

METALS AS ANODES  
IN  
NON-AQUEOUS MEDIA

by  
CARL WALTER NELSON

*at the*  
*2 three o'clock*  
*Jan. 1953*

SUBMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF  
BACHELOR OF SCIENCE  
at the  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
(1953)

Signature of Author.....  
May 25, 1953

Signature of Professor  
in Charge of Research.....  
*[Handwritten signature]*

Signature of Head of Department.....

TABLE OF CONTENTS

	Page
I. Acknowledgement . . . . .	1
II. Abstract . . . . .	2
III. Introduction . . . . .	3
IV. Experimental Work and Discussion of Results	
1. Copper as Anode in Non-Aqueous Solutions . .	5
a. The Preparation of a Copper Deriva- tive of Formamide $\text{HCONH}_2\text{-Cu (HNOCH)}_2$ . .	5
b. The Preparation of Tetraformamide Copper (II) Bromide $\text{Cu (HCONH}_2)_4 \text{Br}_2$ . .	7
2. Uranium as Anode in Non-Aqueous Solutions . .	10
3. Molybdenum and Tungsten as Anodes in Non-Aqueous Solutions . . . . .	12
4. Niobium and Tantalum as Anodes in Non-Aqueous Solutions . . . . .	14
5. Aluminum as Anode in Non-Aqueous Solutions . .	17
6. Nickel as Anode in Non-Aqueous Solutions . .	18
V. Suggestions for Further Work . . . . .	19
VI. Bibliography . . . . .	20

I

ACKNOWLEDGEMENT

My sincere thanks are due to my Thesis Supervisor, Professor R. C. Young, for his constant advice and encouragement during the course of the Research.

## II

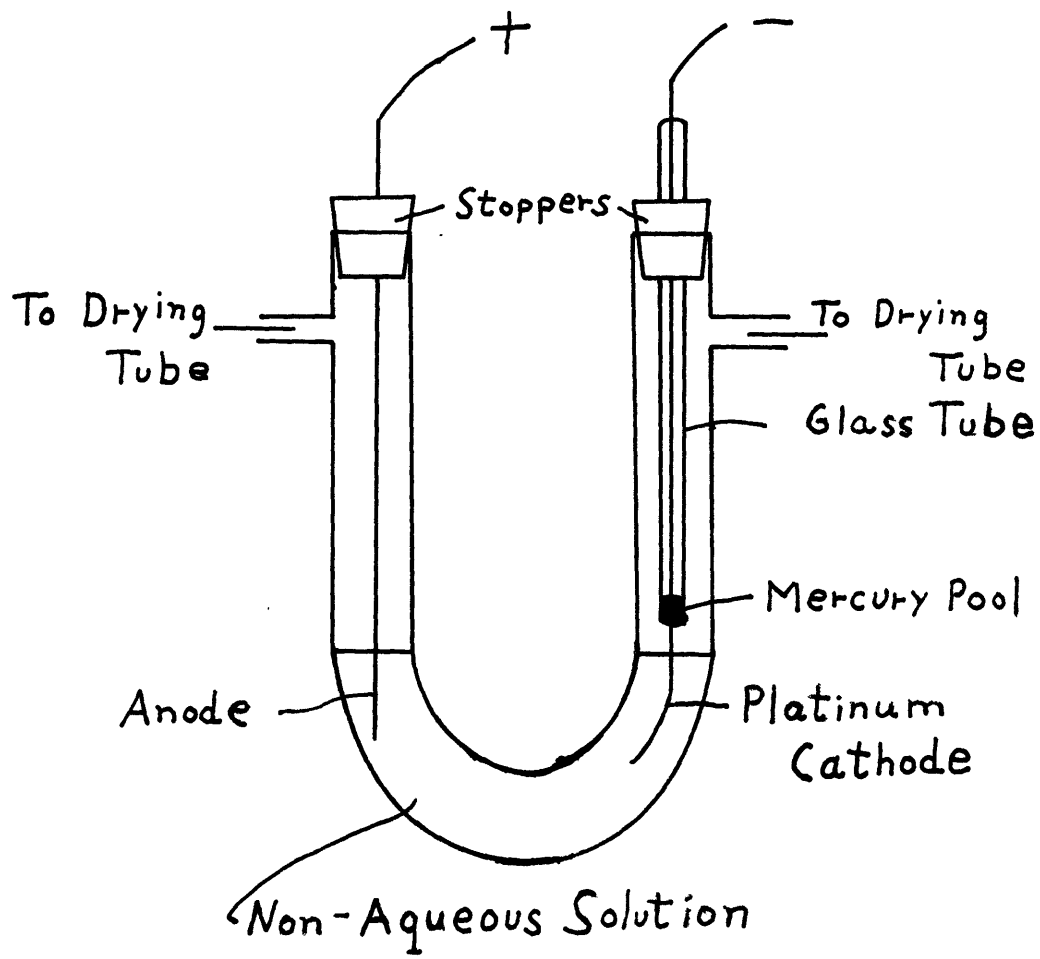
### ABSTRACT

The experimental work described in this thesis consists of the preparation of a copper derivative of formamide and a cupric formamide complex, tetraformamide copper (II) bromide; and the investigation of the metals aluminum, niobium, tantalum, molybdenum, tungsten, uranium, nickel, and copper as anodes in non-aqueous media. The non-aqueous media employed were 100% ethyl alcohol, anhydrous methyl alcohol, ethylene diamine, formamide, and N,N-dimethyl formamide. These organic solvents were chosen because of their relatively high dielectric constants, and, hence, their ability to dissolve ionic compounds to yield conducting solutions.

### III

#### INTRODUCTION

The objective of the work in this thesis was to prepared compounds of metals in their lower oxidation states by the anodic oxidation of the metals in non-aqueous media. It was thought that by this method a lower valence metal compound that is unstable in aqueous solution may be prepared. This was suggested by the evidence of the existence of unipositive aluminum by the anodic oxidation of the metal in anhydrous acetic acid solutions given by A. W. Davidson and F. Jirik.<sup>1</sup> J. Kleinberg<sup>2</sup> has suggested this method as a possible means of obtaining lower valence metal compounds. In the experimental work that follows there is evidence that uranium in the tripositive state may have been prepared by the anodic oxidation of the metal.



## IV

### EXPERIMENTAL WORK AND DISCUSSION OF RESULTS

#### 1. Copper as Anode in Non-Aqueous Solutions

##### a. The Preparation of a Copper Derivative of Formamide

Copper wire was used as the anode and platinum wire as the cathode in formamide,  $\text{HCONH}_2$ . A diagram of the apparatus used showing the arrangement of the electrodes in the U-tube is shown on the preceding page. In order to prevent the thermal decomposition of the formamide by the  $I^2R$  heating of the formamide during the course of the electrolysis, the formamide was cooled by placing the U-tube in a beaker of ice water. A potential of 80 volts D.C. was applied across the electrodes and a current of 0.10 ampere was observed on the ammeter.

Immediately at the anode a white insoluble substance was formed and at the cathode hydrogen gas was liberated. After a few seconds the white insoluble substance surrounding the anode acquired a bluish appearance. By a half minute it had dissolved in the formamide and the formamide had become blue throughout. Then bright copper was deposited on the cathode. The copper that deposited on further electrolysis was spongy and non-adherent.

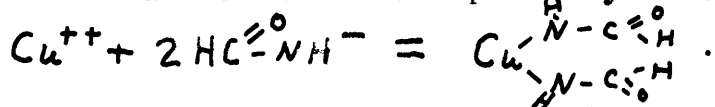
The electrolysis was stopped, the copper deposit was removed, and the blue formamide was placed in a stoppered test tube in a Dewar flask packed with ice. Two weeks later nothing had crystallized out. Thereupon, the blue formamide was diluted with an equal volume of alcohol and cooled again. Several days later blue crystals were seen on the walls of the test tube. Thirty mg. of blue crystals were obtained from 20 cc. of blue formamide. The crystals were washed with alcohol, pumped dry, and analyzed for copper.

	<u>Calculated for HCONH<sub>2</sub> · Cu (HCONH)<sub>2</sub></u>	<u>Found</u>
Cu	32.3%	32.5, 32.2%
M.W.	196.7	195.7, 196.0

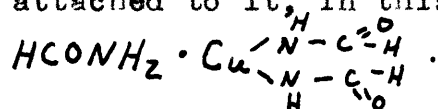
In order to establish conclusively the existence of this compound a C,H,N analysis should be made. The electrolytic reaction taking place at the cathode may possibly be



The Cu<sup>++</sup> ion from the anode probably reacts in this way,



and when the copper derivative crystallizes out of solution, a formamide of crystallization is attached to it, in this way,



In order to learn more about the possibility of the existence of the above reactions and of the copper derivative, N,N-dimethyl formamide was used in place of formamide. It was thought that in N,N-dimethyl formamide the methyl groups



attached to the nitrogen would not be as apt to be removed as would be the hydrogen atoms attached to the nitrogen in formamide by the electrolytic reduction at the cathode. This was indeed true. No reaction or gas evolution of any kind was observed at either electrode at applied potentials up to 120 volts D.C. This is further evidence for the existence of the derivative.

A conducting solution resulted when the  $\text{HCON}(\text{CH}_3)_2$  was saturated with  $\text{NH}_4\text{Br}$ . The bromine liberated at the anode formed a distinct layer at the bottom of the cell. The solution around the copper anode became green in color. The green eventually diffused over to the cathode, where copper was plated out. At no time during the electrolysis was a blue color seen. When the green solution of  $\text{HCON}(\text{CH}_3)_2$  was diluted with alcohol and cooled, a non-crystalline green substance precipitated out.

b. The Preparation of Tetraformamide Copper (II) Bromide

The same procedure employed in the preceding electrolyses was used here except that a saturated ammonium bromide solution of formamide was used. A potential of 20 volts D.C. was applied across the electrodes and a current of 0.17 ampere was observed on the ammeter.

Immediately at the copper anode a green soluble substance was formed and at the cathode hydrogen gas was liberated. At the same time bromine liberated at the bottommost part of the anode formed a layer at the bottom of the U-tube. As soon as

the green substance had diffused throughout the whole solution a color change to blue was noted at the cathode and bright copper was deposited on the cathode. The blue color intensified with time, the whole solution becoming a brilliant blue. On further electrolysis the blue color lessened in intensity and finally the solution throughout became colorless. The electrolysis was stopped at this point and the large mass of red-brown spongy copper which had deposited on the cathode was removed from the solution.

The colorless solution on standing in the stoppered vessel became blue in color. An electrolysis was performed again on the solution, but this time no color change was observed. However, a few brilliant violet crystals were formed on the cathode. The electrolysis was stopped and the blue solution together with the crystals was placed in a stoppered test tube and allowed to stand.

On standing several weeks nothing more had crystallized out. In an endeavor to obtain more of the crystals the formamide solution was diluted with an equal volume of alcohol and the test tube with its contents was placed in a Dewar flask packed with ice. Two weeks later a sizeable quantity of the violet substance had crystallized out. The crystals were washed with alcohol and allowed to dry on filter paper. They were stable in that their appearance was not changed with time. A few blue crystals which had crystallized out with the violet

crystals were mechanically removed. The violet crystals were pumped dry by means of a vacuum pump and analyzed.

Copper was determined by the ignition of a weighed amount of the crystals to cupric oxide. Bromine was determined by the precipitation of silver bromide in acid solution by silver nitrate. Nitrogen was determined by hydrolyzing a weighed amount of the crystals by sodium hydroxide, distilling the ammonia into a measured volume of standard hydrochloric acid and back titrating with standard sodium hydroxide.

	<u>Calculated for Cu (HCONH<sub>2</sub>)<sub>4</sub> Br<sub>2</sub></u>	<u>Found</u>
Cu	15.75%	15.90%
Br	39.61%	39.30%
N(as NH <sub>3</sub> )	13.89%	14.58%
M.W.	403.56	400.2, 406.8

When the crystals were dropped into dilute nitric acid solution for the bromine determination, a white precipitate was formed, probably Cu(OOCH). The white precipitate was collected on filter paper and was allowed to stand. Within a few minutes the precipitate became red in color. The red color probably was due to the formation of Cu<sub>2</sub>O. The formic acid that was formed when the crystals were hydrolyzed in acid solution probably reduced the cupric copper to cuprous copper, precipitating CuOOCH which probably is unstable and decomposes to the red oxide. This is further evidence for the existence of tetraformamide copper (II) bromide.

## 2. Uranium as Anode in Non-Aqueous Solutions

When uranium was electrolyzed, in the same way as copper in Section 1, in saturated ammonium bromide solutions of anhydrous methyl alcohol, ethyl alcohol, and formamide, a definite purple soluble substance was formed immediately at the uranium anode. The purple substance lasted less than a half minute and apparently was oxidized up to the insoluble black uranous oxide,  $UO_2$ . Large quantities of the same black substance was formed at the cathode in each of the above mentioned organic solvents. On standing several weeks, in stoppered test tubes, the black substances changed to lemon-yellow insoluble substances, probably uranic oxide,  $UO_3$ . The colorless solutions changed to lemon-yellow solutions. The color is probably due to uranyl bromide,  $UO_2Br_2$ .

The purple soluble substance formed at the beginning of the electrolyses is of interest in that it probably is trivalent uranium bromide,  $UBr_3$ . Uranium in the + 3 oxidation state is known, and the tribromide has been prepared at high temperatures. However, it is unstable in a moisture containing atmosphere and in aqueous solution. When  $UBr_3$  is dissolved in water it forms a purple solution which is unstable, the  $UBr_3$  being oxidized to  $UO_2$ .

The purple color at the uranium anodes indicates that uranium metal goes into solution in the + 3 oxidation state, rather than the + 4 state as is thought. Further research using

a cell from which all oxygen has been excluded in order to prevent oxidation of the  $\text{UBr}_3$  in non-aqueous media would indeed be fruitful. The purple substance probably may then be isolated in quantity and analyzed.

When uranium was electrolyzed in a saturated  $\text{NH}_4\text{Br}$  solution of ethylene diammine no reaction other than gas evolution at the cathode was observed.

When uranium was electrolyzed in sodium acetate solutions of anhydrous  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and  $\text{HCONH}_2$ , the solution surrounding the anode became green in color. (characteristic of the  $\text{U}^{+++}$  ion) and a black insoluble substance, probably  $\text{UO}_2$ , formed at the cathode in each one of the solvents. On standing several weeks the green solutions changed to colorless ones, and the black precipitates took on a greenish appearance. The precipitates are probably a mixture of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ .

### 3. Molybdenum and Tungsten as Anodes in Non-Aqueous Solutions

When molybdenum and tungsten were electrolyzed in saturated ammonium bromide and potassium bromide solutions or anhydrous methyl alcohol, ethyl alcohol, ethylene diamine, and formamide, immediately bromine was liberated at the anode and hydrogen was evolved at the cathode. In each case shortly after the beginning of the electrolysis, a white insoluble substance was formed at the cathode.

The white substances that resulted from the molybdenum electrolyses dissolved in the organic solvents on standing in closed vessels. However, they could be made again by electrolyzing the solutions again. The substances containing molybdenum were found to be soluble in water, acid, and base, while those containing tungsten were not.

When the substances were collected, dried, and ignited in a crucible, the yellow oxides,  $\text{MoO}_3$  and  $\text{WO}_3$  respectively, were formed. On standing in stoppered test tubes several weeks molybdenum and tungsten blues were formed in many of the non-aqueous solutions.

At an applied potential of 100 volts D.C., a black insoluble substance was formed on the cathode in each one of the electrolyses. The black substances were all insoluble in 6N HCl, but soluble in the hot acid. Each gave a positive flame test for their respective metals. Since there are no known black compounds of either molybdenum or tungsten, it is likely that the black substances are the metals in a finely

divided state. This is of interest and worthy of further investigation, for both molybdenum and tungsten do not deposit cathodically as metals in aqueous solution.

After two hours of electrolysis of formamide alone at an applied potential of 100 volts D.C., a molybdenum green was formed at the molybdenum anode. The olive green color is characteristic of the + 3 oxidation state. The color is indicative of the molybdenum going into solution in the + 3 state. The cathode became coated with a black substance that was insoluble in 6N HCl. The black substance gave a positive molybdenum flame test. As soon as the green color appeared at the anode, a brown precipitate formed at the cathode. The brown precipitate is worthy of further investigation, for there are no known brown molybdenum compounds.

Tungsten electrolyzed in formamide under the same conditions produced no color change in the formamide. The yellow oxide,  $WO_3$ , was formed at the anode. Hydrogen was evolved at the cathode.

#### 4. Niobium and Tantalum as Anodes in Non-Aqueous Solutions

When niobium and tantalum as anodes were electrolyzed in saturated ammonium bromide and potassium bromide solutions of anhydrous methyl alcohol, ethyl alcohol, ethylene diamine, and formamide, immediately, bromine was formed at the anode and hydrogen gas was evolved at the cathode. In each electrolysis carried out with an applied potential of 20 volts, about a half hour was required to detect a further reaction taking place. At this point white flocculent substances were formed at both anode and cathode and throughout the solution. By this time the bromine had formed a distinct layer at the bottom of the cell and no more bromine was liberated. The white substances are quite stable and do not dissolve in the organic solvents on standing. They are insoluble in hydrochloric acid and sodium hydroxide.

When each one of the white substances was collected, washed with water, and ignited in a crucible, the white oxides of niobium and tantalum,  $Nb_2O_5$  and  $Ta_2O_5$  respectively, resulted except in the case of the substances from the formamide electrolyses. Here black substances, probably carbides, resulted from the ignition. This suggests the presence of something organic in the white insoluble substances from the formamide electrolyses. Perhaps niobium and tantalum derivatives of formamide are formed which upon ignition yield the carbides. The white insoluble substances from the other electrolyses



are probably oxides in the first place.

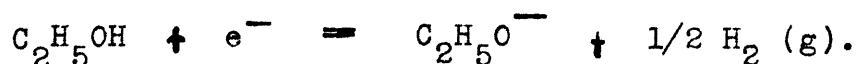
Anhydrous methyl alcohol, ethyl alcohol, ethylene diamine, and formamide solutions of a basic salt, sodium acetate, were electrolyzed by use of tantalum as the anode. In each case the current passed through the solution decreased to zero very rapidly. Even at an applied potential of 120 volts D.C., the current decreased rapidly to zero. Upon inspection of the surface of the tantalum electrode it was noted that it had dullened in appearance. Apparently a protective coating of an oxide which prevents the passage of current is formed on tantalum in basic solutions.

The electrolysis of formamide alone by use of a tantalum anode at an applied potential of 100 volts D. C. produced immediately the white insoluble substance at the anode. Hydrogen gas was evolved at the cathode throughout the electrolysis. After two hours something quite remarkable happened at the cathode. The formamide surrounding the cathode became red in color. In time the red color diffused over to the anode. Several hours later a sizeable amount of a brown insoluble substance had collected at the cathode. The brown substance is of interest in that there are no known <sup>brown</sup> tantalum compounds. The red colored formamide is certainly worthy of further investigation, for the red color may be due to tantalum pentanitride,  $Ta_3N_5$ , or to a tantalum derivative of formamide. Tantalum pentanitride is known to exist and is formed when the

metal is heated in nitrogen at  $1000^{\circ}$  C. It is bright red in color and unstable in aqueous solution. In this electrolysis, the pentanitride of tantalum may have been prepared at the cathode at room temperature. An analysis of the red species, providing it can be isolated from the formamide, would solve the problem.

## 5. Aluminum as Anode in Non-Aqueous Solutions

Aluminum ethoxide,  $(C_2H_5O)_3Al$ , was formed at the cathode in the electrolysis of a saturated potassium bromide solution of anhydrous ethyl alcohol. The reaction that took place at the cathode is as follows:



Aluminum ion liberated at the anode combined with the ethoxide ion to form aluminum ethoxide. The analogous reactions took place when anhydrous methyl alcohol was substituted for ethyl alcohol in the cell.

No reaction other than the evolution of hydrogen at the cathode was observed in the electrolysis of saturated ammonium bromide and potassium bromide solutions of anhydrous ethylene diamine. The aluminum anode was attacked, however.

A black substance was formed on the cathode in the electrolysis of formamide. This is of interest in that there are no known black aluminum compounds. Since a sizeable amount of the black substance was made, the possibility of it being from an impurity present in the aluminum seems to be ruled out. The black may be carbon, but it seems unlikely that formamide is reduced cathodically to carbon.

## 6. Nickel as Anode in Non-Aqueous Solutions

Attempts at the preparation of a nickel derivative of formamide and a nickel formamide complex were made. Nickel was electrolyzed in a saturated ammonium bromide solution of formamide at the same applied potential and with the same arrangement as was used with the copper cell. Bromine liberated at the nickel anode formed a distinct layer at the bottom of the cell. Around the anode a green soluble substance was formed. Eventually the green color diffused over to the cathode where metallic nickel was deposited and hydrogen was evolved. A small amount of a violet flocculent substance was formed at the anode. When the violet substance was collected and dried on filter paper, it quickly changed to green.

The electrolysis was stopped and the metallic nickel which had dropped from the cathode was removed by filtration. The green solution was diluted with an equivalent volume of alcohol and the resulting solution was cooled in a Dewar flask packed with ice. On standing several weeks in the flask nothing crystallized or precipitated out.

Formamide containing no dissolved salt was electrolyzed between a nickel anode and a platinum cathode. The formamide became green in color like that of the above. Metallic nickel was deposited and hydrogen was evolved at the cathode. Attempts at the crystallization and/or the precipitation of the green substance out of the formamide were unsuccessful.

SUGGESTIONS FOR FURTHER RESEARCH

The isolation and determination of the soluble purple substance formed at the uranium anode in ammonium bromide solutions of non-aqueous solvents is of most importance. If the color is due to the formation of uranium tribromide, it would indicate that tripositive uranium is formed when the metal is anodically oxidized.

The red tantalum species from the electrolysis of formamide is next in order of importance. The formation of the red nitride in formamide would be analagous to the formation of the nitride in liquid ammonia.

The black and brown substances formed at the cathode when aluminum, molybdenum, and tungsten are anodically oxidized in formamide are worthy of further investigation. The electrolytic reactions of the transition metals in formamide should be explored.

VI

BIBLIOGRAPHY

1. A. W. Davidson and F. Jirik:  
J. Am. Chem. Soc., 72, 1700 (1950)
2. J. Kleinberg: J. Chem. Education, 27, 32 (1950)