

**INTERNAL OXIDATION OF METALLIC PRECURSORS OF HIGH  
TEMPERATURE SUPERCONDUCTING CERAMICS UNDER SILVER  
SHEATH**

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The thesis "INTERNAL OXIDATION OF METALLIC PRECURSORS OF HIGH  
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## ACKNOWLEDGEMENTS

All the thanks to my parents, wife, children, thesis committee, and friends,  
with respect.

## DEDICATION

Now I lay me down to study,  
I pray the Lord I won't go nutty,  
If I should fail to learn this junk,  
I pray the Lord I will not flunk.  
But if I do, don't pity me at all,  
Just lay my bones down in the study hall;  
Tell my teacher I did my best,  
Then pile my books upon my chest.  
Now I lay me down to rest  
And pray I'll pass tomorrow's test.  
If I should die before I wake,  
That's one less test I'll have to take.

Sufferin' Student

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## ABSTRACT

### INTERNAL OXIDATION OF METALLIC PRECURSORS OF HIGH TEMPERATURE SUPERCONDUCTING CERAMIC UNDER SILVER SHEATH

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Making high temperature superconducting pellets by using powdered materials is a relatively easy process. However, most industrial applications require wire or coil. Also, superconducting oxides have a tendency to deteriorate from weathering and need to be protected from atmospheric effects. So far, all attempts at producing high temperature superconducting wires of sufficiently good quality for wide scale application have failed. Therefore, in this study an effort was made to apply electrochemical methods to obtain a deposit of silver, copper, yttrium, and barium on a silver substrate. Also, investigations of the process of internal oxidation of copper through the silver sheath were explored. Theoretical calculations were performed to determine feasibility of the experimental approaches and establish some parameters of the experiments.

Solutions of cupric nitrate,  $\text{Cu}(\text{NO}_3)_2$ , barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , and yttrium nitrate,  $\text{Y}(\text{NO}_3)_3$ , in dimethyl sulfoxide (DMSO) were used for the deposition of copper, yttrium, and barium on a silver wire. The deposition process of copper yielded a good quality copper layer. The deposits of barium and yttrium were of lower quality. Silver, deposited on the surface of the copper layer, was of high quality.

Internal oxidation of the metal under the silver sheath was explored. Copper was chosen to be oxidized under the silver sheath using an electrochemical technique as well as high temperature annealing. The oxidation of copper during high temperature annealing was satisfactory.

The experimental results demonstrate that an electrochemical route to high quality high temperature superconducting wires is feasible.



## INTRODUCTION

### 1.1 What are superconductors ?

Superconductors are materials that undergo a remarkable transformation at extremely low temperatures. Superconductors have a number of unique characteristics but their most notable property, and the origin of their name is the ability to conduct electrical current with no loss of energy. Nothing else in nature can perform this feat.

Superconductivity was discovered by a Dutch scientist, Kamerlingh Onnes, in 1911. He found that the electrical resistance of mercury (Hg) disappeared suddenly at 4.2 degree kelvin (K) (-269 degree celsius [C]), a temperature accessible only through immersion in liquid helium<sup>(1)</sup>. Significant progress occurred in the 1950s, new materials were discovered that displayed superconductivity at temperatures as high as 20 K, almost 5 times higher than the temperature of superconductivity in mercury.

In the years between 1960 and 1986, several hundred materials were found to be superconductive at low temperatures. However, the highest critical temperature (i.e., the temperature below which a material becomes superconducting,  $T_c$ ) achieved in this period was 23 K, which still required either liquid helium or liquid hydrogen cooling.

Recently, new materials have been discovered that have substantially higher  $T_c$ s. The highest stable value to date that has been independently confirmed was 95 K (-178 C). A large number of the so called high-temperature superconductors are now known to exist, all of them are variations of two basic types (the so-called 40 K and the 95K [or 1-2-3] materials). Those with  $T_c$  greater than 77 K are based on only one structure, with copper (Cu) and oxygen (O) as a constant feature. The new materials present an enormous scientific opportunity and open new vistas for potential applications<sup>(2)</sup>. Because our understanding of superconductivity has been challenged in so fundamental a fashion, with the present theoretical understanding of superconductivity being insufficient to explain the properties of the new materials, there is hope that what has been achieved in such a short time can be extended. There have been several preliminary reports of superconductivity at still higher temperatures, but at present there is no consensus as to their validity. It is likely that

room-temperature superconductivity would make possible a much broader range of applications.

### **1.2 What is zero resistance ?**

Resistances of common materials vary wildly. A piece of copper might have a resistance of only a few millionths of an ohm. A piece of glass, on the other hand, can easily have a resistance in millions of ohms. Yet, all conductive materials have one thing in common: they have some electrical resistance, which is a form of friction and which leads to heat and loss of energy. Zero is zero, which is not an easy number to measure. All instruments have their limits and zero is below the resolution of any measuring device. Nevertheless, not even the most careful experiments using the most sensitive instruments have ever found any electrical resistance in a superconductor. For superconductors, the higher the temperature value, the lower the application cost.

### 1.3 WHY ARE SUPERCONDUCTORS NEEDED ?

Superconductivity brings unique advantages, because resistive conductors such as copper, dissipate large amounts of energy as heat when carrying large currents. Superconductors are also useful in high-Q cavities because of their low alternating current losses at high frequencies compared to those in normal metals<sup>(1)</sup>. Superconductors also eliminate resistive current losses in electronic lines and device anteconnections. Finally, superconductors will save energy, make the world cleaner , less noisy, and save a lot of money.

## BACKGROUND

The discovery of several classes of oxide compounds with superconducting transition temperatures in excess of the boiling point of liquid nitrogen has led to intense basic and applied research activity. However, as remarkable as advances in this field have been, considerable improvement in many areas is required before the new superconductors appear in commercial technology. A crucial area is the development of high-quality synthesis and processing methods which yield materials with high critical current densities and useful shapes, such as wires and films.

### 2.1 Synthesis of high temperature superconductors

High- $T_c$  ceramic superconductors are normally prepared by the solid-state reaction of mixtures of oxides, carbonates, or nitrates of the constituent cations at high temperatures (above-800C). In this case, the constituents, thoroughly mixed in appropriate ratios, are initially heat-treated in the range 800 to 950 C to decompose the carbonates or nitrates and to promote interdiffusion, leading to relevant phase formation and chemical homogenization. Often, it is necessary to re-grind and re-calcine the reacted powder to subdivide any aggregated products and to improve



chemical homogeneity. The as-obtained ceramic particles are then shaped into useful forms and are finally densified into solid forms by sintering. For most high- $T_c$  superconducting ceramics, an additional annealing step, at moderate temperatures under a controlled oxygen atmosphere, is also required to optimize the oxygen stoichiometry<sup>(3,4)</sup>.

The main advantage of this usual ceramic route is that the synthesis of materials is relatively easy. However, subsequent examination often reveals that even materials with acceptable superconducting transitions are multi-phased and poorly sintered, being both porous and friable. The resulting sintered materials also have the same drawbacks as typical ceramics with respect to brittleness and forming problems. Although oxide superconductors alone will not have the flexibility that is necessary for these shaping operations. The mechanical properties of single or poly-crystalline YBa<sub>2</sub>Cu<sub>3</sub>O are comparable to those of typical brittle ceramics. It is conceivable, however, that flexibility and toughness required for good workability can be achieved when the oxide is protected by a noble metal. Indeed, it appears that this is one form in which the low temperature superconductors achieve the mechanical and electrical performance required in service.

With the aim of avoiding the disadvantages associated with the classic ceramic preparation method, several research groups have developed other techniques for preparing high-T<sub>c</sub> superconducting oxides<sup>(5-7)</sup>. For example, methods such as sol-gel process, which often refers to the use of metal alkoxides as the precursors, allows a decrease of the sintering temperature and time, and yields fine powders in which the components are mixed at the molecular level. Because of this atomic scale mixing, this process is frequently used to study doping effects for which a uniform distribution of the dopant through the lattice is required. But in the case of Y Ba Cu O the alkoxide precursors are both very expensive and difficult to obtain. In addition, the copper alkoxides are very sparingly soluble in organic solvents and the yttrium alkoxides are readily hydrolyzed by very small amounts of water. Thus, the preparation of homogeneous oxides of the required formula is difficult. Fabrication of shaped or preformed superconductors has been attempted using screen-printing and tape-casting techniques<sup>(8,9)</sup>. Attempts were made to produce coils by mixing the powder of 1-2-3 superconductivity material with organic materials and shaping the mixture into variety of forms. Another technique is the thermal spray, where a powdered superconducting materials are fed into either plasma spray or hypersonic flame spray system, which deposits the materials onto suitably prepared substrates. A post-spray anneal yields coatings with transition temperatures above the boiling point of liquid nitrogen<sup>(10)</sup>. However, maintaining today technological advances require new

methods of synthesis of high temperature superconductors. As a requirement for many electric devices, these superconductors should be thin and have a high degree of homogeneity. Thin films of copper oxides may be prepared by using electrochemical deposition techniques. That suggests that electrochemistry may provide a novel synthesis route for superconducting thin films<sup>(11-14)</sup>. A synthesis of superconductors via electrochemical methods bring with it the advantages of molecular mixing of oxides, and the films should have no area devoid of critical atoms. As a result, a superconducting product by this method may be expected to be of high quality and have the optimum quality of superconducting phases.

## **2.2 Preparation of superconducting wires**

Large-scale applications, requires flexible superconducting wires or cables. For these applications a superconductor is covered with a tube or pipe of a classic conductor which can also act as a conduit for the coolant.

In addition to the ability to be shaped into a useful configuration, or to have significant resistance to brittle fracture, good workability includes the ability of a material to be joined and readily connected to electrical terminators. Experimental



work to date on the high- $T_c$  superconductors has shown that it is difficult to make low-resistance contacts between metals and superconducting oxides. This is due, in large part, to the chemical instability of the surfaces of the oxides<sup>(15,16)</sup>. Electrical connections and joining operations may be facilitated by using a noble metal (i.e. silver) as a sheath.

When put into service, the useful lifetimes of the superconducting oxides will be limited if they do not exhibit sufficient chemical stability, strength, fracture toughness, and electrical performance for a particular application. Coating will certainly be needed to prevent contact of the superconducting oxides with water vapor and carbon dioxide, thereby inhibiting environmental degradation of the oxides. In applications such as motor and magnet windings, the wires or cables will be subjected to tensile stresses originating from magnetic fields. In many cases, the tensile stresses will be high enough to cause failure of the oxides unless special design precautions are taken. The protective sheath will help to satisfy these mechanical property requirements.

### 2.3 Electrodeposition method

The electrodeposition of thin-film superconductors has considerable practical potential, particularly in the fabrication of large nonplanar devices, as well as other electronic device applications<sup>(17)</sup>. In principle, electrodeposition from both aqueous and nonaqueous solutions is possible, although aqueous solutions are apparently unsuitable because the reduction of water is kinetically more favorable on most electrode materials than are the metals. Yet, the electrodeposition of superconducting films from nonaqueous media has been more encouraging<sup>(18)</sup>. The electrodeposition process offers the ability to plate a film of controllable thickness on conductive substrates such as continuous wires, on planar or irregular surfaces, and patterned substrates. Other potential processing advantages include adaptability to large-scale processing, relatively low cost and simplicity<sup>(19)</sup>. Thus the synthesis of superconductors by electrodeposition process has a promising future

## RESEARCH OBJECTIVE

The goal of this research involves the deposition of the three elements; yttrium, barium, and copper by applying potential to a silver wire which serves as a substrate and is a working electrode in solutions containing yttrium, barium, and copper. A silver sheath is deposited on the three elements using electrochemical cell. The silver sheath should completely cover the three elements alloy wire. An electrochemical oxidation of the alloy will be conducted at room temperature to stimulate the diffusion of oxygen through the silver sheath. A further step will take place to complete the oxidation process using a thermal method (annealing).

## THEORETICAL

### 4.1 Theoretical evaluation of the deposition of copper, barium, and yttrium from aqueous solutions

An attempt was undertaken to predict if it was possible to deposit metals of Cu, Ba, and Y, from their aqueous solutions using the Nernst equation:

The Nernst equation is<sup>(20)</sup>:

$$[E = E^{\circ} + \frac{RT}{nF} \ln(\text{ox/red})]$$

where,

R- gas constant, T- temperature (K), n- the number of electrons involved in the electrochemical reaction, F- the Faraday constant, ox- the activity of the oxidized species, red- the activity of reduced species,  $E^{\circ}$ - the standard reduction potential. The reduction reactions for the ions of  $\text{Cu}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Y}^{3+}$ , are:



and the reduction reaction for hydrogen ions is:



Calculations were made for copper, yttrium, barium, and hydrogen to determine the relation between electro-deposition potential and ion concentration for each reaction. The calculated values of potentials in a function of concentrations ranged from 0.01 M to 2.5 M for the reduction reactions are shown in Table (1). A dependence between the potential and the concentration of barium ions is shown in Figure (1,a). The potential values increase with increasing concentration of  $\text{Ba}^{2+}$ . Large increases of the potential with  $\text{Ba}^{2+}$  concentrations are observed up to 0.5 M  $\text{Ba}^{2+}$ . Above 0.5 M  $\text{Ba}^{2+}$  the potential increases slightly with increasing concentrations of  $\text{Ba}^{2+}$ . A similar dependence is observed for the other ions e.g,  $\text{Cu}^{2+}$ ,  $\text{Y}^{3+}$ , and  $\text{H}^+$ , which is shown in Figures (1, b, c, and d) respectively. The highest values of the potentials in the function of the ion concentrations are observed for  $\text{Cu}^{2+}$ , and the lowest for  $\text{Ba}^{2+}$ . The potential for  $\text{Y}^{3+}$  is higher than the potential for  $\text{Ba}^{2+}$  and lower than the potential for  $\text{H}^+$  at any concentration of their solutions, which is shown in figure (1,e). These results indicate that the deposition process of yttrium and barium from aqueous solutions of their salts is infeasible due to the hydrogen evolution, since hydrogen is reduced first. Therefore, DMSO will be a candidate to be used as a non-aqueous solvent for depositing Cu, Ba, Y, metals on the silver substrate.



Table 1. Ion Concentration vs Potential

Ion Conc.	Potential (Voltage)			
	$\text{Y}^{3+}$	$\text{Ba}^{2+}$	$\text{Cu}^{2+}$	$\text{H}^{+}$
0.01	-2.411	-2.9642	0.2778	-0.0592
0.05	-2.397	-2.5435	0.2984	-0.0385
0.10	-2.391	-2.9346	0.3074	-0.0296
0.20	-2.385	-2.9256	0.3163	-0.0206
0.30	-2.382	-2.9204	0.3215	-0.0154
0.40	-2.379	-2.9167	0.3252	-0.0117
0.50	-2.377	-2.9140	0.3280	-0.0089
0.60	-2.376	-2.9110	0.3304	-0.0065
0.70	-2.375	-2.9090	0.3324	-0.0045
0.80	-2.374	-2.9078	0.3341	-0.0028
0.90	-2.373	-2.9060	0.3356	-0.0013
1.00	-2.372	-2.9505	0.3370	0.0000
1.20	-2.370	-2.9020	0.3390	0.0023
1.40	-2.369	-2.9000	0.3410	0.0043
1.60	-2.368	-2.8980	0.3430	0.0060
1.80	-2.367	-2.8970	0.3445	0.0075
2.00	-2.366	-2.8960	0.3460	0.0089
2.50	-2.364	-2.8930	0.3480	0.0117

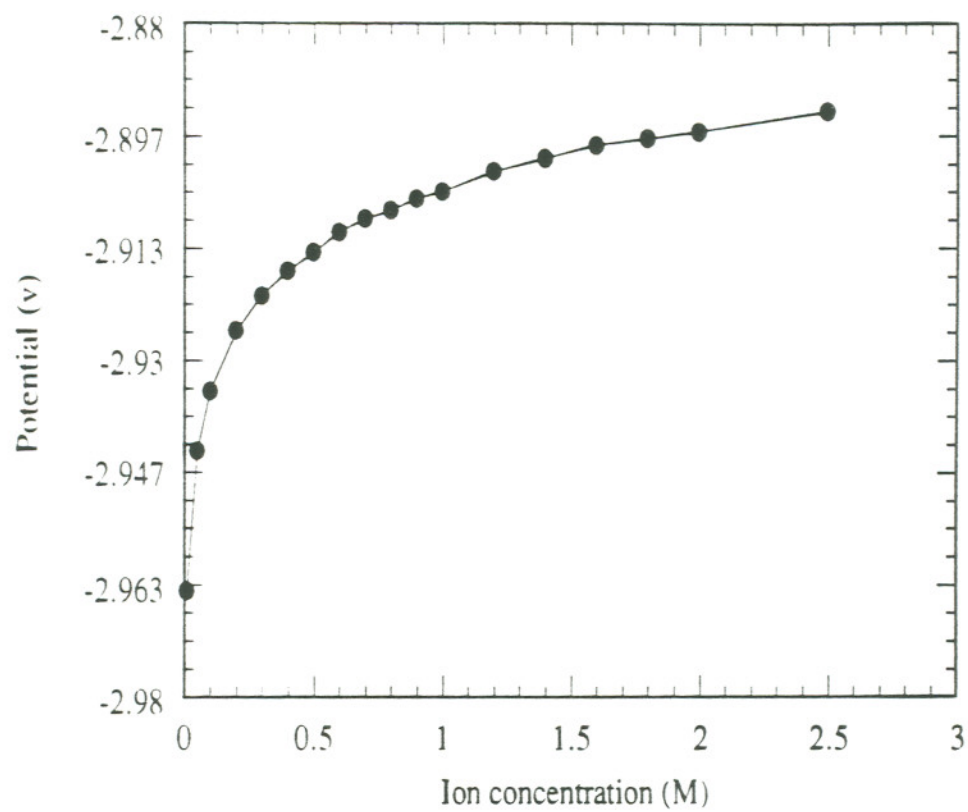


Figure 1.a. A Dependence Between the Potential and the Concentration of Barium Ions

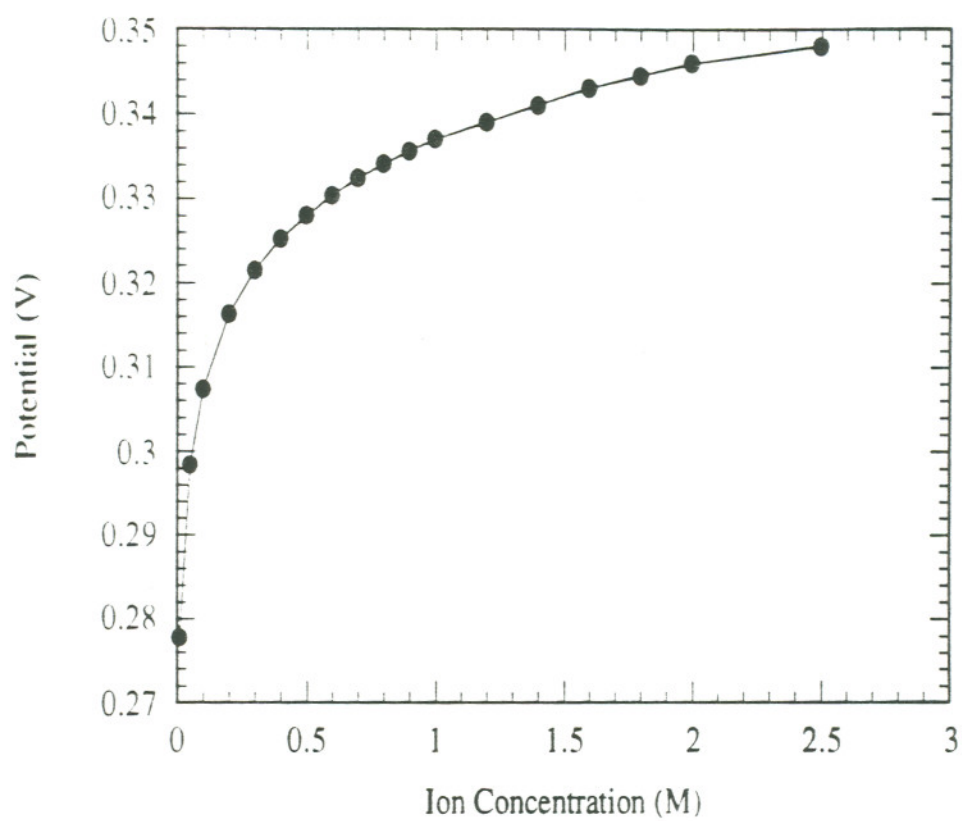


Figure 1.b. A Dependence Between the Potential and the Concentration of Copper Ions



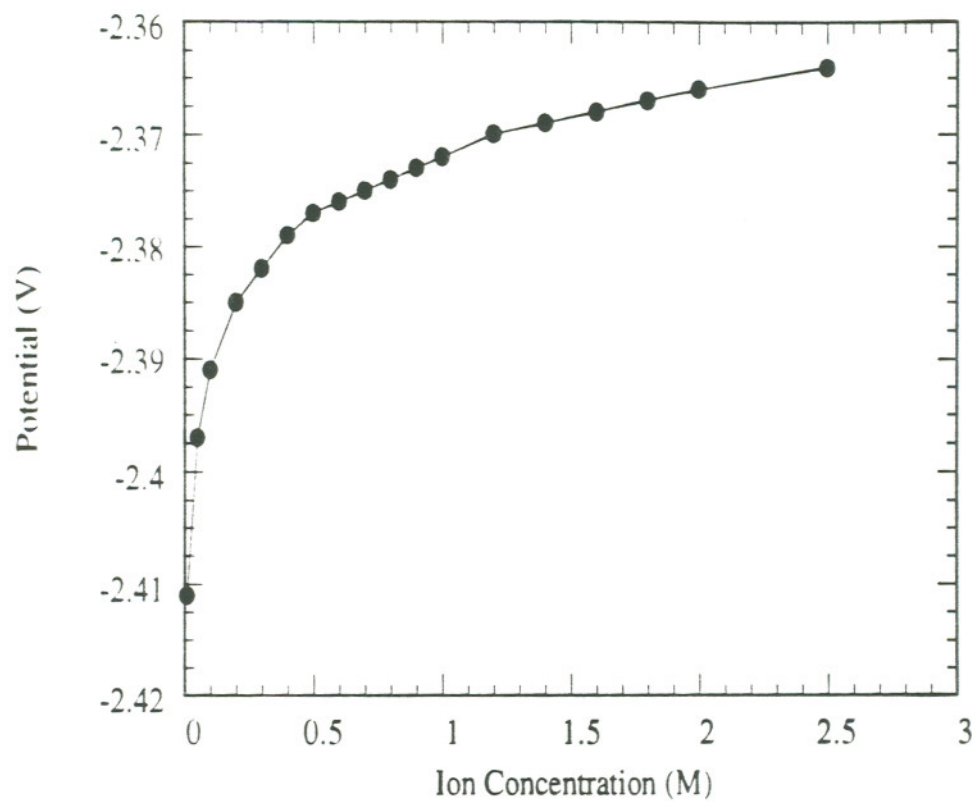


Figure 1.c. A Dependence Between the Potential and the Concentration of Yttrium Ions

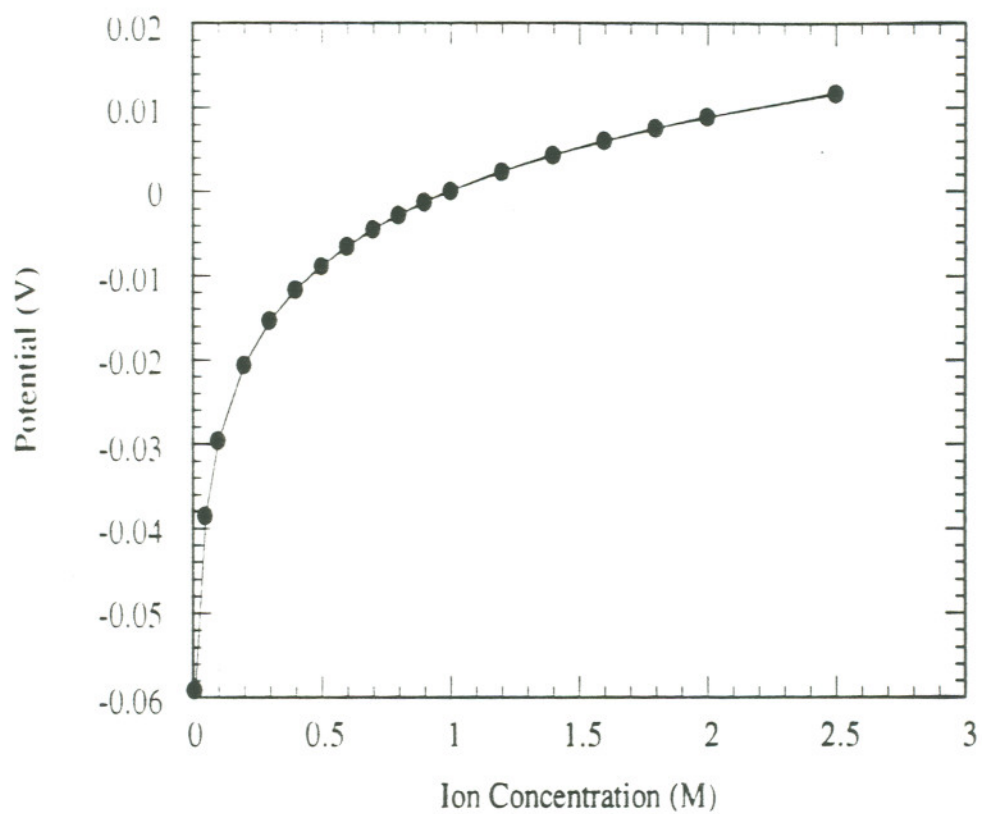


Figure 1.d. A Dependence Between the Potential and the Concentration of Hydrogen Ions

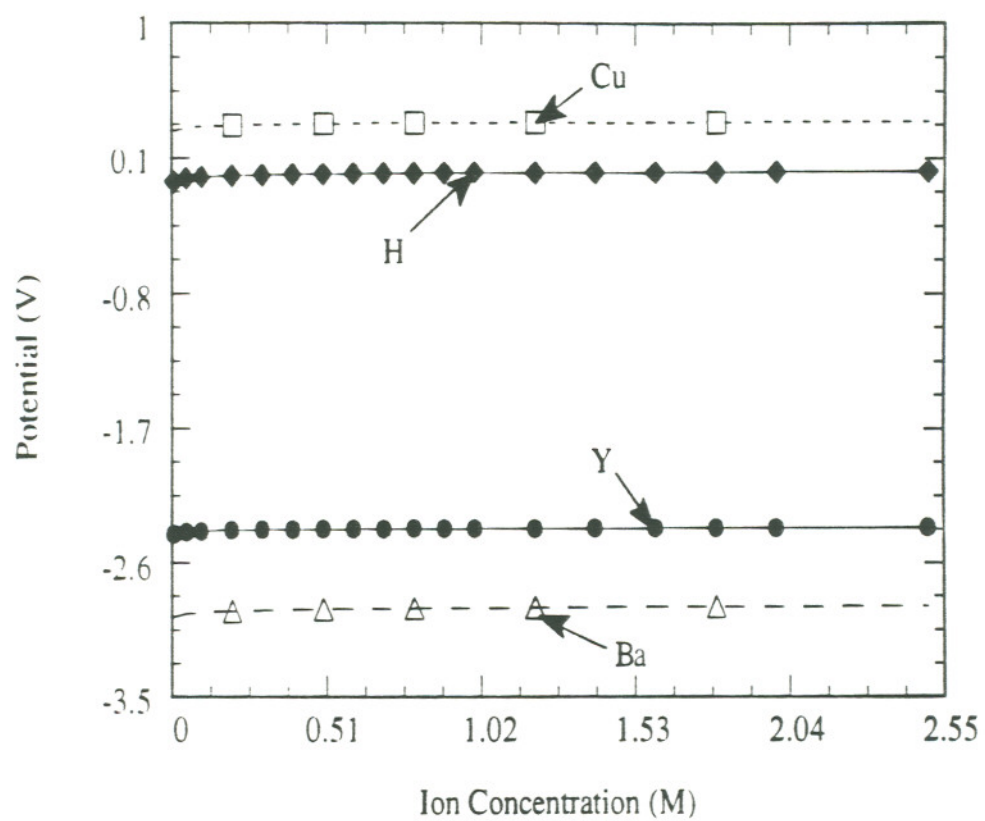


Figure 1.e. An Overlay Graphs Between the Ion Concentration of Cu, H, Ba, and Y, Versus the Potential

#### 4.2 Diffusion of oxygen through the silver sheath

To complete the oxidation process of the metallic precursor under the silver sheath, one more step will be undertaken, using high temperature oxidation. It has been noted that oxygen can penetrate silver at high temperatures. The kinetics of this process can be influenced by different factors, concentration of defects, pressure, and temperature. The calculations of the diffusivity of oxygen into the silver sheath was based on the oxidation of copper under the silver layer, since copper is the most difficult element to be oxidized compared to the other two elements, yttrium, and barium. Equation [1] was used to calculate the diffusivity of oxygen in a function of temperature<sup>(21,22)</sup>:

$$D_o = 3.2 \times 10^{-3} e^{-0.5\text{ev}/KT} \text{ cm}^2/\text{s} \quad [1] \quad \text{where}$$

$D_o$  = Diffusivity,  $K$  = Boltzman constant, and

$T$  = Temperature (K)

Figure (2), indicates the relationship between the diffusivity of oxygen in silver and temperature. From the graph, increasing the temperature will increase the diffusivity of oxygen in the solid silver.

### 4.3 Pressure exerted on superconducting ceramics

Pressure generated by the silver sheath on superconducting ceramics due the stress and strains after the high temperature oxidation was calculated using equation<sup>(23)</sup> [2]

$P = \text{Yield strength of silver lb/in}^2 \times [(r_2 - r_1)/r_1]$  [2] where

$P = \text{Pressure, psi, } r_1 = \text{Alloy radius, } r_2 = \text{Silver sheath radius}$

Figures (3), shows the relationship between the thickness of the silver sheath and the pressure generated from the silver sheath onto the deposited alloy. The graph shows that by increasing the thickness of the silver sheath, the pressure on the alloy will increase in a linear manner.

Figure (4), shows the relationship between the thickness of the deposited alloy and the pressure generated from the silver sheath. The graph shows that by increasing the thickness of the deposited alloy the pressure will tend to decrease. Calculations were made for a constant radius of the silver sheath  $r_2$  and a changing radius of the oxidized alloy. Any pressure exerted by the silver sheath reduces porosity of the ceramic formed in the process of the internal oxidation.

Figure (5), shows a cross section of the expected wire after the oxidation process.

$r_1$  = radius of the deposited alloy (thickness)

$r_2$  = radius of the silver sheath (thickness)

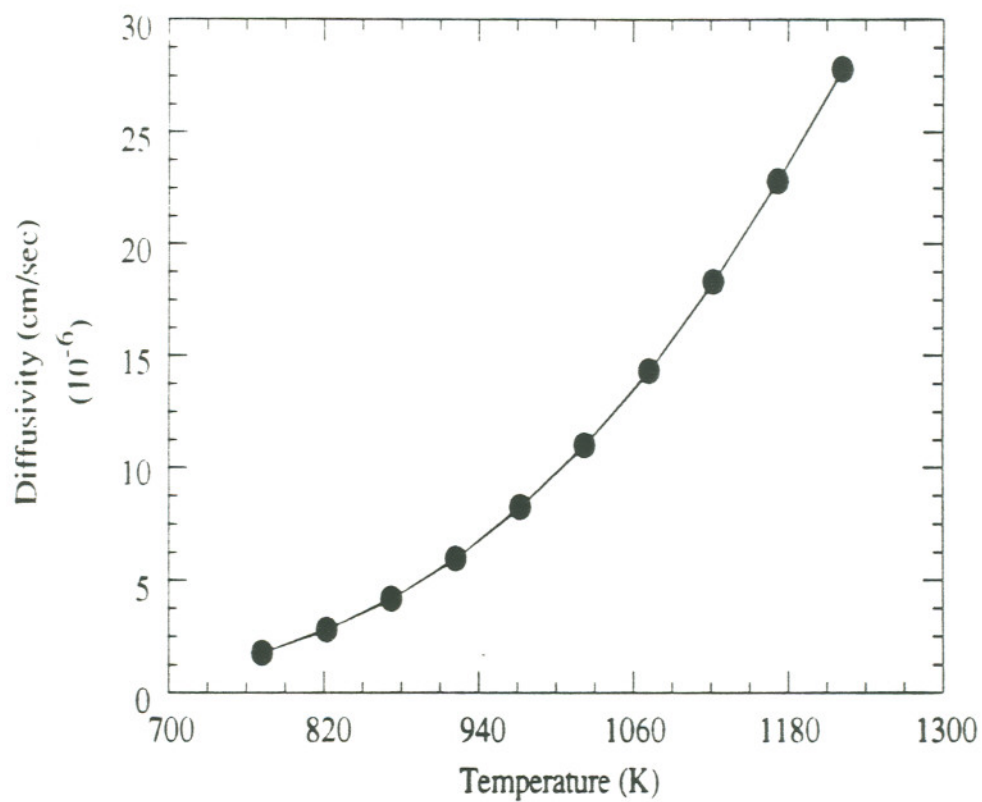


Figure 2. Diffusivity of Oxygen Versus Temperature (K)

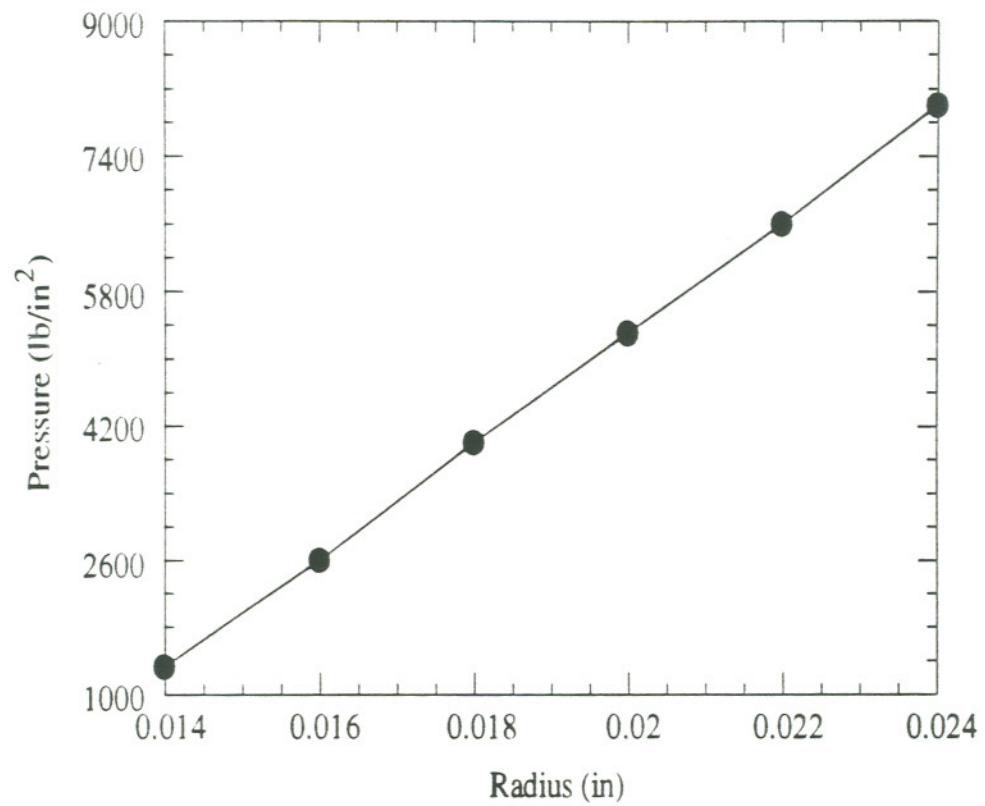


Figure 3. Pressure Profile on the Oxidated Alloy  
Generated by Changing the Silver Sheath  
Thickness

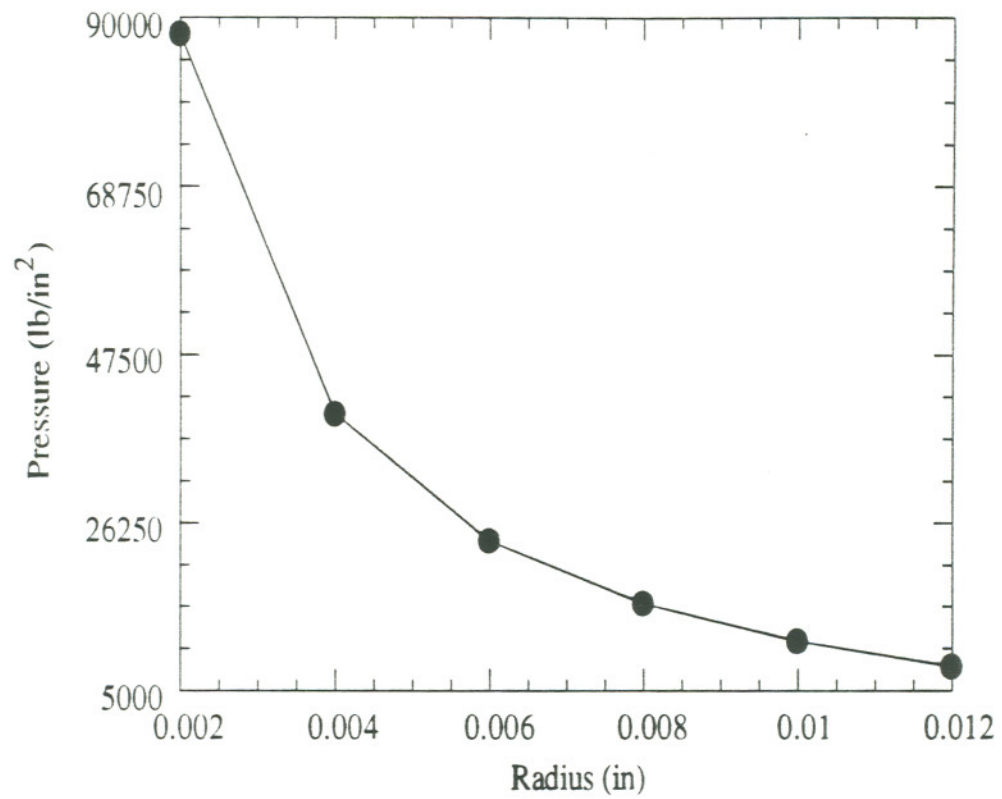


Figure 4. Pressure Profile on the Oxidated Alloy  
Generated by Changing the Deposited Alloy  
Thickness



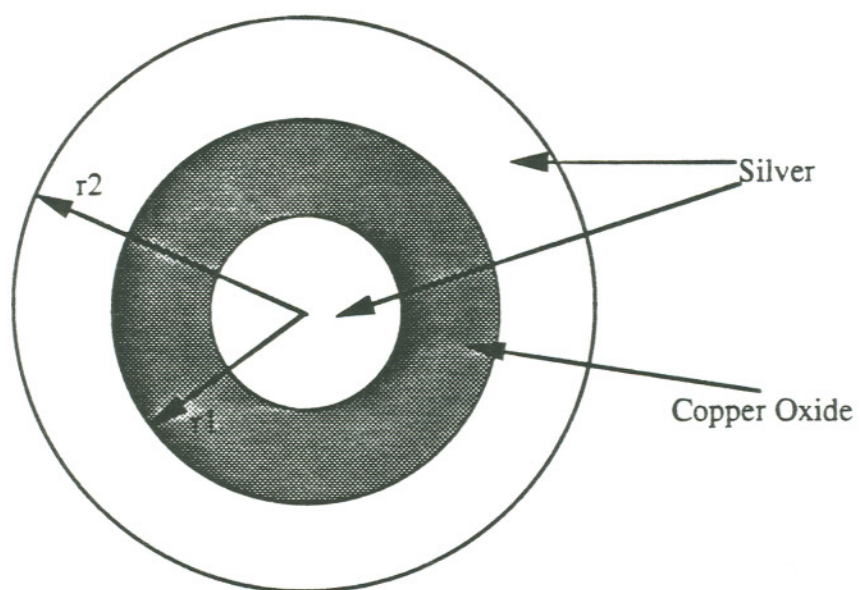


Figure 5. Transverse Section of Expected Wire After the Oxidation Process

## EXPERIMENTAL PROCEDURES

### 5.1 Materials

The following materials were used in the experiments: A silver wire from Aldrich company with a diameter of 0.25 mm and a purity of 99.9%. A copper wire with a diameter of 0.5 mm (commercially supplied).

### 5.2 Solutions

Experiments were conducted in non-aqueous and aqueous solutions. The non-aqueous solution was made of dimethyl sulfoxide (DMSO), with purity of 99.9%, from Sigma-Aldrich inc., which has been used as a solvent for preparing the cupric nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  with purity of 99.5%, from Baker Analyzed, yttrium nitrate,  $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  with purity of 99.9%, from Aldrich Chemical Company, and barium nitrate  $\text{Ba}(\text{NO}_3)_2$  with purity of 99.1%, from Baker Analyzed. Prior to the preparation of the non-aqueous solutions, the DMSO was dried by using an activated alumina, from Scientific Supply Co. which is commonly used as drying agent. The drying

process was performed by shaking the DMSO in the presence of the activated alumina for 12 hours. The solution was then filtered.

Several concentrations of solutions were prepared for each nitrate salt (e.g. cupric nitrate, yttrium nitrate, and barium nitrate). 0.5 M, 0.1 M, and 0.05 M for the cupric nitrate, 1.0 M for yttrium nitrate, and 0.5 M, 1.0 M for barium nitrate.

Three different types of aqueous solutions were prepared using deionized water. First, sodium hydroxide, NaOH with purity of 98.9%, from Baker Analyzed was used. The concentration of the solution was  $10^{-5}$  M with a pH range 9 to 10. Second, 1 M cupric nitrate  $\text{Cu}(\text{NO}_3)_2$ , was prepared. Third, a solution containing a mixture of 50 g of silver chloride, AgCl, with purity 99.5%, from Mallinckrodt Chemical Works, 500 g of Sodium Thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , with purity 97.0%, from EM Science, and 30 g of Potassium Meta-Bisulfite,  $\text{K}_2\text{S}_2\text{O}_5$ , with purity of 96.2%, from Baker Analyzed, g/L for the solution<sup>(24)</sup>.

### **5.3 TECHNICAL TERMS**

#### **5.3.1 Potentiostatic Technique**

This technique applies a constant potential to the metal-solution interface and measures its electrochemical behavior as a function of time. The current resulting from the applied potential is plotted versus time.

#### **5.3.2 Potentiodynamic Technique**

This technique is used to determine the electrochemical behavior of a given metal/solution system. The applied potential versus the logarithm of the measured current is plotted.

#### **5.3.3 Galvanostatic Technique**

This technique applies a constant current to the metal-solution interface and measures its electrochemical behavior as a function of time. The potential resulting from the applied current can be plotted versus time. This type of technique can be applied to electroplating experiments.

#### 5.4 Apparatus

Experiments were conducted in 0.050 l, three-neck flask. Pt wire was used as a counter electrode. As a reference electrode, saturated calomel electrode (SCE) as well as silver-silver nitrate electrode,  $\text{Ag}/\text{AgNO}_3$ , were used. The electrode potential of silver-silver nitrate electrode was 0.1074 V versus SCE. The working electrode was the test material, either silver wire or copper wire with a diameter of 0.25 mm, 0.5 mm respectively, an approximate length of 30 mm for both wires.

Potentiodynamic and potentiostatic experiments were carried out using EG&G PRINCETON Potentiostat/Galvanostat Model 273A, connected to an IBM compatible PC computer. The schematic diagram of the set up is shown in figure (6). During the potentiodynamic experiments the potential was monitored by using HEMICO voltmeter model HDS-90L. The galvanostatic experiment were performed using Potentiostat Model-553. In this technique only two electrodes were used with Pt wire as counter electrode and test specimens as working electrode, figure (7).



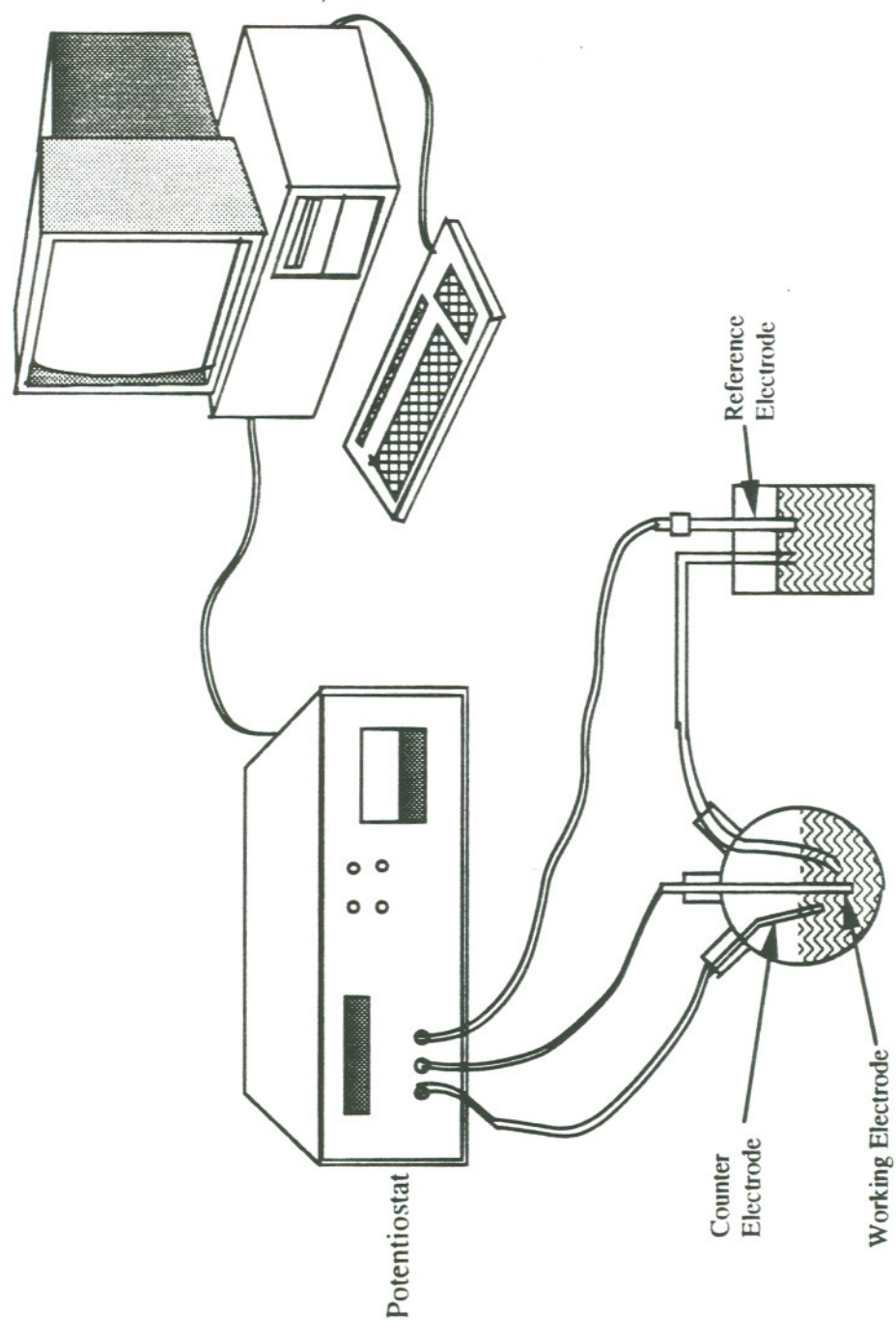


Figure 6. Experimental Set Up



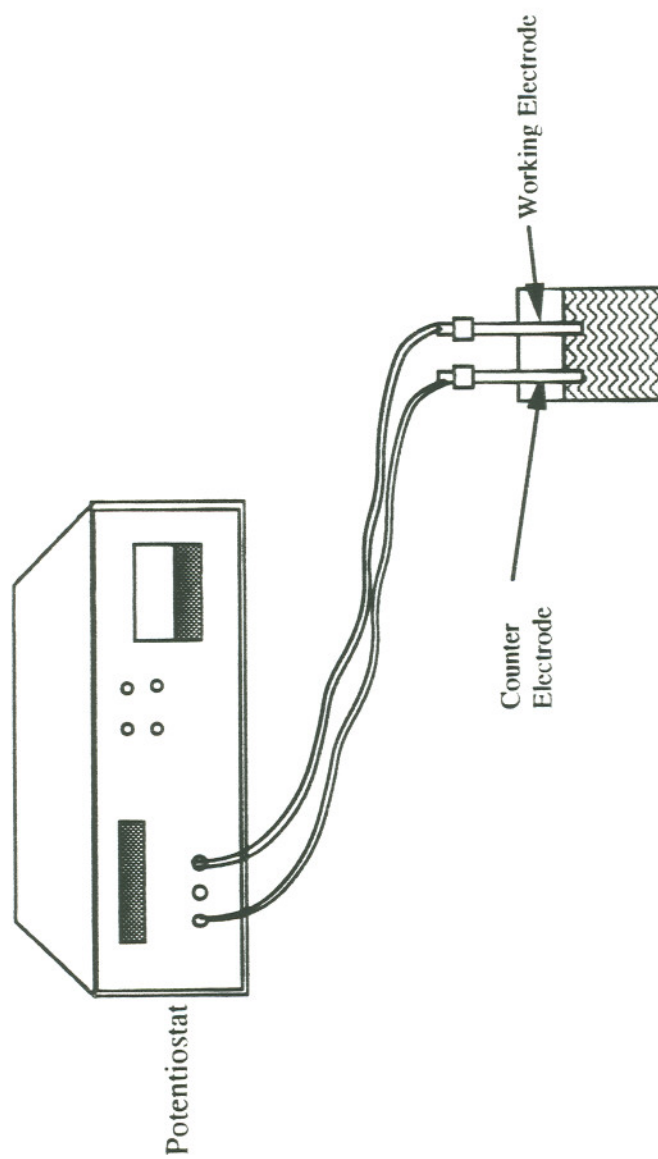


Figure 7. Experimental Set Up

Experiments were performed in the potentiodynamic experiments conducted in non-aqueous solutions (DMSO), the potential was scanned in the cathodic direction from the open circuits potential of substrate at different scan rates. The scan rate for potentiodynamic experiments conducted in cupric nitrate solutions ranged from  $3 \times 10^{-4}$  mV/s to  $1.2 \times 10^{-3}$  mV/s, in yttrium nitrate solutions the scan rate ranged from  $2.0 \times 10^{-4}$  mV/S to  $5.0 \times 10^{-4}$  mV/S, and in barium nitrate solutions the scan rate ranged from  $2 \times 10^{-4}$  mV/s to  $10^{-3}$  mV/s.

In the potentiodynamic experiments conducted in aqueous solutions  $10^{-5}$  M NaOH, the potential was scanned in the anodic direction. The test materials were the silver wire and the copper wire. The initial potential (I.P), was 50 mV more negative than the open circuit potential (O.C) of the test material. The final potential (F.P) was determined by the evolution of oxygen.

Potentiostatic experiments were also conducted in an aqueous and non-aqueous solutions. In aqueous solution  $10^{-5}$  M NaOH, the test materials were silver and copper wires respectively. The constant potentials applied were 0, 50, 100, 200, 1000 mV versus SCE. The specimen was held at a constant potential for 1 hour. In non-aqueous, the potential held constant at -4.8 V versus SCE. The time ranged from 1 hour to 2 hours.

In the galvanostatic experiments two electrodes were used, Pt wire as a counter electrode and the test materials, which was silver wire, as a working electrode. The galvanostatic experiments were performed in  $10^{-5}$  M NaOH. A constant current was set at  $2.0 \text{ A/dm}^2$  for two hours for the deposition of copper  $\text{Cu}^{2+}$  solutions. The current was set at  $1.25 \text{ A/dm}^2$  for 24 hours for the silver deposition  $\text{Ag}^+$  solution.

The oxidation process of the copper under the silver sheath was explored by employing two methods. Namely, electrochemical and thermal. In the electrochemical method, constant potential was at 300 mV and 1000 mV, respectively. The thermal oxidation of copper was performed by holding a specimen at  $600^\circ\text{C}$  in air for 16 hours.

## RESULTS

### 6.1 Deposition stage for copper, barium, and yttrium, using potentiodynamic technique

#### 6.1.1 Copper

Potentiodynamic experiments were carried out in the copper nitrate solutions with the following concentrations: 0.5 M, 0.1 M, and 0.05 M, at the scan rates vary from  $3 \times 10^{-4}$  mV/s to  $1.5 \times 10^{-3}$  mV/s. Figure (8) presents cathodic polarization curves of the silver wire obtained in 0.5 M  $\text{Cu}(\text{NO}_3)_2$  at the scan rate of  $3 \times 10^{-4}$  mV/s. The initial potential, which represents the open circuit potential, was -0.36 V. Two peaks are observed in the polarization curve at -0.3 V and -0.4 V, respectively. The formation of the copper layer started from -0.5 V. Gravimetric measurements of the layer indicate that the weight was 0.1487 g. The calculated thickness of the layer was 0.52 mm. Visual examination of the deposited layer showed that the layer was dark brown to black color, very porous, non-uniform, and did not result in a good attachment to the silver wire. The porosity and the lack of the good attachment to the surface of the silver wire was caused by the high thickness of the deposited layer. In order to reduce the thickness of the deposited layer, the scan rate of the

potentiodynamic experiment was increased and the concentration of the copper nitrate solution was reduced. Figure (9) shows the cathodic polarization curve obtained in 0.1 M  $\text{Cu}(\text{NO}_3)_2$  at the scan rate of  $10^{-3}$  mV/s. There is one peak present at the potential of -0.3 V. As expected, the weight of the layer obtained at a higher scan rate and lower concentration was smaller and equaled to 0.1064 g. The calculated thickness of the deposited layer was 0.41 mm. The visual examination of the layer indicated that the layer was not very well attached to the silver wire. Changing the scan rate did not significantly effect the electrochemical characteristics of the cathodic curves obtained in 0.5 M. Figure (10) shows the polarization curves at different scan rates  $5 \times 10^{-4}$ ,  $8 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $1.5 \times 10^{-3}$ , and  $2 \times 10^{-3}$  mV/s. The weight and thickness of the layers as a function of scan rate are shown in Table (2). The potentiodynamic experiments were also performed in 0.05 M and 0.01 M of  $\text{Cu}(\text{NO}_3)_2$  solutions at the scan rate of  $1.2 \times 10^{-3}$  mV/s. Figure (11) shows the cathodic polarization curve taken in 0.05 M  $\text{Cu}(\text{NO}_3)_2$  at scan rate of  $1.2 \times 10^{-3}$  mV/s. A peak was observed at a potential of -0.4 V similar to the cathodic polarization curve obtained in 0.1 M  $\text{Cu}(\text{NO}_3)_2$ , which is shown in figure (9). The deposited layer of the 0.01 M concentration had a good attachment and a uniform thickness of 0.32 mm. The color of the layer was dark brown to black.



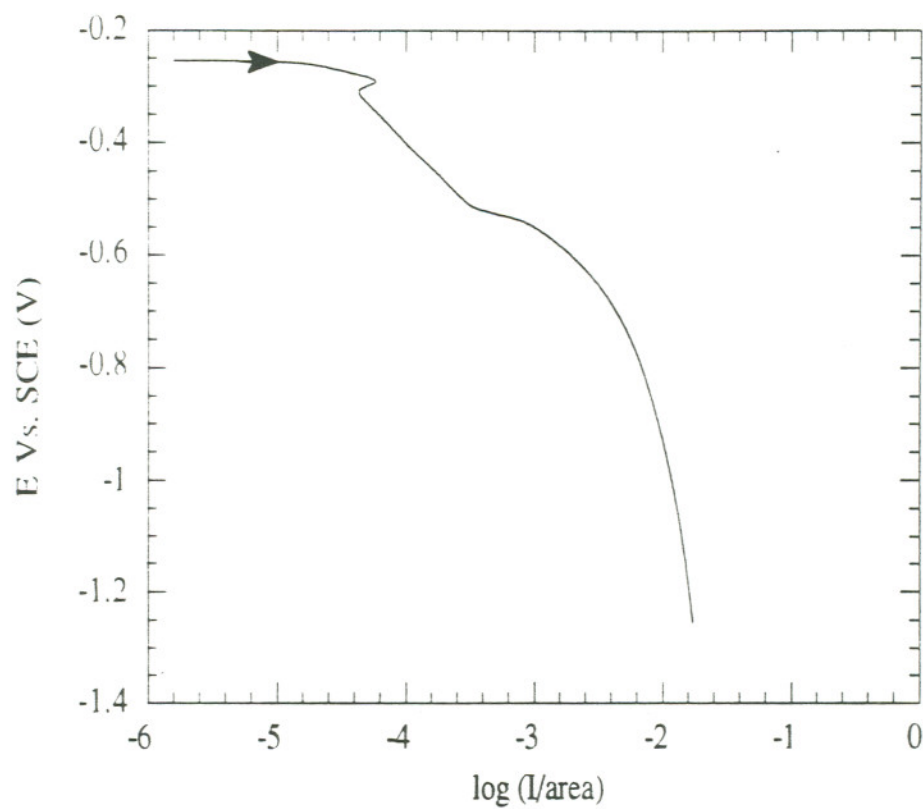


Figure 8. Cathodic Polarization curve for Silver wire in 0.5 M Cupric Nitrate Solution, Scan Rate  $10^{-3}$  mV/s



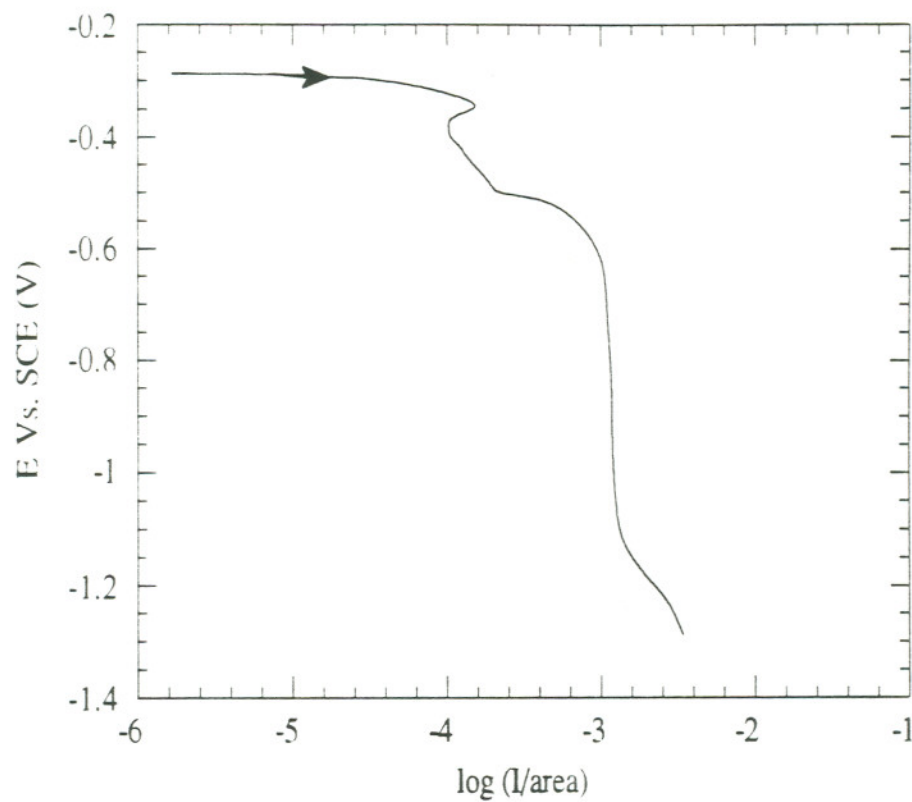


Figure 9. Cathodic Polarization Curve for Silver wire in 0.1 M Cupric Nitrate Solution, Scan Rate  $1.2 \times 10^{-3}$  mV/s

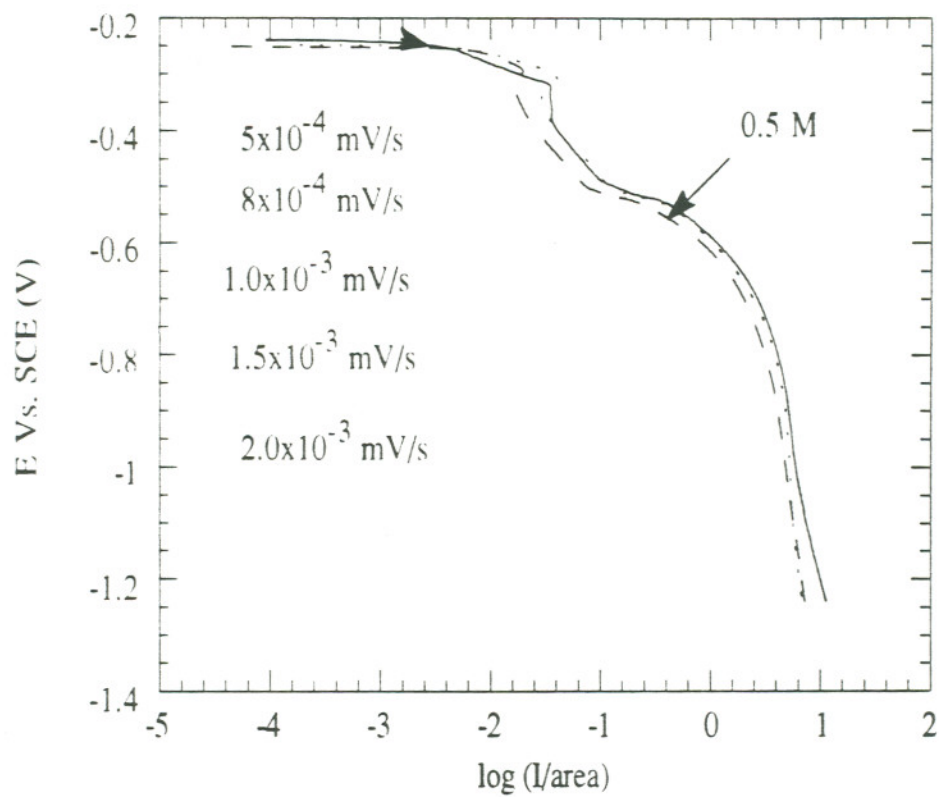


Figure 10. Cathodic Polarization Curves for Silver Wire with the Different Scan Rates and the Same Concentration in Cupric Nitrate Solution

**Table 2. Weight and Thickness as a Function of  
Scan Rate**

Scan Rate (mV/s)	Weight (g)	Thickness (mm)
$5 \times 10^{-4}$	0.1418	51
$8 \times 10^{-4}$	0.1354	48
$1 \times 10^{-3}$	0.1315	47
$1.5 \times 10^{-3}$	0.1286	45
$2 \times 10^{-3}$	0.1253	44

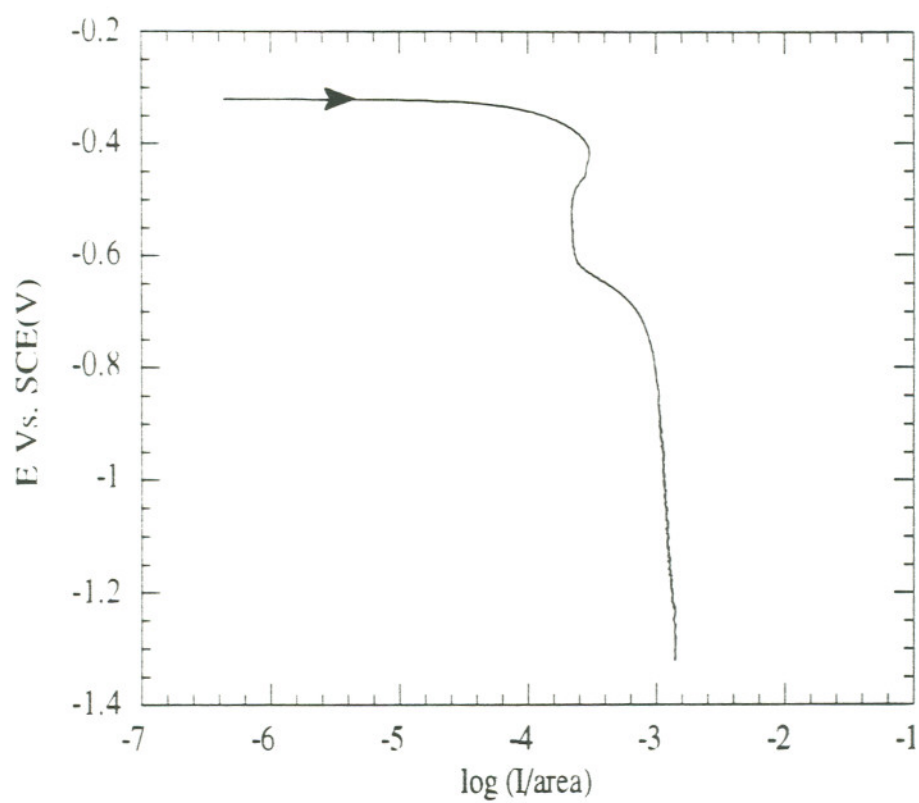


Figure 11. Cathodic Polarization Curve for Silver Wire in 0.05 M Cupric Nitrate Solution, Scan Rate  $1.2 \times 10^{-3}$  mV/s

It was found that changing the concentration of solutions altered the final current, which is shown in figures (12) and (13) respectively. Thicker, less uniform layers obtained in more concentrated solutions.

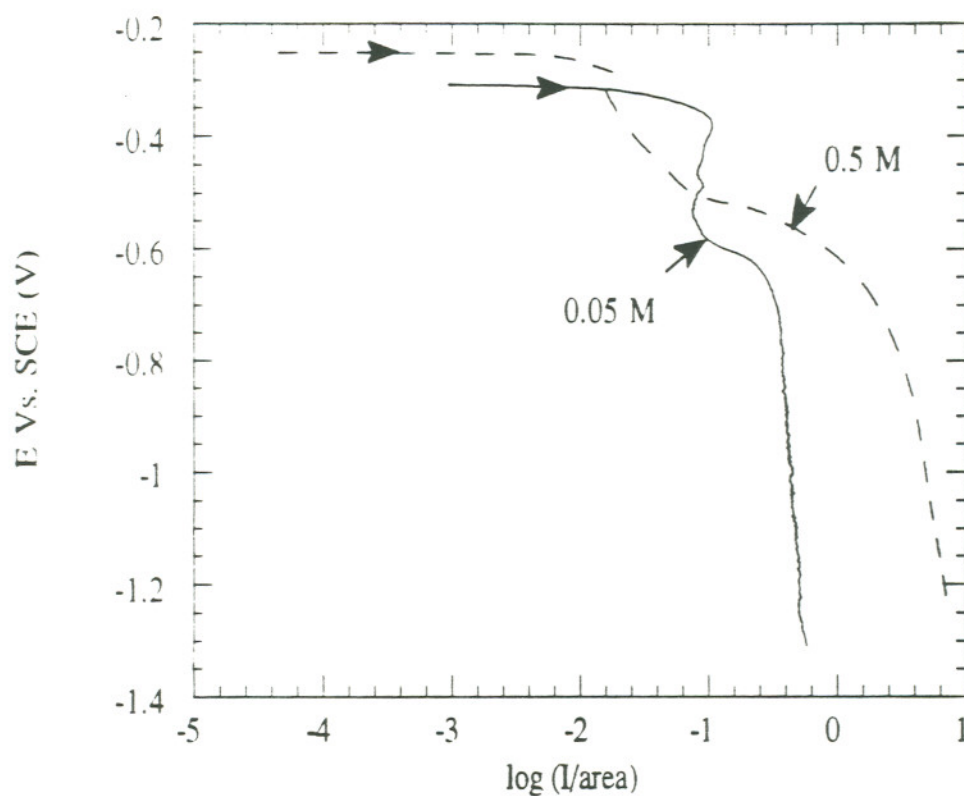


Figure 12. Cathodic Polarization Curve for Silver Wire  
with the Same Scan Rate  $8 \times 10^{-4}$  mV/s  
and Different Concentrations in Cupric  
Nitrate Solution

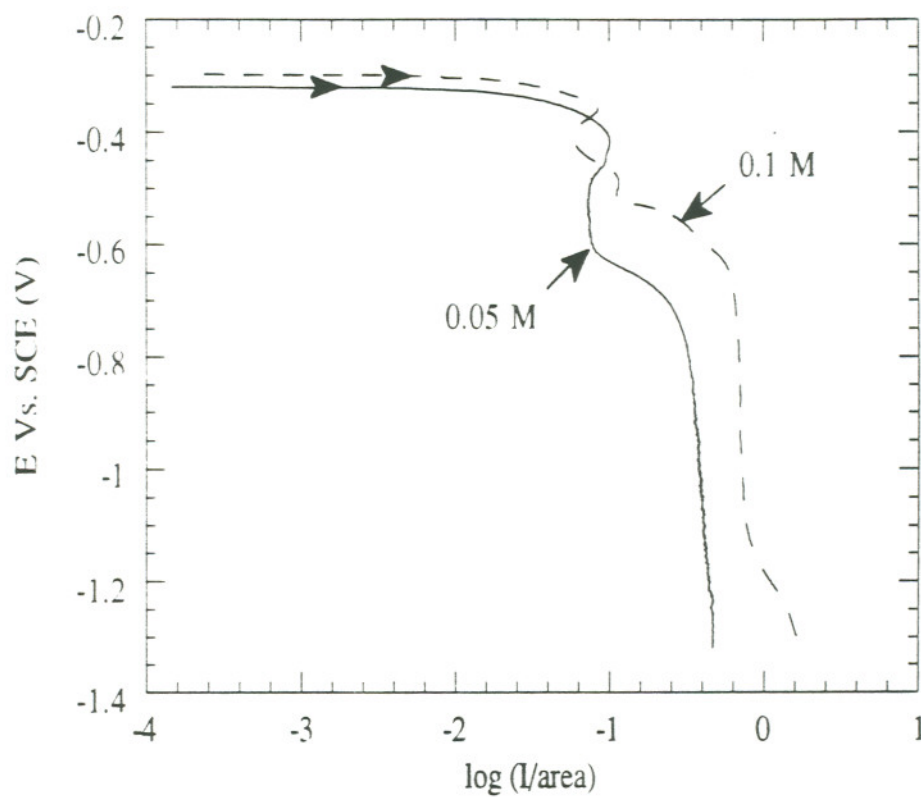


Figure 13. Cathodic Polarization Curve for Silver Wire  
with the Same Scan Rate  $1.2 \times 10^{-3}$  mv/s  
and Different Concentrations in Cupric  
Nitrate Solution



### 6.1.2 Barium

Cathodic polarization curves were performed in 0.5 M and 1.0 M of  $\text{Ba}(\text{NO}_3)_2$  solutions at 25°C. Figure (14) represent the polarization curve obtained in 0.5 M  $\text{Ba}(\text{NO}_3)_2$ . The scan rate was  $2.0 \times 10^{-4}$  mV/s. The initial potential which was the open circuit potential of the silver wire, was -0.77 V. An increase in the current was observed from the initial potential down to -1.0 V. Before the -1.0 V value, a constant current with decreasing potential value was observed down to the final potential, which was -2.2 V. Gravimetric measurement showed no weight gain indicating that no deposited layer was obtained during the experiment. Also, visual examination of silver wire showed no deposited layer; the surface of the silver wire was shiny. By increasing the concentration of the solution from 0.5 M to 1.0 M, the general characteristics of the polarization curve obtained in 1 M  $\text{Ba}(\text{NO}_3)_2$  changed slightly with comparison to the polarization curve obtained in 0.5 M. Figure (15) represents the polarization curve obtained in 1.0 M  $\text{Ba}(\text{NO}_3)_2$ . The values of current increased with decreasing potential from the open circuit potential, which was -0.67 V to approximately -0.9 V. Below this potential, the current is constant to -1.4 V. A peak is observed at -1.5 V. Visual examination showed some deposition with a gray color, which was non-uniformly distributed on the surface of the silver wire. The Average weight of the deposition was  $6.4 \times 10^{-4}$  g.

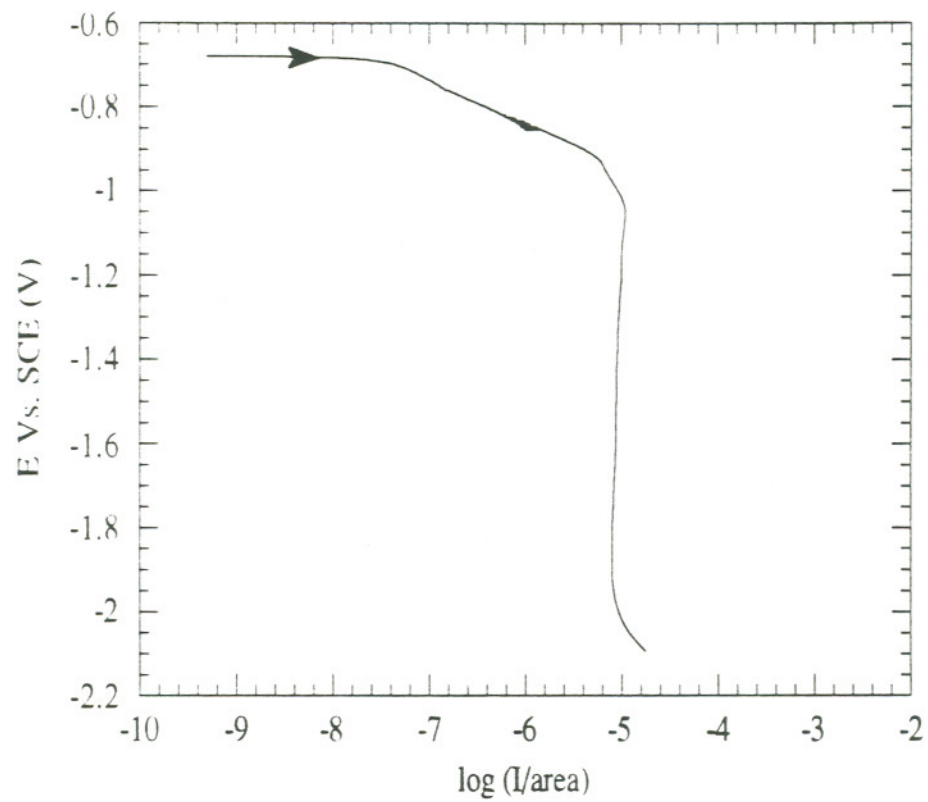


Figure 14. Cathodic Polarization Curve for Silver wire in 0.5 M Barium Nitrate Solution, Scan Rate  $2.0 \times 10^{-4}$  mV/s

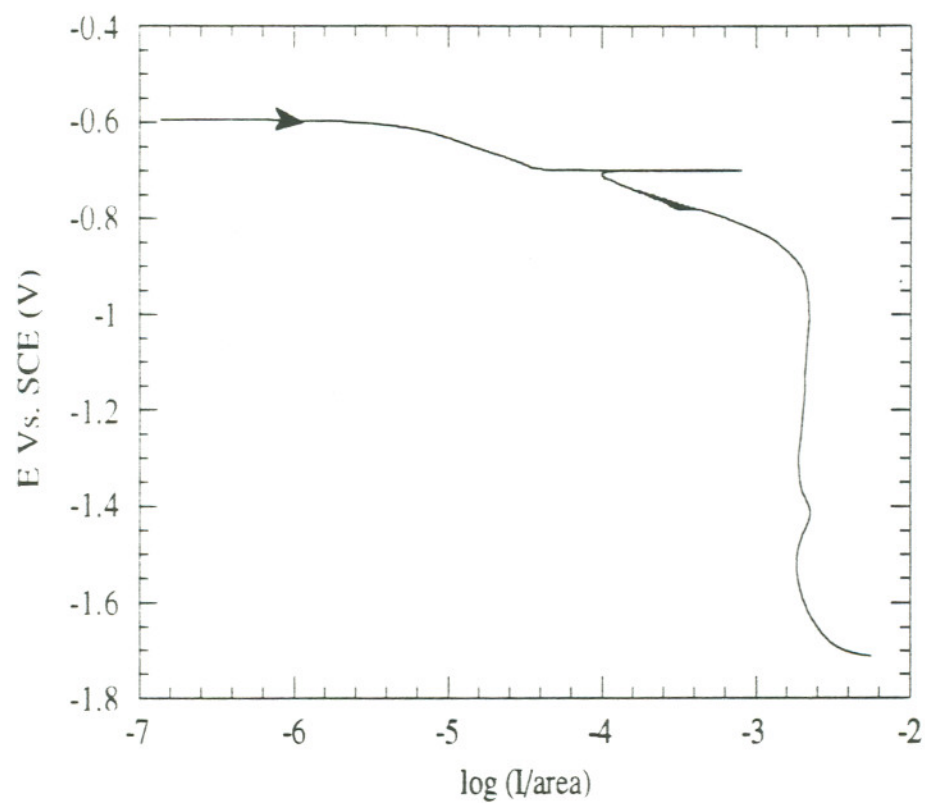


Figure 15. Cathodic Polarization Curve for Silver Wire in 1.0 M Barium Nitrate Solution, Scan Rate  $2.0 \times 10^{-4}$  mV/s

### 6.1.3 Yttrium

The cathodic polarization curve was obtained for the silver wire in 1.0 M  $\text{Y}(\text{NO}_3)_3$ , which is shown in figure (16). The open circuit potential was -0.549 V. An increase in the current with decreasing potential was observed to -0.7 V. Constant current occurs in a range of potentials -0.7 - 1.1 V. A steady increase in the current was observed to the final potential, which was 2.2 V. Visual examination showed that the surface of the silver wire had some deposition. The deposited layer did not cover the entire surface of the silver wire. Gravimetric measurements showed that the weight of the deposited layer was  $1.0 \times 10^{-3} \text{g}$ .

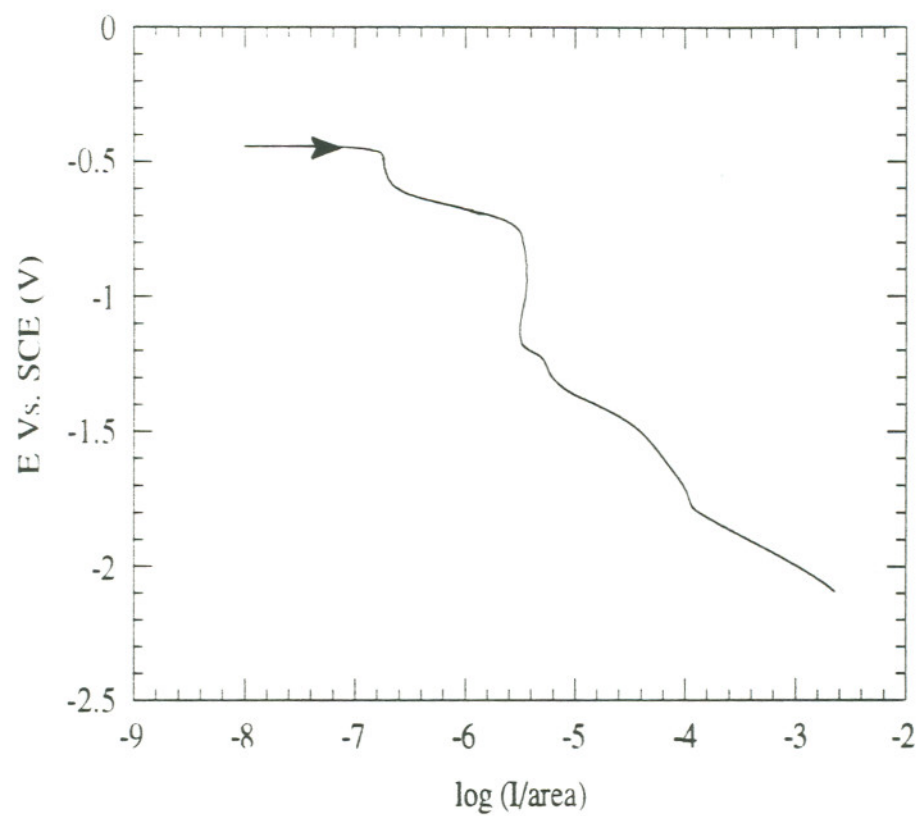


Figure 16. Cathodic Polarization Curve for Silver wire in 1 M Yttrium Nitrate Solution, Scan Rate  $2.0 \times 10^{-4}$  mV/s

## 6.2 Determination of potential values for oxidation of copper

Potentiodynamic experiments were performed on a silver and copper wires in aqueous solution ( $10^{-5}$  M NaOH), in order to determine the potential values at which copper would be oxidized under the silver sheath in potentiostatic experiments. Figure (17), represent the anodic polarization curves of the silver wire. The initial potential was  $5 \times 10^{-2}$  V more negative than the open circuit potential. The scan rate was  $2 \times 10^{-4}$  mV/s. The current decreased from the initial potential to 0.315 V. Then, a high and steady increase in current was observed up to 0.65 V. Above the potential 0.65 V, the current was almost constant to the final potential, which was 1.25 V. During the experiment, a black uniform layer started to form when the potential reached value of 1.1 V. Gravimetric measurements showed that the silver wire had a slight gained weight of  $3.2 \times 10^{-4}$ g. Visual examination showed a uniform black layer with a good attachment the silver wire. The anodic polarization curve of the copper wire in NaOH solution is shown in figure (18). The initial potential was  $5 \times 10^{-2}$  V more negative than the open circuit potential. The scan rate was  $2 \times 10^{-4}$  mV/s. Four stages are presents in the polarization curve. First stage represents the decay of current to -0.1 V. The second stage a very sharp increase to the first peak at 0.2 V. The third stage a steady increase in the current is followed the sharp increase to the second peak at 0.35 V. The fourth stage started from the second peak, the current did not change up to the



final potential, which was 2.0 V. Visual examination showed a dark green to black color layer covering the surface of the copper wire, the layer had good attachment to the wire. Gravimetric measurements showed that the deposited layer weighted  $1.2 \times 10^{-2}$  g. Figure (19) is an overlay graph for figures (17) and (18), the anodic polarization curves of the silver wire and the copper wire. It shows that the open circuit potential for the copper wire, which is -0.042 V, and is far below the open circuit potential for the silver wire, which is 0.315 V. The current for the copper wire is lower than the current for the silver wire up to 0.6 V. Above this value the silver wire indicate a slightly higher current than the copper wire.

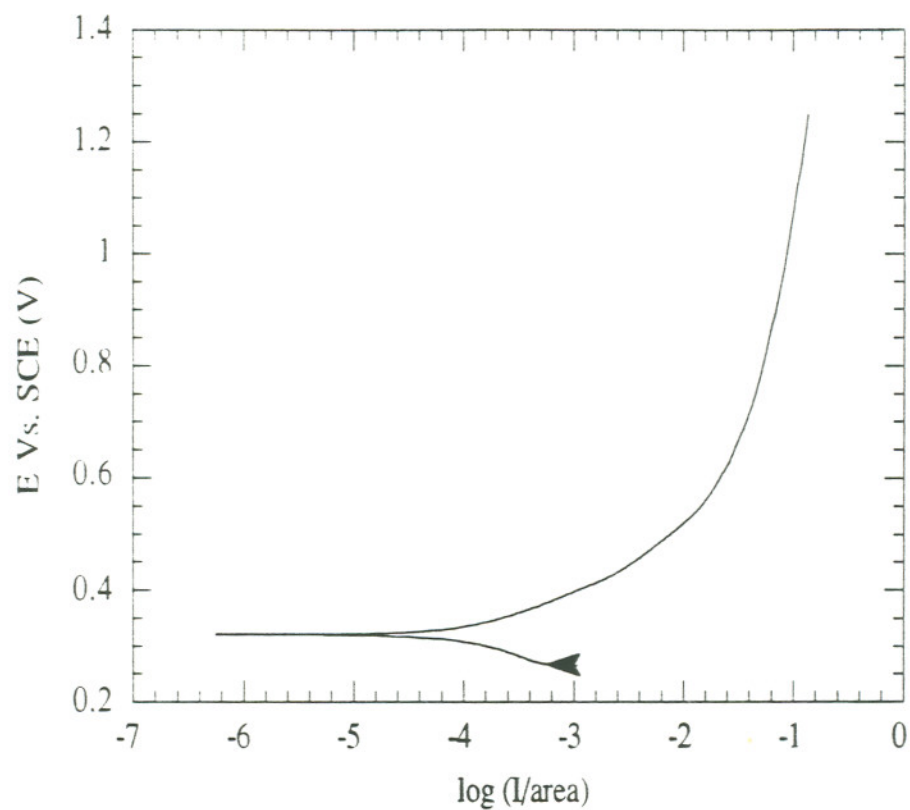


Figure 17. Anodic Polarization Curve for Silver

Wire in  $10^{-5}$  M NaOH Solution,

Scan Rate  $2.0 \times 10^{-4}$  mV/s

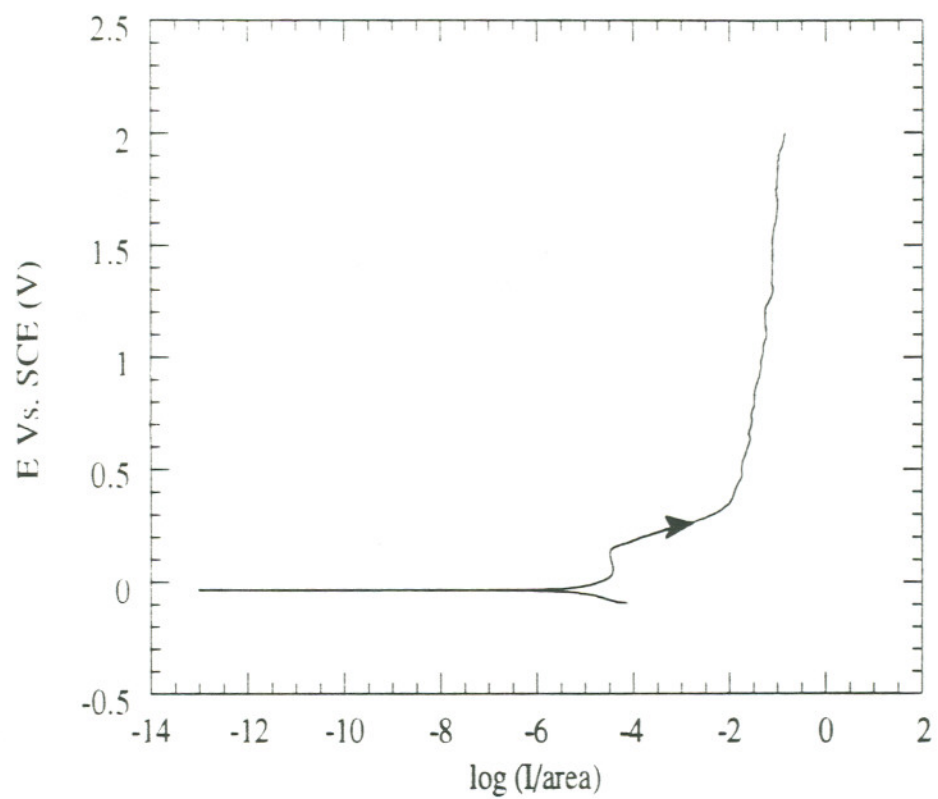


Figure 18. Anodic Polarization Curve for Copper

Wire in  $10^{-5}$  M NaOH Solution,

Scan Rate  $2.0 \times 10^{-4}$  mV/s

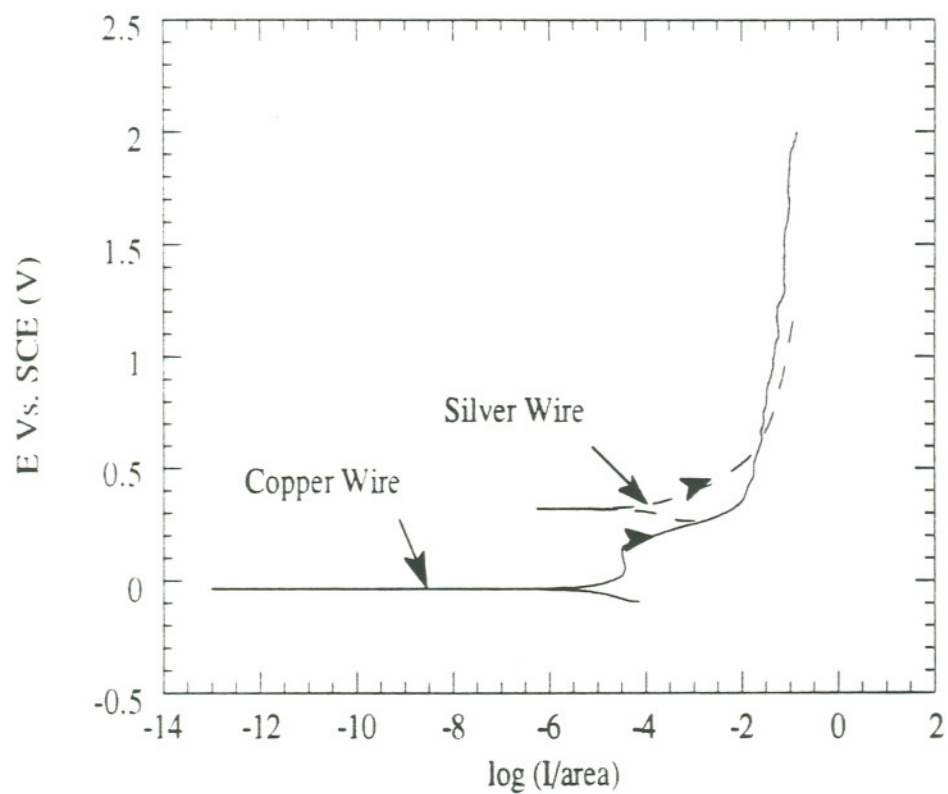


Figure 19. Comparison of Anodic Polarization Curves for  
Copper and Silver Wires in  $10^{-5}$  M NaOH  
solution, Scan Rate  $2.0 \times 10^{-4}$  mV/s

### 6.3 Potentiostatic experiments

According to the results of the polarization curves obtained for the silver and copper wires, in  $10^{-5}$  M NaOH solution, potentiostatic experiments were conducted to observe the electrochemical behavior of the two metals at very specific potentials. Five different potentials were chosen namely: 0.0, 50, 100, 200, and 1000 mV, and the experimental time was set for one hour. Figures (20, a, b, c, d, e), shows the behavior of the cathodic current as a function of time (I-t) under potentiostatic condition for the silver wire in  $10^{-5}$  M NaOH solution. Figure (20,a), represent the (I-t) curve obtained at 0.0 mV. An immediate increase in the cathodic current density was observed from  $67.0 \mu\text{A}/\text{cm}^2$  to  $6.0 \mu\text{A}/\text{cm}^2$  during the first five minutes, followed by a constant current of  $6.0 \mu\text{A}/\text{cm}^2$  to the end of the one hour experiment. Visual results showed no change on the surface of the silver wire. Also, gravimetric measurements indicated no change in the weight of the wire. Figures (20, b, c, d) present the (I-t) curves of the silver wire obtained at the applied potentials of 50, 100, 200 mV respectively. The results of the experiments were the same as in the experiment conducted at 0.0 mV. There was no change either to the surface or to the weight of the silver wire. However, Figure (20, e), represents the experiment with the applied potential of 1000 mV. The current density had a sharp increase into the first peak at  $0.156 \text{ A}/\text{cm}^2$ , then a steady but slow increase to the second peak at 0.17

A/cm<sup>2</sup>, followed by a sharp drop to the end of the one hour experiment. Visual observation showed a dark gray uniform layer, indicating sufficient attachment to the substrate surface. Gravimetric measurement for the silver wire showed 10<sup>-3</sup>g weight gain.



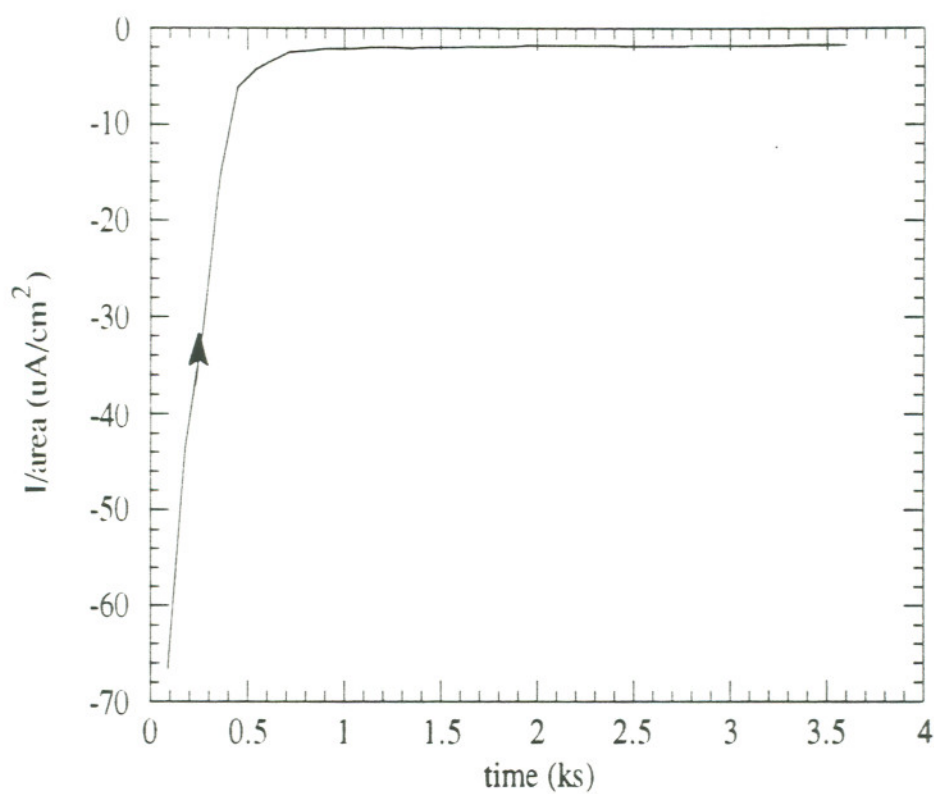


Figure 20.a. Current Under Potentiostatic Conditions, 0.0 mV  
for Silver Wire in  $10^{-5}$  M NaOH Solution

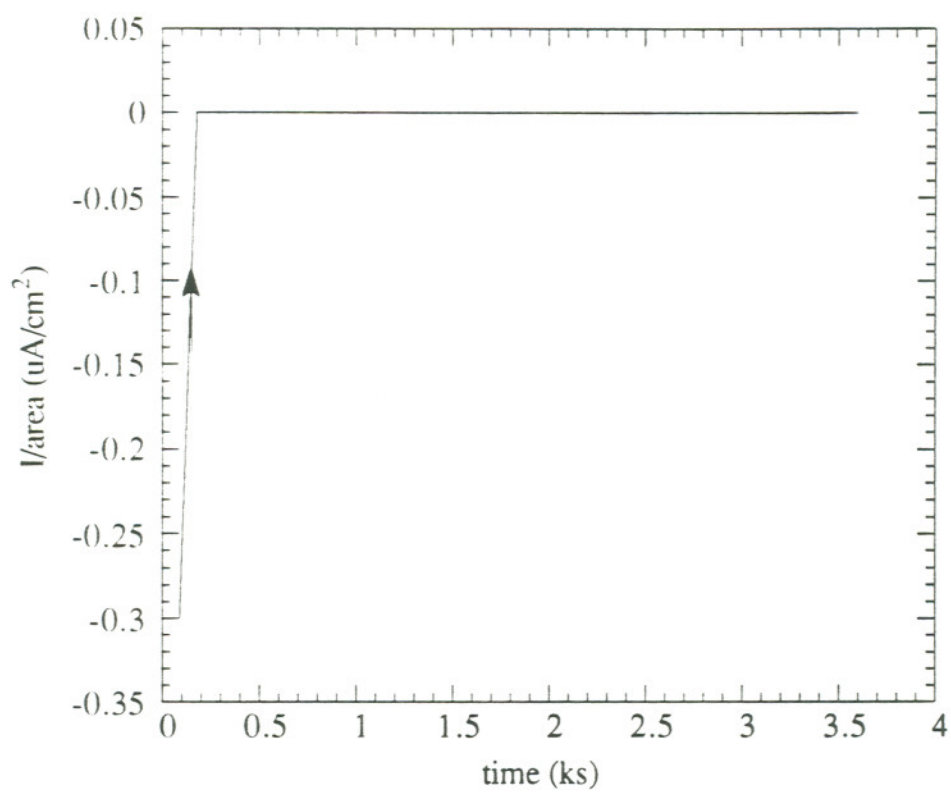


Figure 20.b. Current Under Potentiostatic Condition, 50 mV  
for Silver Wire in  $10^{-5}$  M NaOH Solution

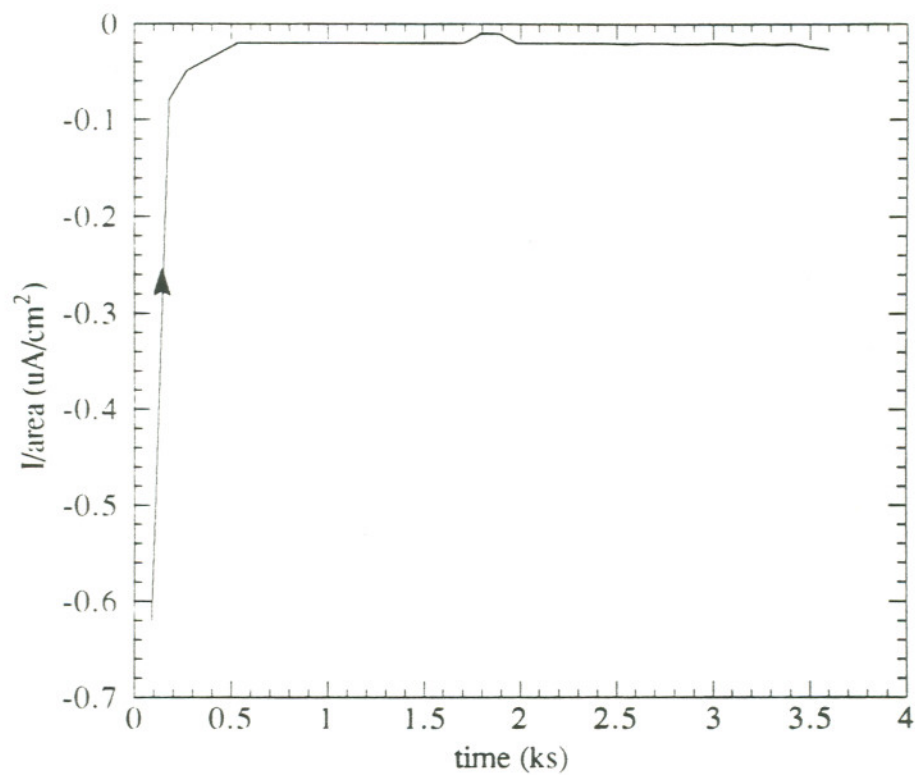


Figure 20.c. Current Under Potentiostatic Condition, 100 mV  
for Silver Wire in  $10^{-5}$  M NaOH Solution

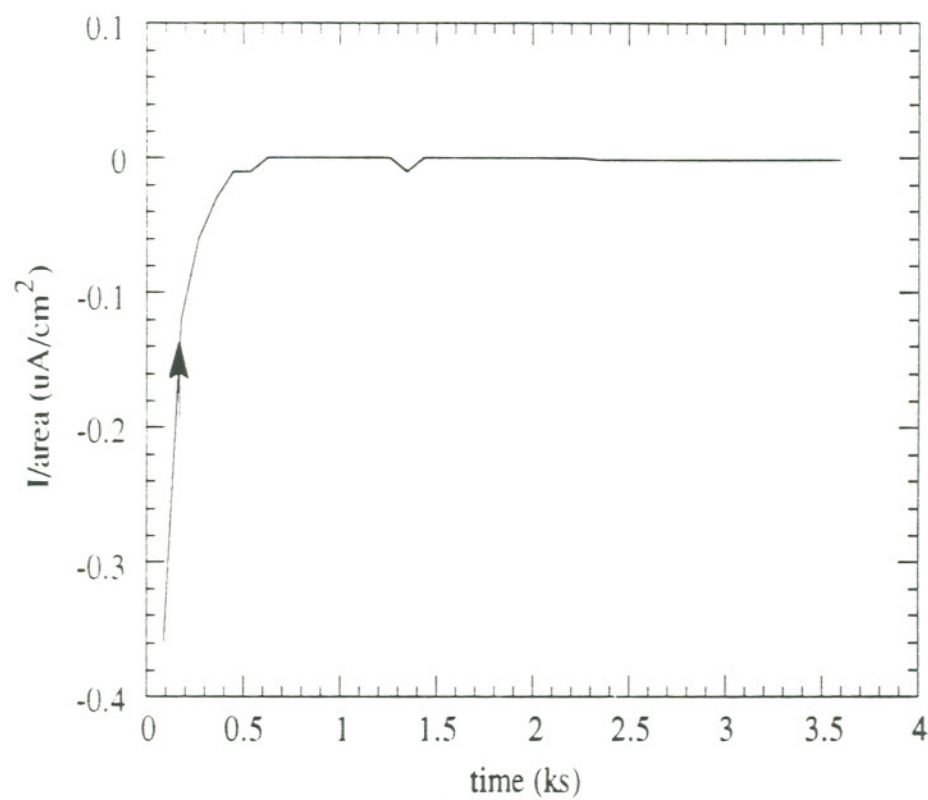


Figure 20.d. Current Under Potentiostatic Condition,  
200 mV for Silver Wire in  $10^{-5}$  M NaOH  
Solution

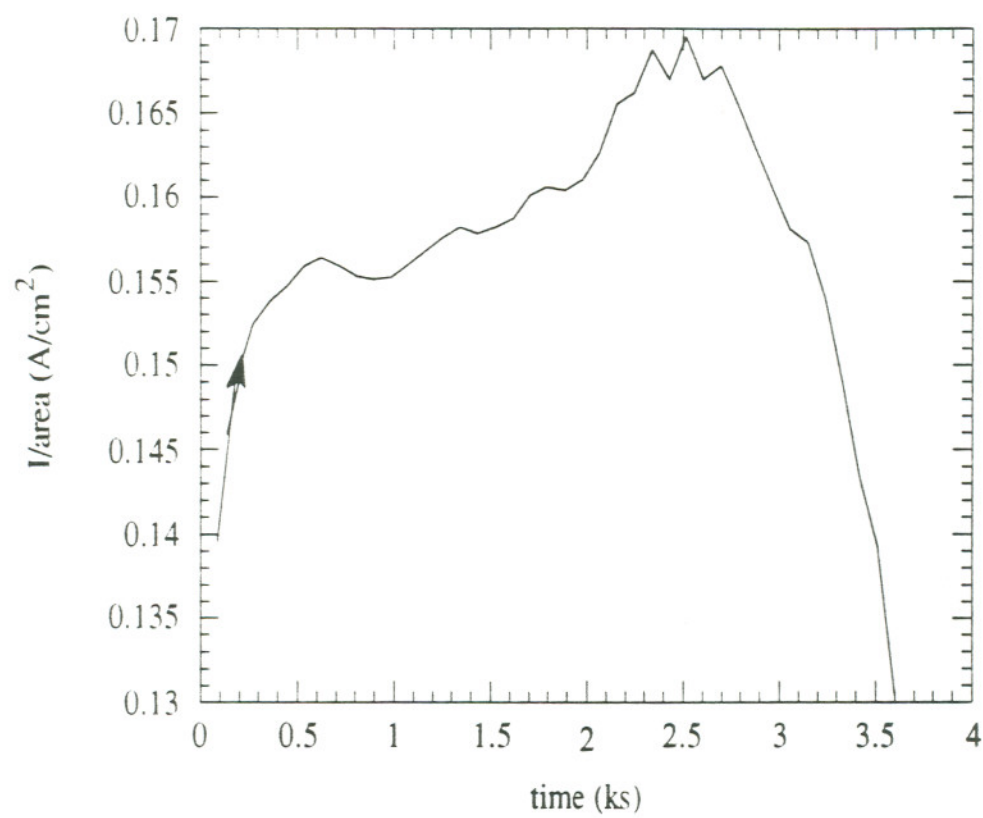


Figure 20.e. Current Under Potentiostatic Condition,  
1000 mV for Silver Wire in  $10^{-5}$  M NaOH  
Solution

In the case of the copper wire, Figures (21, a, b, c) represent the (I-t) curves at the applied potentials of 0.0, 50, and 100 mV, respectively. In general, the current in those experiments indicated in the same trend. First, an immediate decrease from the initial current to a first peak, then a constant current to the end of the experiment. Visual examination did not show any change in the appearance of the surface of the wire before and after the experiment. Also, gravimetric measurements showed no change in the weight of the copper wire. Figure (21, d), shows the (I-t) curve has different characteristic of current versus time is observed at applied potential of 200 mV. In this experiment, current increases with increasing time up to  $4.5 \text{ A/cm}^2$ . Then, a constant current is observed until 3 Ks. After that time current increases to reach a final value of  $5.2 \text{ uA/cm}^2$ . Visual results showed some spots on the surface of the copper wire. Gravimetric measurements showed a gain in weight equal to  $5.3 \times 10^{-3} \text{ g}$ . Figure (21, e) represent the (I-t) curve obtained at applied potential of 1000 mV. The current was not very stable. Visual examination showed a very thick and porous dark greenish to black color layer. Gravimetric examination showed a 0.1g gain in weight.



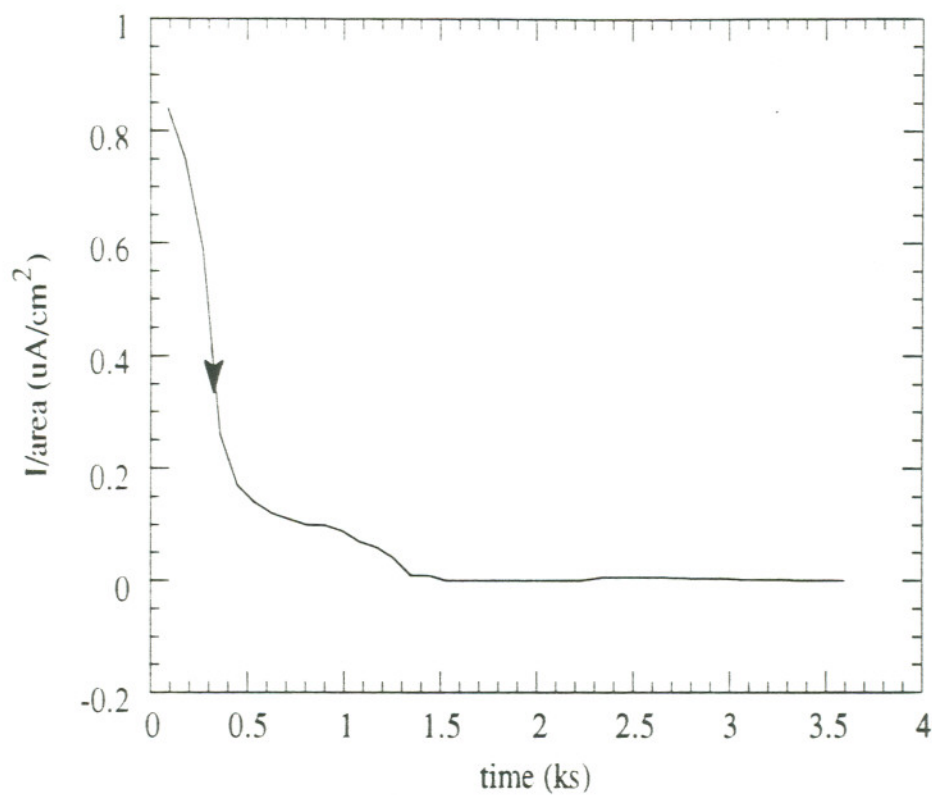


Figure 21.a. Current Under Potentiostatic Condition,  
0.0 mV for Copper Wire in  $10^{-5}$  M NaOH  
Solution

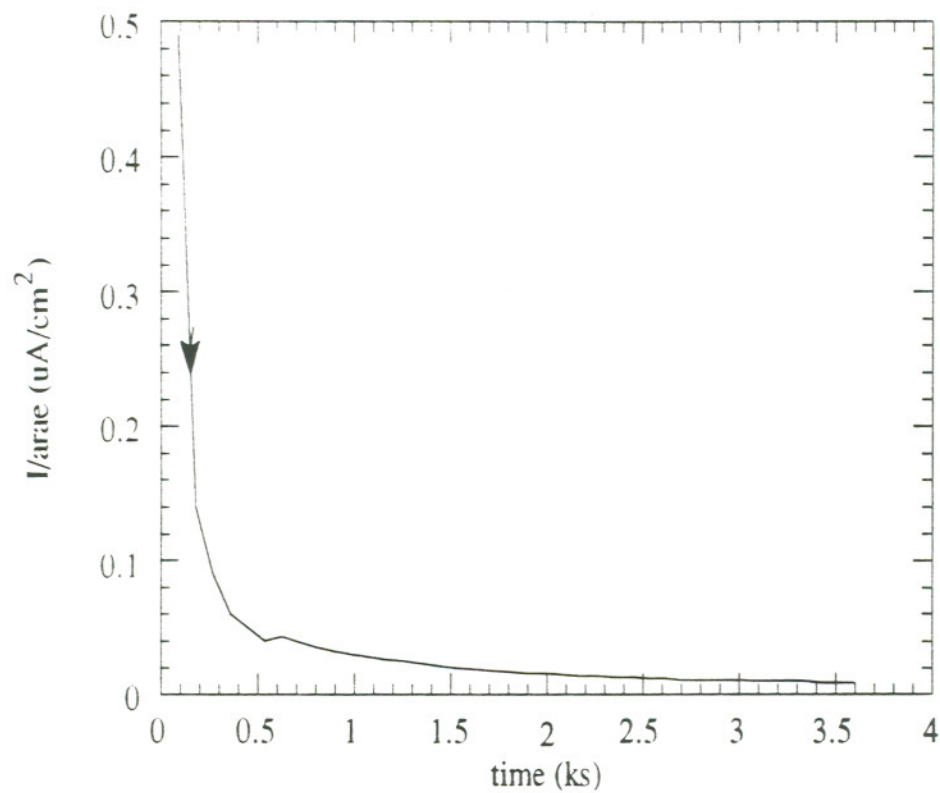


Figure 21.b. Current Under Potentiostatic Condition,  
50 mV for Copper Wire in  $10^{-5}$  M NaOH  
Solution

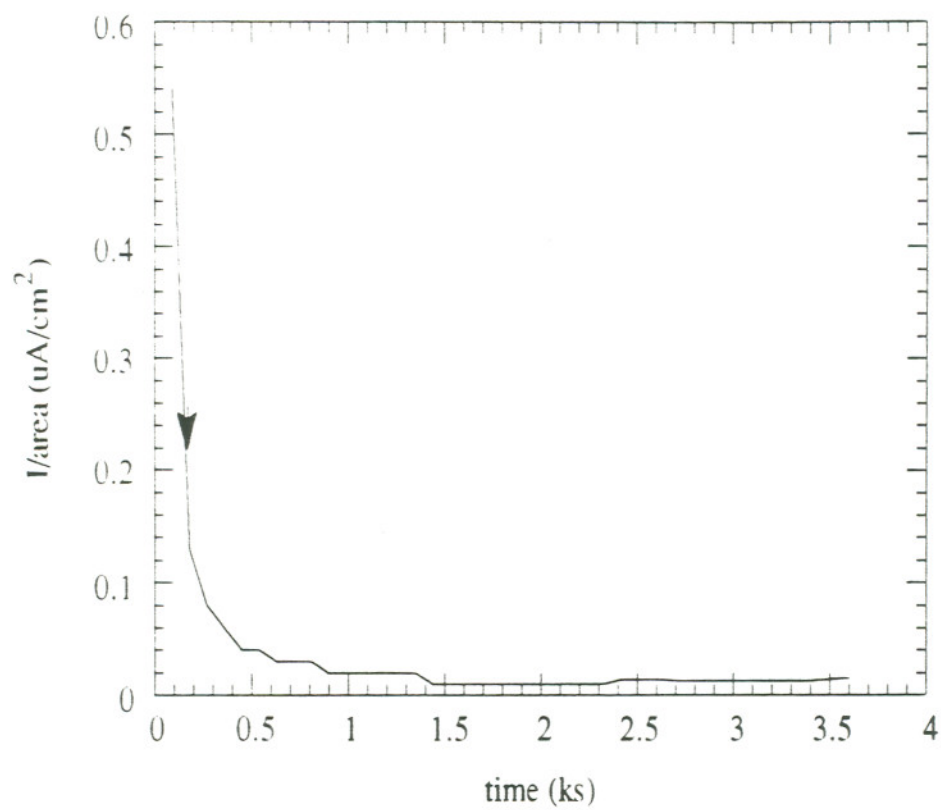


Figure 21.c. Current Under Potentiostatic Condition,  
100 mV for Copper Wire in  $10^{-5}$  M NaOH  
Solution

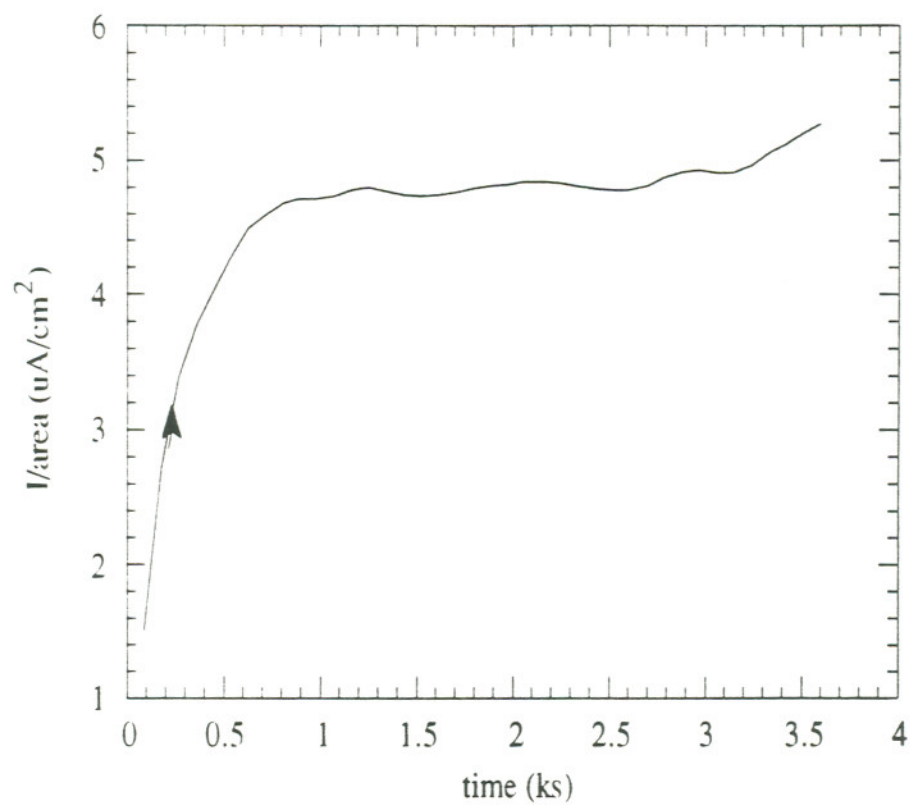


Figure 21.d. Current Under Potentiostatic Condition,  
200 mV for Copper Wire in  $10^{-5}$  M NaOH  
Solution

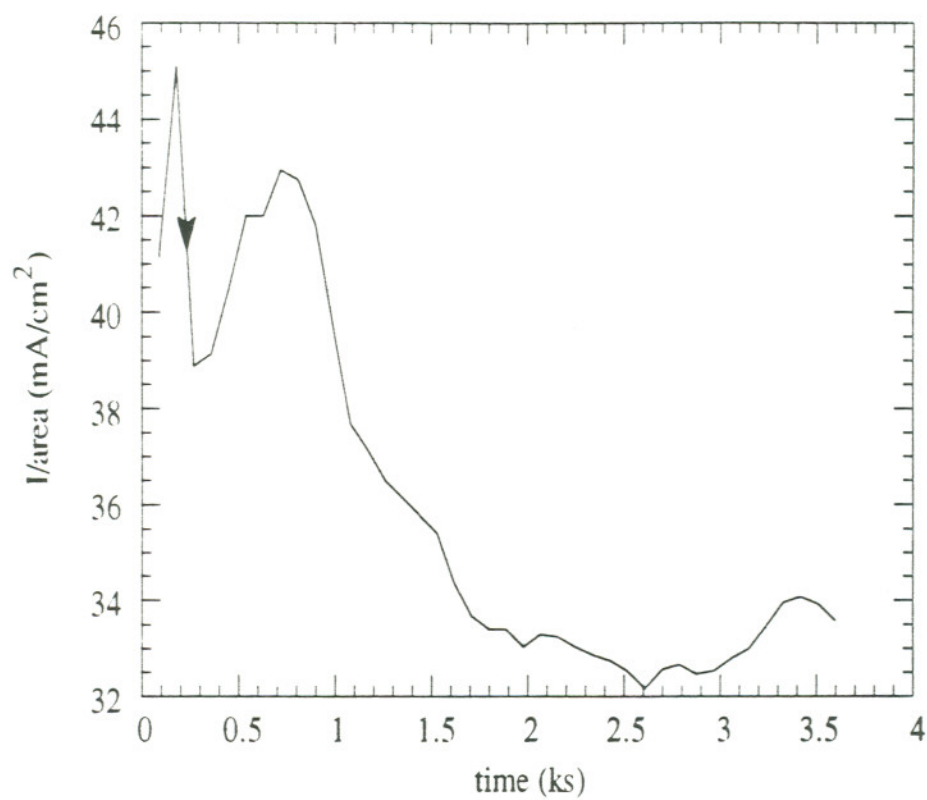


Figure 21.e. Current Under Potentiostatic Condition,  
1000 mV for Copper Wire in  $10^{-5}$  M  
NaOH Solution

#### 6.4 Galvanostatic experiments (deposition process)

Galvanostatic experiments were performed using two electrodes; the counter electrode and the working electrode. The counter electrode was a platinum rod and the working electrode was a silver wire. Galvanostatic experiments where a deposition process took place, consisted of two parts. The first part of the experiment was conducted to deposit a copper layer on the surface of the working electrode (Ag) using 1.0 M cupric nitrate  $\text{Cu}(\text{NO}_3)_2$  solution. The constant applied current was set at  $-2.0 \text{ A/dm}^2$ . The time for the deposition process was set for two hours. Visual examination showed that a deposited layer had a shiny copper color with a good attachment to the silver wire. The layer weighted  $3 \times 10^{-2} \text{ g}$  and had a thickness of 0.22 mm. The second part of the experiment was conducted to deposit a silver sheath on top of the deposited copper layer. The solution for the silver deposition was a mixture of  $\text{AgCl}$  50;  $\text{Na}_2\text{S}_2\text{O}_3$  500; and  $\text{K}_2\text{S}_2\text{O}_5$  30 g/L. The constant applied current was set at  $-1.25 \text{ A/dm}^2$ . The time for the deposition process was set for 12 hrs. Visual observations of the experiment showed a presence of a light gray color layer with a good attachment to the wire. The thickness of the layer was 0.15 mm. Gravimetric measurement showed that the silver layer weighted  $3.5 \times 10^{-2} \text{ g}$ . The final product was a silver wire covered with copper layer, and a silver sheath covering the entire copper



layer. A cross section of the final product is shown in Figure (22). The next step was to oxidize the copper layer under the silver sheath.

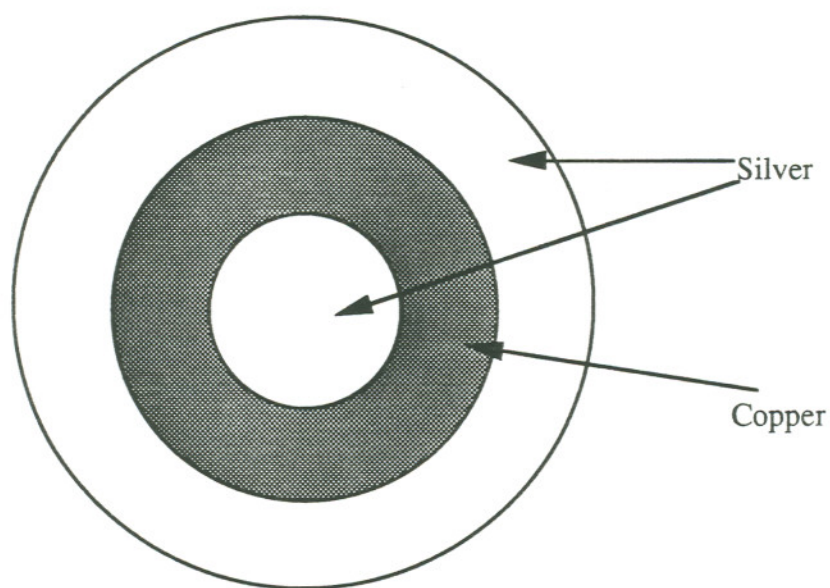


Figure 22. Transverse Section of the Wire Before the Oxidation Process

### 6.5 Oxidation process of copper under the silver sheath

Two different techniques were used for the oxidation process, namely: Electrochemical process and Thermal process.

First, electrochemical oxidation process was carried out using the potentiostatic technique. Two potentials were applied, 300 mV and 1000 mV. The experiments were conducted in aqueous solution of  $10^{-5}$  M NaOH for two hours. Figure (23) represent the (I-t) curve for the experiment with the applied potential of 300 mV. An immediate decrease in the current occurred in the first five minutes, followed by a steady current to the end of the experiment. Visual examination did not show any change in the surface of the sample. Also, when a cross section of the sample was examined under the optical microscope, the results showed no sign of oxide film on the copper layer. Figure (24) represents the (I-t) curve for the experiment with the applied potential of 1000 mV. A high increase in the current was observed up to the first hour, followed by a smaller but steady increase to the end of the experiment. Visual examination showed a heavily corroded and damaged silver layer.

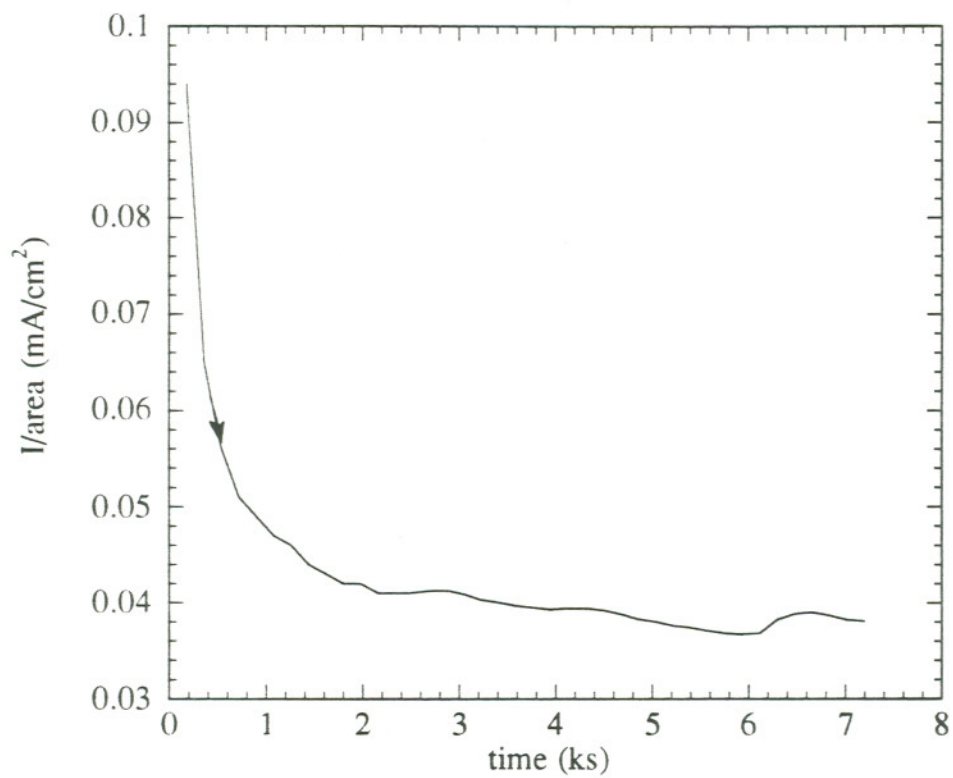


Figure 23. Current Under Potentiostatic Condition, 300 mV for the Silver Wire, Plated With Copper Layer Under the Silver Sheath in  $10^{-5}$  M NaOH Solution

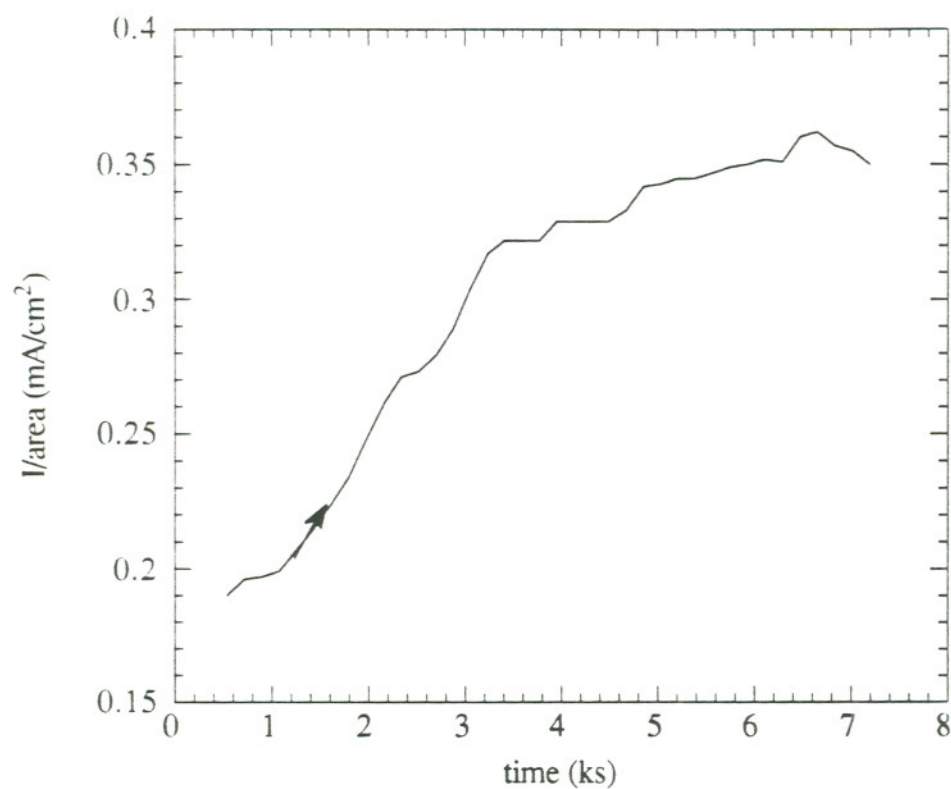
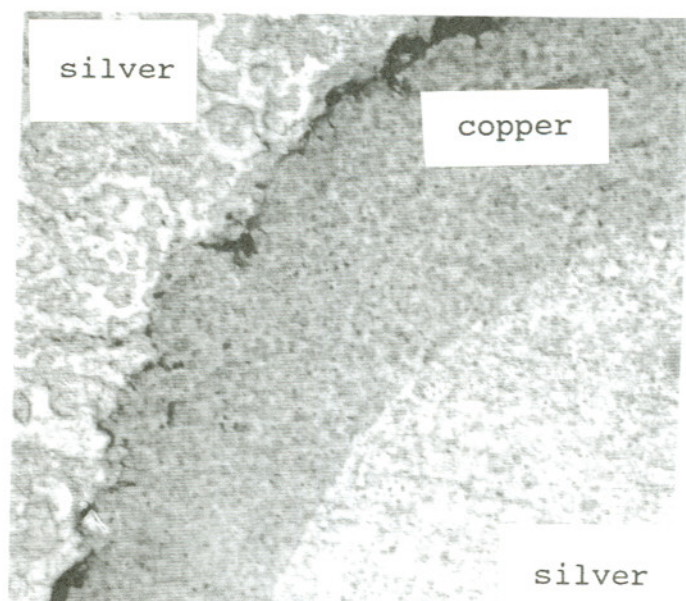


Figure 24. Current Under Potentiostatic Condition, 1000 mV for the Silver Wire, Plated with copper layer under the Silver Sheath in  $10^{-5}$  M NaOH Solution

Second, thermal oxidation process was conducted at high temperature of 600° C. The samples obtained after the deposition process were atmospherically heat treated for 16 hours at 600° C. After the heat treatment, a cross section of the sample was observed under an optical microscope. Figure (25,a), shows an optical micrograph of the specimen before the thermal oxidation process. All the three layers, silver sheath, copper layer, and the silver wire have a good shiny color. However, figure (25,b), shows an optical micrograph of the specimen with a black color on the copper layer, while the silver wire is in the center and the silver sheath on top of the copper layer are very shiny.



(a)



(b)

Figure 25. (a) An optical micrograph of the specimen before oxidation

(b) An optical micrograph of the specimen after oxidation



## DISCUSSION

According to figure (1,e), using the Nernst equation to calculate potentials versus ions concentration in aqueous solution and applying potentiodynamic technique, copper ions are the first to be reduced and deposited, and barium ions are the last to be deposited. In other words barium ions are the most difficult to be reduced and copper ions are the easiest to be reduced. This phenomena is related to the standard reduction-oxidation, table (3), the higher the standard potential of the metal the easier to be reduce. There are some difficulties in reducing metal ions with low potential in aqueous solution, specially if the metal potential is lower than the hydrogen potential, as is yttrium and barium. The hydrogen ions will be reduced first, which cause the evolution of hydrogen, preventing the deposition process from completion. Figure (26), shows Pourbaix diagram for the thermodynamic stability of water, at low potential, below line (a) hydrogen evolution will take place in the electrochemical reaction. However using a non-aqueous solution as the DMSO should eliminate the problem of the hydrogen evolution.

Table 3. ELECTROCHEMICAL SERIES

Electrode Reaction	Stnd. Potential (V)
$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	0.337
$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0.000
$\text{Y}^{3+} + 3\text{e}^- = \text{Y}$	-2.372
$\text{Ba}^{2+} + 2\text{e}^- = \text{Ba}$	-2.912

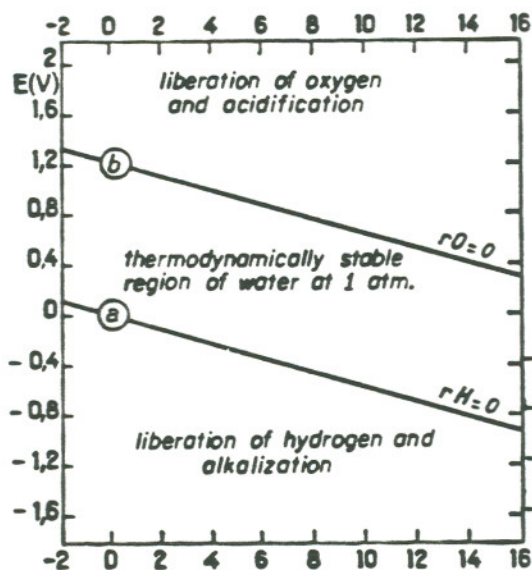


Figure 26. Pourbiax diagram for the stability of water

Although the deposition process for  $\text{Cu}^{2+}$  faced no problems, the deposition of  $\text{Y}^{3+}$  and  $\text{Ba}^{2+}$  had difficulties due to the hydrogen evolution, even though the DMSO is a non-aqueous solution and should not cause any problems with the hydrogen evolution. Unfortunately, the humidity and moisture from the atmosphere contributed to the contamination of the DMSO. Drying the DMSO using activated alumina did help solve the problem, but not eliminate it. The experiment was run for 1 hr to 2 hrs, which is enough time for the DMSO to be contaminated with moisture. However, a light deposition for yttrium and barium was observed.

Changing the concentration of the ion solution had a major role on the deposited layer. It has been found that increasing the concentration of the salts, caused a higher deposition rate.

Potentiodynamic experiments for copper and silver were conducted to observe the electrochemical behavior of the two metals. Figure (19) shows that the open circuit potential for copper  $-0.042$  V is lower than the open circuit potential for silver  $0.315$  V. This difference in potential indicates that copper can be oxidized before silver. The region between the copper open circuit potential and the silver open potential can have two interpretations. 1. There is an anodic region related to the copper metal and a cathodic region related to the silver metal. This suggest that, in

the potentiostatic experiments applying potentials from this specific region should not oxidize the silver wire. However, the same applied potential should oxidize the copper wire. From this prospective, potentiostatic experiments were conducted for the silver and copper wires using the following values of potentials (0.0, 50, 100, 200, 1000 mV). It was not surprising that the surface of the silver wire did not change its properties at 0.0, 50, 100, and 200 mV. This happened because the applied potentials fell in the cathodic region which was below the open circuit potential of silver. In the case of copper the 0.0, 50, 100 mV potentials had no effect on the wire, due to the active dissolution of copper, even though they fall in the anodic region. Increasing the potential to 200 mV resulted in oxidation of the surface of the copper wire. Applying the potential at 1000 mV, to the silver wire and the copper wire caused the formation of oxide films on both wires. The silver wire showed a presence of black layer where the copper wire showed a presence of a dark greenish to black layer.

### 7.1 Deposition process for Cu and Ag

Galvanostatic experiments were conducted to deposit copper from 1 M cupric nitrate  $\text{Cu}(\text{NO}_3)_2$  solution, and silver from a mixture of 50 g of silver chloride  $\text{AgCl}$ , 500 g of Sodium Thiosulfate  $\text{Na}_2\text{S}_2\text{O}_3$ , and 30 g of Potassium Meta-Bisulfate  $\text{K}_2\text{S}_2\text{O}_5$ .



using a two electrode system. This method was used for metal plating because of its simplicity, since the deposition rate is not a major factor. Yet, it provides an excellent outcome. The deposition process for copper on the silver wire, and the deposition of silver on top of the copper layer, resulted in high quality layers, as expected.

## 7.2 Oxidation process

Copper was chosen to be the candidate for the oxidation process under the silver sheath, because it's most difficult to be oxidized with comparison to yttrium and barium. The reason is that  $\text{Cu}/\text{Cu}^{2+}$  has higher standard potential than  $\text{Y}/\text{Y}^{3+}$  and  $\text{Ba}/\text{Ba}^{2+}$  at any ion concentration, which is shown in Figure (1,e). Two different techniques were used for the oxidation process of copper beneath the silver sheath. The electrochemical process was a candidate for a low temperature oxidation method. Two potentials were applied, 300 mV and 1000 mV, in the potentiostatic experiments. Those two potentials were chosen because of the results obtained in the potentiodynamic experiments, Figure (19), indicate that the oxidation process of copper under the silver sheath applying a potential of 300 mV should occur. However, the copper layer did not show any sign of oxidation after the experiment. This is due to the silver sheath, which played a role in reducing the hydrogen ions, since the applied potential is more negative than the open circuit potential of silver,

Figure (17). This reduction process caused the evolution of hydrogen, which prevented the oxidation process from completion. Yet the results of the 1000 mV applied potential experiment agreed with what was expected. The silver sheath and the copper layer were damaged due to the high applied potential, which fall in the anodic region for both metals.

Another approach was undertaken to oxidize copper under the silver sheath by applying high temperature annealing. It has been indicated that oxygen has the ability to penetrate solid silver under high temperature. According to the results, it is possible to oxidize copper under the silver sheath without oxidizing or damaging the silver sheath. The results showed that the color of the copper layer after the thermal oxidation is black, which was different from the color before the oxidation process. Moreover, the silver wire as a substrate and the sheath were not affected by the thermal oxidation process.



## CONCLUSIONS

- 1- Electrodeposition of copper, barium, and yttrium in non-aqueous solution by potentiodynamic technique:

The deposition process of copper yielded a better result than barium and yttrium. This is due to the atmospheric moisture effect, which was a major factor in preventing the complete deposition of barium and yttrium.

- 2- Potentiodynamic experiments for silver and copper wires:

Potentiodynamic experiments showed that copper wire could be oxidized before silver wire in aqueous solutions.

- 3- Galvanostatic experiments:

The deposition of copper on a 0.25 mm diameter silver wire and the deposition of the silver sheath using the galvanostatic technique produced a good outcome.

4- Potentiostatic experiments:

The wire obtained from the galvanostatic experiments was subjected to a constant potential in aqueous solution using the potentiostatic technique. This technique was implemented to oxidize the copper layer under the silver sheath, utilizing the results obtained from the potentiodynamic experiments for silver and copper wires. However, evolution of hydrogen was a major factor in preventing the copper layer under the silver sheath from being oxidized. To avoid hydrogen evolution, the applied potential was increased above the open circuit potential of the silver wire. This resulted in damaging the silver sheath.

5- Oxidation by thermal process produced a good result in oxidizing the copper layer under the silver sheath. No oxidation or damage to the silver sheath or the silver wire substrate was evident.

6- The silver sheath is an excellent protection from weathering and corrosion of the deposited alloy, especially for superconducting oxides, which are easily effected by the environment.

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The author will use his knowledge to help bring a better future for Kuwait and for the whole world.