V vs MSE in 0.5M H$_2$SO$_4$ for 20hours. For Cu$_{70}$Pt$_{25}$ it was run 032203-a, dealloyed at 0.2V vs. MSE in 1M H$_2$SO$_4$ for 18hours. For Cu$_{71}$Pt$_{29}$ it was run 061702-a, dealloyed at 0.6V vs. MSE in 0.5M H$_2$SO$_4$ for 20hours. The only common characteristic from these experiments is the solution. We had originally setup experiments to measure the percolating cluster size in 1M HClO$_4$ due to its low surface diffusivity for Pt found in the literature in the vicinity of $10^{-19}$cm$^2$/s, but that this behavior does not hold for our data. For more details on the experiments please see Appendix E.

Table 4.1 shows the experimental percolating cluster size determined form the SANS data vs. the calculated via equation (3.1).

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Experimental $r_0$ (nm)</th>
<th>Calculated $\xi_{Perc}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{80}$Pt$</em>{20}$</td>
<td>2.67</td>
<td>2.29</td>
</tr>
<tr>
<td>Cu$<em>{70}$Pt$</em>{25}$</td>
<td>2.37</td>
<td>1.78</td>
</tr>
<tr>
<td>Cu$<em>{71}$Pt$</em>{29}$</td>
<td>2.09</td>
<td>1.50</td>
</tr>
</tbody>
</table>

4.3.2. Determination of the maximum pore size

The minimum pore size is set by the percolating cluster size. In this section we would like to address what is the maximum pore size supported by the porous Pt structure. In porous Au we have found that pores in the vicinity of 1$\mu$m are attainable. We know that the best method to alter the pore size in a drastic manner is by temperature coarsening. The thought is that after a long enough time the structure will not be able to support the developing pore size and it will sinter.
We dealloyed four $Cu_{80}Pt_{20}$ samples in 1M HClO$_4$ at 0.6V vs. MSE for 20 hours; the average charge removed per sample was 215 C/cm$^2$. Post dealloying the samples were coarsened in a furnace at 800C for 15m, 30m, 1h, 3h. The coarsened samples were placed in transmission geometry in a evacuated chamber to conduct USANS experiments. The samples were then cleaved with tape to expose new surface and viewed with the aid of the FESEM.

![Figure 4.6](image.png)

Figure 4.6. Ultra Small Angle Neutron Scattering Data, for $Cu_{80}Pt_{20}$ samples dealloyed in 1M HClO$_4$ at 0.6V vs. MSE for 20 hours and coarsened at 800C for various times

Form the USANS data we notice that the smallest peak corresponds to the 15m heat treatment as would be expected; as we continue to coarsen the structure the peak develops reaching maximum pore size and intensity at 1h. There is a distribution of ligaments in the structure created through the selective dissolution process with an average critical size. Ligaments above this critical size will grow at expense of the smaller ones, below the critical size, that become unstable and dissolve. This process can only persist for so long, eventually the smaller ligaments will be consumed, leaving the structure unsteady and it begins to slowly collapse. This behavior can be seen for the
three-hour heat treatment, the peak has ceased to shift to smaller Q’s and the intensity of the peak begins to decay indicating the densification of the structure. The FESEM images confirm this expectation.

\[ \text{Figure 4.7: Sample 051602-b, Cu}_{80}\text{Pt}_{20} \text{ samples in 1M HClO}_4 \text{ at 0.6V vs. MSE for 20 hours, and coarsened at 800C for 15m} \]

\[ \text{Figure 4.8: Sample 052102-b, Cu}_{80}\text{Pt}_{20} \text{ samples in 1M HClO}_4 \text{ at 0.6V vs. MSE for 20 hours, and coarsened at 800C for 30m} \]
Figure 4.9: Sample 052802-b, Cu₈₀Pt₂₀ samples in 1M HClO₄ at 0.6V vs. MSE for 20 hours, and coarsened at 800°C for 1h

Figure 4.10: Sample 060302-b, Cu₈₀Pt₂₀ samples in 1M HClO₄ at 0.6V vs. MSE for 20 hours, and coarsened at 800°C for 3h
The average pore sizes calculated from the FESEM images and verified through the USANS data are compiled in Table 4.2. For more details on the dealloying procedure for these samples see Appendix C

Table 4.2 Maximum pore sizes achieved through heat treatment at 800C of dealloyed Cu$_{80}$Pt$_{20}$

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Heat Treatment at 800C</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>051602-b</td>
<td>15m</td>
<td>160</td>
</tr>
<tr>
<td>052102-b</td>
<td>30m</td>
<td>175</td>
</tr>
<tr>
<td>052802-b</td>
<td>1h</td>
<td>203</td>
</tr>
<tr>
<td>060302-b</td>
<td>3h</td>
<td>210</td>
</tr>
</tbody>
</table>

4.4 Conclusions

We have experimentally determined the minimum and maximum pore size in the Cu-Pt system. The minimum approximates that of the percolating cluster size in the percolation model, defined by the random high-density packing of the less noble element. The percolation model is the only model to predict an initial pore size. All three alloys approximated the theoretical value by less than 6Å. These values were obtainable due to the low surface diffusion of Pt.

The maximum pore size was achieved through high temperature coarsening at 800C. The final pore size after 3 hours was of approximately 210nm. The structure begins to collapse and smoothen as we try to obtain larger length scales as determined through the USANS data and FESEM images. These pore sizes are significantly smaller than the ones achievable in the Au system. We would expect that if the structure does self-similar coarsen then the pores would continue to grow until they reach the size of the dealloyed layer, this is not the case.
A.1 Introduction to Cardiac Pacing Leads

The synchronized contraction and relaxation of the muscle tissue in each of the heart’s chambers is essential for proper pumping and cardiac output. The sequence of the heart includes time delays that enable chambers to fill before emitting blood as the result of the pumping action. These delays allow cardiac output to vary according to the volume of blood the body requires.

Problems in cardiac pacing occur when any of the components involved in the synchronized sequence fail. A faulty SA node could result in a very low heart rate, which would yield an insufficient blood supply for the body. A faulty conduction path in the myocardial walls could prevent the action potentials from traveling fast enough to induce contraction at the proper time. These defective mechanisms and others can lead to irregularities in heart pacing or heart failure. An implantable cardiac pacemaker is designed to detect and restore the natural rhythm of the human heart. The implanted pacemaker [80] Figure A.1, consists of two main subunits, the pulse generator (battery, electronics, pulse generator) and the leads (attached in or on the heart). The system works together to sense and detect arrhythmias and then to deliver the appropriate therapy (pacing pulses or a high energy shock in the case of fibrillation).

Figure A.1: a) Implantable Cardiac Pacemaker. b) Leads
To assure safe and reliable stimulation to the heart at all times the generators output voltage is usually twice that of the cardiac threshold. The cardiac threshold is defined as the lowest voltage at a given pulse duration that is necessary to depolarize the myocardium. The current state of the art lead has a threshold of approximately 0.5V for a 0.5msec duration pulse; this has decreased from a value of 3V at 1.8msec in the 1960’s [81]. The geometric size, and total surface area of the lead ultimately affect the threshold values for stimulation, the longevity of the battery and the sensing efficiency. These are discussed below.

Cardiac Pacing Electrodes have been undergoing a consistent reduction in size through the 1970’s and 1980’s from a hemispherical area of 90mm² to as small as 1.5mm² with the introduction of porous electrodes.

Although it is accepted that porosity is important for the improved performance of the pacing electrodes, it is not known what the optimal pore morphology should be. No systematic studies have been performed on the effect of pore morphology, size and distribution, on the pacing lead performance, sensing and stimulation.

The various functions of the pacing system require different size scale porosity for optimum performance. Improved sensing requires large capacitance, large surface area, and therefore, small scale porosity; while improved tissue ingrowth requires larger micro scale porosity that favors fibroblast attachment [82]. Not only is the effect of pore size important, sensing electrodes act as high pass filters [83] which can be used to optimize sensing by attenuating the relatively large amplitude low frequency component of the electrogram. The filtering behavior depends on the electrode impedance, which in turn is a function of frequency. The electrode impedance is determined by the average pore size, pore distribution and pore length [84, 85,86]. Other effects of porosity on cardiac electrode performance are: reduced electrode polarization, reduced sensing signal attenuation, and increased delivery to cardiac cells for a given pulse duration. These issues are discussed in more detail below. However, some of these effects such as longevity of the pulse generator, threshold, sensing, polarization considerations, and
biocompatibility effects can only be studied in vivo, but we present them for
completeness and motivation. We will address effects as the impedance behavior of
porous electrodes as function of pore morphology that can be pursued in vitro.

A.2 Longevity of Pulse Generator Battery

The longevity of the pulse generator depends directly upon the current required to
pace the patient. By equating the energy drain from the battery and the required energy
for pacing we can find the pacing current given by equation (A.1)[81]

\[ I_t = \frac{V_0^2 t}{V_b Z_p L} \]  

(A.1)

\( I_t \) is the current that goes to the patient, \( V_0 \) is the output pacing voltage, \( t \) is time,
\( V_b \) is the battery voltage, \( Z_p \) is the pacing impedance, and \( L \) is the cycle length. Of these
terms, the performance of the lead will affect the output voltage, twice the threshold
voltage, and the pacing impedance. In order to increase the longevity of the battery we
must design stable, low threshold, high pacing impedance leads. Battery longevity of 7-
10 years is considered acceptable.

A.3 Electrode Size and Threshold Considerations

Theoretically a lead’s chronic threshold should vary as a function of the size of
the stimulating electrode. Equation (A.2) states that the electric field \( \varepsilon \) necessary to
depolarize the myocardium is a function of the applied voltage \( V \), the radius of the
stimulating electrode \( r_0 \) and the thickness \( d \) of the fibrous capsule covering the implant,
Irnich [87]. This fibrous capsule, also called virtual electrode, is conductive but not
stimulatable, it has the effect of increasing the radius of the electrode. Hence, decreasing the electric field by the square of its thickness.

\[
\varepsilon = \frac{V}{r_0} \left( \frac{r_0}{r_0 + d} \right)^2 \quad \text{(A.2)}
\]

If we consider a constant fibrous capsule layer thickness, the equation predicts an increasing electric field, decreasing threshold voltage, as the electrode is reduced in size. The optimal size of the lead would be that of a radius equal to the thickness \(d\) of the fibrous capsule, below this value, the electric field decreases rapidly. A typical value for \(d\) is in the order of 1mm, which gives the electrode a surface area of 6.3mm\(^2\). However, the chronic thresholds measured for porous, steroid-eluting electrodes as small as 1.5mm\(^2\) have been shown not to be significantly different than that of 8mm\(^2\) electrodes [88], and were shown to sense as well as if not better than larger electrodes [89]. The important point here is that as long as we are not increasing threshold values by reducing the size of the lead, we are benefiting from the increase in impedance values, and therefore increased longevity. The specific effect of porosity on sensing and stimulation is discussed following.

### A.4 Electrode Polarization and Sensing Considerations

Electrode polarization is a phenomenon that can increase thresholds and interfere with sensing. Mathematically, electrode polarization equation (A.3) can is represented as capacitive reactance \(X_c\), where \(f\) is the frequency of the signal, and \(C\) is the capacitance of the electrode which is proportional to \(A\) the electrolyte contacting surface area.

\[
X_c = \frac{1}{(2\pi fC)} \quad \text{(A.3)}
\]
Pulse generators are capacitively coupled devices. Electrode polarization occurs with these devices as increasing impedance as a function of pulse duration. The trailing edge voltage is higher with a polarizing electrode. However, this polarization overvoltage is not available for tissue stimulation. Hence, more voltage must be applied to overcome these polarization effects and a subsequent increase in threshold voltages. In addition the polarization overvoltage decays exponentially after the pulse and can be sensed as a false cardiac signal. *Polarization can be minimized by increasing the capacitance of the electrode, i.e. increasing the surface area of the lead by the addition of porosity.*

Electrode polarization may also have a negative effect on sensing to impedance mismatch. The impedance is a function of frequency equation (A.4), where \( R \) is the pacing system resistance dominated by the fibrous capsule, \( f \) and \( C \) are defined above.

\[
Z = \sqrt{\frac{R^2 + 1}{(2\pi f C)^2}} \tag{A.4}
\]

The pacing pulse has a relatively high frequency content. However the cardiac electrogram is a low frequency signal. As a result, the sensing impedance \( Z_s \) can be much higher than the pacing impedance, \( Z_p \). It seems that there is greater focus on the pacing impedance to reduce current drain and increase battery longevity. However, the sensing impedance should not be ignored, if it reaches values near the input impedance of the generators amplifier, it may attenuate the pacing signal. *Increasing the capacitance by introducing porosity can minimize attenuation issues as described in equation (A.3).*
A.5 Effect of Porosity on Biocompatibility

The type of tissue response to an implanted biomaterial is one of the most important questions regarding long-term success of implants in the body. The contact between the heart’s tissue and the implanted lead is influenced by the micromorphology of the surface e.g. microporosity and micrometer scale roughness. This response in turn affects the acute and chronic stimulation threshold values. Typically the stimulation thresholds increase in the first three months post implantation due to the inflammatory response at the tissue electrode interface, as the inflammation subsides stimulation thresholds plateaus to a chronic level [90]. The effect of micromorphology on biocompatibility is not fully understood, micrometer scale roughness has shown to affect fibroblast attachment by allowing intimate contact between the fibroblast and the interface showing mechanical interlocking of cells, and hence improve the mechanical integrity of the interface [91]. However studies on electrodes with porosity too small to allow tissue ingrowth has shown to decrease threshold values over their corresponding polished electrodes of the same material, indicating that we do not fully understand the role of micro- scale and nano-scale porosity on biocompatibility. An added difficulty has been that electrodes with different size scale porosity are composed of different materials.

The technique proposed will allow us to produce porous platinum at any size scale from 3 nm to 300nm allowing for fundamental in vivo study on the role of morphology on biocompatibility for a phase II of this research. We can predict that an electrode with microscale surface porosity (maximizing fixation via fibroblast attachment and tissue ingrowth) and nanoscale bulk porosity (maximizing capacitance, reducing electrode polarization) may optimize stimulation. This process is also compatible with existing technology on of steroid elution, which has a marked effect on controlling the tissue response to implanted leads [90].

In a previous section we discussed the impedance of the pacing electrode assuming it was a smooth polished electrode with capacitance $C$, equation (8), which demonstrated that the impedance is expected to decrease as we increase the signal frequency or increase surface area. This general trend will hold for porous electrodes, however, the capacitance is now a function of frequency, which in turn is a function of pore radius, pore length, pore shape and pore distribution. This frequency dependence has been studied in detail for simplified cylindrical geometries[84-86]. Song [86] gives the impedance for the simple case of constant pore diameter, non-connected pore and in the absence of faradaic reactions equation (A.5) as

$$Z_p = \alpha \left[ \frac{\sinh(\omega) - \sin(\lambda)}{\cosh(\omega) - \cos(\lambda)} - j \frac{\sinh(\omega) + \sin(\lambda)}{\cosh(\omega) - \cos(\lambda)} \right]$$

(A.5)

where $\alpha = \frac{\omega}{C_d} \quad \text{and} \quad \lambda = \frac{1}{2} \sqrt{\frac{k r}{C_d \omega}}$, $k$ is the pore solution conductivity, $r$ is the pore radius, $C_d$ is the double layer capacitance, $\omega$ is the angular frequency, $\lambda$ is the penetration depth, and $l_p$ is the pore depth. Figure A.2 is a bode plot simulated in Mathematica using Song’s reduced formula to the transmission line model corresponding to values of $\alpha$ of 2.25 and 225.
The equation shows the general trend of increasing impedance with decreasing frequency. Also evident is a break-point frequency that corresponds to the shift from planar to porous behavior. For frequencies below the break point, the electrical signal penetrates the entire porous structure “seeing” the total porous surface area and sharply increasing the magnitude of the impedance; for frequencies above this value, the porous electrode acts as a polished one. As we increase the values of $\alpha$, by either increasing the porous layer thickness or decreasing the pore radius, the overall impedance at a given frequency will decrease and the break-point frequency will shift to smaller values as shown in Figure A.2. An understanding of the frequency dependence of the specific porous system used on pacing lead is critical to tailoring the overall behavior of the pacing system. This frequency dependence of the pacing lead results in the electrode acting as a high-pass filter on the electrogram [83]. Proper tailoring of the position of the break point allows for strong attenuation of the large amplitude low frequency of the electrogram. The exact position of the break point depends on the cardiac system, but for Medtronic systems a value of less than 1Hz is desired. The ability to tailor the depth of penetration and pore size will allow us to pinpoint and control the break-point frequency for a desired cardiac pacing system.
We must stress that our system is not simple cylindrical pores so we are fundamentally interested in the impedance response of the highly interconnected porosity.

**A.7 Porous Pacing Tips**

Even though we believe that we can remove most of the Cu from the alloy, this system is not appropriate for cardiac management technologies due the toxic nature of any remaining Cu that may have been left behind from the dealloying process. However, as a proof of concept, we successfully produced nanoporous platinum on cardiac pacing tips, and rings, shown in Figure A.3, and defibrillator rings. The nanoporous platinum was produced by dealloying sputter deposit Pt$_{0.25}$Cu$_{0.75}$ films of thickness ranging from (8000-12000)Å.

![Figure A.3](image)

*Figure A.3*: Cardiac Pacing Tips and sensing rings used as substrates for the porous metal formation.

Electrochemical Impedance measurements confirmed the existence of porosity on the pacing tips rings and coils. Figure A.4 shows the impedance behavior of the tips prior to dealloying and post dealloying. The presence of porosity can be seen as the break point frequency shifts to lower frequencies. We can calculate the change in surface area by the ratio of the capacitance, assuming that the double layer capacitance does not
change prior and post dealloying, hence the change in capacitance is due only to a change in surface area, the calculated change in surface area for a 8000 Å tip is of 2cm². This appears to be a viable and promising method for producing porous Pt on cardiac electrodes. Unfortunately, the presence of Cu contaminates makes any further conclusion about their potential performance difficult.

Figure A.4 Impedance data from a 8000Å dealloyed cardiac pacing tip, note the shift to lower frequencies in the Bode Plot, implying porosity; the change in surface area is in the order of 2cm²
APPENDIX B: Microprobe Data

This Appendix displays the composition of the alloys as confirmed through Wavelength Dispersive Spectroscopy (WDS) utilizing a Cameca SX-50 electron microprobe operating at 15kV and 20nA. The X-ray intensities were calculated using the PAP general method which uses a modified version of the $\phi(\rho z)$ polynomial used in the standard ZAF correction scheme.

The foils were probed along the surface and cross section; these are the results.

Figure B.1 Composition of Cu$_{80}$Pt$_{20}$ alloy across the foil surface
Figure B.2 Cross section Composition of Cu₈₀Pt₂₀ alloy

Figure B.3 Composition of Cu₇₅Pt₂₅ alloy across the foil surface
Figure B.4 Cross section Composition of Cu$_{75}$Pt$_{25}$ alloy

Figure B.5 Composition of Cu$_{71}$Pt$_{29}$ alloy across the foil surface
Figure B.6 Cross section Composition of Cu$_{71}$Pt$_{29}$ alloy
APPENDIX C: Dealloying and SANS Data

C.1 Reproducibility Data

041902-a or PCS-0.5, 042302-a or 2PCS-0.5

Cu$_{80}$Pt$_{20}$ dealloyed at 0.5V in 1M H$_2$SO$_4$ for 20 hours. The two graphs represent potential and current versus time.

Sans data corresponding to PCS-0.5

Ligament histogram for PCS-0.5
Data: PCS0_B
Model: Lorentz

\[ \chi^2/\text{DoF} = 73121.86804 \]
\[ R^2 = 0.99087 \]

\[ y_0 = -254.16426 \pm 66.72902 \]
\[ x_c = 12.78377 \pm 0.21003 \]
\[ w = 21.0777 \pm 0.79447 \]
\[ A = 288205.88798 \pm 9551.03728 \]

Filename: 2PCS-0.5

scale factor: \( 8 \times 10^{-7} \)
background: 0.062

Schultz\( \alpha = 0.595116 \)  \( \sigma \rightarrow 5 \)  mean: \( 0.166276 \)  \( A \rightarrow 0.566395 \)  \( B \rightarrow 0.541066 \)
Data: A2PCS05_B
Model: Lorentz

\[ \text{Chi}^2/\text{DoF} = 45433.36206 \]

\[ R^2 = 0.99481 \]

\[ y_0 = -207.77472 \pm 55.3933 \]

\[ x_c = 12.73301 \pm 0.13985 \]

\[ w = 18.00289 \pm 0.52338 \]

\[ A = 259004.83987 \pm 6587.63267 \]
PCS-02

scalefactor : $3.8 \times 10^{-7}$  
background : \{minfitq, maxfitq\} : \{(1, 3)\}

Schultz $\alpha$: 0.595116  
$\sigma$ -> 10  
mean -> 0.188299  
$A$ -> 0.871647  
$B$ -> 0.700062

Data: PCS0_B
Model: Lorentz

Chi^2/DoF = 58354.93174
R^2 = 0.99544

y0 = -267.4241 ± 60.0986
xc = 13.2417 ± 0.11384
w = 15.59643 ± 0.40979
A = 282471.82216 ± 6353.99197
scalefactor : $4.2 \times 10^{-7}$ background : 0.07 (minfitq , maxfitq ) : (0.9, 3.)

Schultz $\alpha$: 0.595116 $\sigma \rightarrow 10$ kmean $\rightarrow 0.38136$ A $\rightarrow 0.812345$ B $\rightarrow 0.740673$

Data: A2PCS0_B
Model: Lorentz

$\chi^2$/DoF = 62032.58795
$R^2 = 0.99512$

$y_0 = -272.60811 \pm 61.25251$
$x_c = 13.04527 \pm 0.12312$
$w = 16.50203 \pm 0.44762$
$A = 295805.48876 \pm 6880.90379$
C.2 Potential Hold

Filename: POTC0ARS -000
scalefactor :1.3 x 10^-7 background :0.018 {minfitq,maxfitq} :{0.6,3.5}
Schultz α:0.370807 σ → 8 kmean → 0.133354 A → 0.794363 B → 0.805304

Data: POTCOARS000_B
Model: Lorentz

\[ \chi^2/\text{DoF} = 32994.36242 \]
\[ R^2 = 0.99025 \]

\[ y_0 = -123.85828 \pm 37.07906 \]
\[ x_c = 19.8086 \pm 0.23397 \]
\[ w = 28.53588 \pm 0.87146 \]
\[ A = 262205.35987 \pm 6991.87994 \]

Filename: POTCOARS000_B

scalefactor : 1.43197 \times 10^{-7}
background : 0.017
(minfitq, maxfitq) : (0.6, 3.6)

Schultz \( \alpha \) : 0.370807
\( \sigma \) -> 7
kmean -> 0.137581
A -> 0.733126
B -> 0.810214

94
Data: POTCOARS200_B
Model: Lorentz

$\chi^2/\text{DoF} = 24045.24834$

$R^2 = 0.99311$

$y_0 = -116.41906 \pm 29.85781$

$x_c = 20.65344 \pm 0.17773$

$w = 26.15861 \pm 0.6418$

$A = 253347.97841 \pm 5319.96534$

Filename: POTCOARS -430
scalefactor: $1.75 \times 10^{-3}$
background: $0.018$ (minfitq, maxfitq): $(0.6, 3.5)$

Schultz $\alpha = 0.370807$ 
$\sigma \rightarrow 8$ 
$k\text{mean} \rightarrow 0.133834$ 
$A \rightarrow 0.791261$ 
$B \rightarrow 0.76171$
Data: POTCOARS430_B
Model: Lorentz

$\chi^2$/DoF = 22523.2341
$R^2 = 0.9931$

$y_0 = -107.8151 \pm 30.19588$

$xc = 20.94249 \pm 0.18437$

$w = 26.93027 \pm 0.67399$

$A = 247381.34329 \pm 5367.69648$

Filename: potcoars -490

scalefactor = $2.8 \times 10^{-7}$ background = 0.0055 [minfitq, maxfitq] = (0.6, 3)

Schultz $\sigma$: 0.370807 $\sigma$ -> 9 kmean -> 0.135096 A -> 0.85296 B -> 0.885859
Data: POTCOARS490_B
Model: Lorentz

$\chi^2$/DoF = 24295.48631
$R^2 = 0.9933$

$y_0 = -166.91589 \pm 33.49669$
$x_c = 22.02279 \pm 0.18389$
$w = 27.06068 \pm 0.67946$
$A = 257986.66319 \pm 5718.43955$

Filename: POTCOARS
scalefactor : 2.65073 $\times 10^{-7}$ background : 0.023 $(\text{minfitq, maxfitq}) : \{0.6, 3.5\}$
Schultz $\alpha : 0.370807 \quad \sigma \rightarrow 8 \quad \text{kmean} \rightarrow 0.139602 \quad A \rightarrow 0.801985 \quad B \rightarrow 0.759549$
C.3 Halide Coarsening

![Graph showing the Lorentz fit of POTCOARS572_B data.]

- **Data**: POTCOARS572_B
- **Model**: Lorentz
- **Chi^2/DoF**: 27450.69752
- **R^2**: 0.99282
- **y0**: -99.38406 ±31.30773
- **xc**: 19.63363 ±0.17581
- **w**: 25.04934 ±0.63052
- **A**: 256759.47493 ±5480.15847
Filename: Coars-KI
scalefactor: $1.08 \times 10^{-7}$ background: 0.024 (minfitq, maxfitq): (0.5, 3.5)
Schultz $\alpha$: 0.595116 $\sigma$ -> 5 kmean -> 0.135646 A -> 0.587368 B -> 0.671222

Counts vs. Angstroms

Data: COARSKI_B
Model: Lorentz

Chi^2/DoF = 22275.55142
R^2 = 0.993

y0 = -141.4314 ±33.7554
x0 = 16.60117 ±0.18716
w = 24.37821 ±0.70206
A = 214070.38848 ±5408.73837
Filename: COARSK - KCl
scalefactor : 1.2 x 10^-7 background : 0.001495 (minfitq, maxfitq) : (0.7, 3.1)
Schultz α : 0.595116 σ -> 7 kmean -> 0.122403 A -> 0.766609 B -> 0.743844

Data: COARSKCLR_B
Model: Lorentz
Chi^2/DoF = 20304.73909
R^2 = 0.9914
y0 = -137.37621 ± 32.27577
xc = 19.17343 ± 0.21222
w = 26.17761 ± 0.79811
A = 197492.00316 ± 5341.08503
C.4 Effect of Electrolyte

CH-02

scalefactor :3.×10⁻³ background :0.0165 (minfitq ,maxfitq ):[1.3]
Schultz α0.595116 σ → 8 kmean → 0.151126 A → 0.753051 B → 0.683609
Data: CH02_B
Model: Lorentz

\[ \chi^2/\text{DoF} = 37353.27015 \]
\[ R^2 = 0.99309 \]
\[ y_0 = -204.21457 \pm 47.13712 \]
\[ x_c = 16.29736 \pm 0.16582 \]
\[ w = 20.47512 \pm 0.61271 \]
\[ A = 234716.62517 \pm 6169.66651 \]

Counts
Angstroms

scalefactor : 1.1 \times 10^{-7} background : 0.028 (minfitq , maxfitq ) : (0.8, 3.)
Schultz \( \alpha : 0.595116 \) \( \sigma \) -> 7 kmean -> 0.131806 A -> 0.746944 B -> 0.742484
C.5 Effect of Electrolyte Composition
Filename: E05

scalefactor : 6.5 x 10^-8 background : 0.032 (minfitq, maxfitq) : (0.7, 3.5)
Schultz α: 0.476936 σ -> 6 kevau -> 0.15575 A -> 0.595844 B -> 0.707789

Chi^2/DoF = 50445.09563
R^2 = 0.99305
y0 = -201.31454 ± 48.17302
xc = 15.35185 ± 0.16788
w = 21.45685 ± 0.61308
A = 294037.49664 ± 7183.52905

Counts
Angstroms
Data: E050_B
Model: Lorentz

\[ \chi^2/\text{DoF} = 48157.58725 \]

\[ R^2 = 0.99213 \]

\[ y_0 = -197.35943 \pm 53.32439 \]
\[ x_c = 16.31367 \pm 0.19476 \]
\[ w = 23.12127 \pm 0.73605 \]
\[ A = 277531.71497 \pm 7840.21123 \]

Counts
Angstroms

-1000
0
1000
2000
3000
4000
5000
6000
7000
8000

0
20
40
60
80
100
120
140

Angstroms

scalefactor: \(1.2 \times 10^{-7}\)
background: \(0.042\)

Schultz: \(\alpha = 0.476936\)
\(\sigma \rightarrow 7\)
\(kmean \rightarrow 0.156652\)
\(A \rightarrow 0.701024\)
\(B \rightarrow 0.70292\)
C.6 Temperature Coarsening
Filename : Ht5h - c
scalefactor : $1.11211 \times 10^{-7}$ background : $0.038$ [minfitq,maxfitq] : (0.6, 3.6)
Schultz $\alpha : 0.595116$ $\sigma \rightarrow 6$ $kmean \rightarrow 0.161988$ $A \rightarrow 0.666109$ $B \rightarrow 0.620954$
Data: HT5H15H_B
Model: Lorentz

\[ \chi^2/\text{DoF} = 31557.85995 \]
\[ R^2 = 0.99343 \]
\[ y_0 = -165.69067 \pm 38.79326 \]
\[ x_c = 15.41265 \pm 0.16188 \]
\[ w = 21.13858 \pm 0.5919 \]
\[ A = 235036.38958 \pm 5642.69561 \]

Filename: HT5H-15H
scalefactor : \(9.9 \times 10^{-8}\) background : 0.02 \(\{\text{minfitq, maxi f t q}\} : \{0.6, 4.\}\)
Schultz \(\alpha : 0.595116 \quad \sigma \to 6 \quad \text{mean} \to 0.150127 \quad A \to 0.679511 \quad B \to 0.688155\)

Counts
Angles
filename : HT5H-30m
scalefactor : $8.8 \times 10^{-8}$ background : 0.024 (minfitq , maxfitq ) : (0.6, 3.5)
Schultz $\alpha$: 0.595116 $\sigma$ -> 6 kmeean -> 0.153848 A -> 0.673062 B -> 0.715732

Data: HT5H30M_B
Model: Lorentz
Chi^2/DoF = 42448.75381
R^2 = 0.99322
y0 = -186.24957 ± 48.19424
xc = 14.57561 ± 0.16415
w = 20.17617 ± 0.60624
A = 251331.07738 ± 6538.93166
Data: HT5H_B
Model: Lorentz

Chi^2/DoF = 31557.85995
R^2 = 0.99343

y0 = -165.69067 ± 38.79326
xc = 15.41265 ± 0.16188
w = 21.13858 ± 0.5919
A = 235036.38958 ± 5642.69561

Filename: HT5H-15H
scalefactor: 9.9 × 10^{-8}
background: 0.02
(minfitq, maxfitq) = (0.6, 4.)
Schultz: α = 0.595116
σ -> 6 kmean -> 0.150127 A -> 0.679511 B -> 0.688155
Data: HT3HC_B
Model: Lorentz

Chi^2/DoF = 49265.68795
R^2 = 0.9934

y_0 -192.1178 ±49.67786
x_c 13.2043 ±0.15921
w 19.52453 ±0.58388
A 269907.07074 ±6889.77397

Filename: HT3H-C
scalefactor: 6. ×10^{-7} background: 0.013 (minfitq ,maxfitq ):{0.6, 3.6}
Schultz α: 0.59516 σ -> 6 kmean -> 0.143757 A -> 0.680266 B -> 0.652294
Data: HT3H5M_B
Model: Lorentz

Chi^2/DoF = 29079.05223
R^2 = 0.99323

y0 -166.2392 ±37.00457
xc 16.16477 ±0.16772
w 21.96771 ±0.61334
A 230170.3878 ±5526.28

Filename : Ht3h−15m
scalefactor :6.81058 x10−7 background :0.0118 (minfitq ,maxfitq):(0.5,4.5)
Schultz α:0.595116 σ -> 6 kmean -> 0.340285 A -> 0.687279 B -> 0.736436
Data: HT5H15H_B
Model: Lorentz

\[\text{Chi}^2/\text{DoF} = 31557.85995\]

\[R^2 = 0.99343\]

\[y_0 = -165.69067 \pm 38.79326\]

\[xc = 15.41265 \pm 0.16188\]

\[w = 21.13858 \pm 0.5919\]

\[A = 235036.38958 \pm 5642.69561\]
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VITA

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