NATIONAL BUREAU OF STANDARDS REPORT

9889

ELECTRODELESS ELECTROLYSIS OF SOLID ELECTROLYTES

SEMI-ANNUAL

PROGRESS REPORT

November 1, 1967 to May 31, 1968

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract No. R-09-022-052

November 15, 1965

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.
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BY
Abner Brenner and John Sligh

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ELECTRODELESS ELECTROLYSIS OF SOLID ELECTROLYTES

I. INTRODUCTION

In ordinary electrolysis, solid electrodes are used which are considered to be electronic conductors. Metals are most frequently used, but graphite also finds a large application. The products of the electrolysis are formed at the interface between the electrolyte and the electrode.

A matter of fundamental interest is whether electrodes consisting of electronic conductors are essential for electrolysis to occur. It was known that the glass of an electric light bulb (evacuated type) could be electrolyzed under certain conditions by means of a stream of electrons from a hot filament. In our initial work we designed an apparatus for investigating the general application of electron beam electrolysis. However, certain experimental difficulties made the method rather difficult to use. The chief problem was making the positive (+) electrical connection to the solid which was being electrolyzed. Another was the shorting between the electron beam and the positive (+) electrical lead.

The difficulties with the electron beam electrolysis lead us to the development of a glow discharge type of electrolysis. Essentially the electrolyte forms the septum between two partially evacuated chambers (pressure between 50 and 1,000 microns), one of them containing the positive and the other the negative electrical lead.

Between 1,000 and 3,000 volts a glow discharge occurred extending from each electrode through the rarified gas to the electrolyte. A slice of solid silver chloride electrolyzed readily, forming a silver layer on the side toward the negative electrical lead. Glass underwent a dramatic change forming an opaque material mainly on the side facing the anode. A disc of a titanate, which was originally yellow in color, became black throughout and fairly conductive. The change was similar to that resulting from passing hydrogen over the titanate at a high temperature. Some other minerals showed a discoloration but no obvious chemical change. These experiments were all conducted with the electrolyte heated between 400°C and 800°C in order for the ceramic material to become sufficiently conducting. Metal did not separate out on the surface of the ceramic as we had expected.

In some further experiments, salts of the heavy metals were incorporated in fused melts of sodium borates or phosphates which, on cooling, often form glassy solids. The glow discharge electrolysis of these solid materials seemed to yield sodium. There was no evidence of a heavy metal coating on the surface of the electrolyte facing the cathode lead.

The inability of electron beam electrolysis to produce coatings of many metals leaves open the question as to whether the failure was owing to the defects in the specimen or whether the solid materials at temperatures much below their melting points do not conduct ionically.

II. RECENT WORK: GLOW DISCHARGE ELECTROLYSIS OF FUSED ELECTROLYTES

A. Introduction

In the third and final phase of our work we turned our attention to the electrolysis of fused electrolytes, since these are good ionic conductors (having been electrolyzed by conventional means) and, hence, would not involve the difficulty experienced with the ceramic materials. The experimental arrangement consisted of a simple U-tube with an electrode in the top of each limb. The melt which was to be electrolyzed occupied the bend at the bottom of the U-tube. As before, the glow discharge was the means of carrying the current to the fused salt. In order to study each electrode reaction separately, a cell with a glass frit separator between the anode and cathode compartment was employed. In one of these compartments (the one of less interest) a conventional metal electrode was immersed in the melt and the glow discharge was used in the other compartment.

The phenomena of the glow discharge electrolysis of fused salts should be of considerable theoretical interest, if for no other reason than as a comparison with the glow discharge electrolysis of aqueous solutions. The phenomena of the latter process has received a considerable amount of study, which has shown that the process is not a normal electrolysis. Metal does not separate out at the interface between the solution and the glow discharge. The chemical reaction appears in some instances to result in an oxidation, in others

a reduction and the yields are several times greater than that expected from Faraday's law. The results are explained on the basis that reactive materials are produced from the water vapor, such as hydroxyl ions.

Our preliminary results with the glow discharge electrolysis of fused salts indicate that the process is normal electrolysis. In the glow discharge electrolysis of silver chloride (with a glow discharge from both the positive and negative leads) we obtained dendrites of silver, which appeared similar to those obtained in the electrolysis of a water solution.

B. Apparatus

The problem involved in isolating the products of the anode and cathode reaction have already been mentioned and can be solved by the use of a porous diaphragm. For those experiments in which the reaction at only one electrode is being studied the apparatus shown in Figure 1 was devised and found convenient. The empty tube A, which is fashioned from a commercial porous glass filtering tube, is immersed into the molten salt B in the large tube C, and usually the molten salt enters to the same level as in the large tube. The melt which enters the chamber A is thus a filtered melt. A glow discharge is now produced and maintained for one or two hours at a current of 10 to 25 ma and a voltage of 1,000 to 3,000. After the electrolysis the tube A is withdrawn and the melt allowed to drip out. The remainder of the melt is washed out with an aqueous solution.

The solid products of the electrolysis are thus left on the frit and can be removed from the tube and examined.

It will be noted that the volume of melt contained in the tube A is small. This is done purposely, because only a small amount of metal is produced in an experiment. For example, in an electrolysis at 20 ma for an hour, probably less than 50 mg of a metal would be produced. Our preliminary work with cruder apparatus indicated that it was difficult to separate such a small amount of product from about a thousand times larger quantity of melt. The use of the small reaction chamber A (diameter about 1 cm) immersed in the larger volume of melt B solved the problem.

C. Results

In our first experiments, we showed that the electrolysis of a melt containing cobalt chloride yielded a black material which was magnetic. However, a more detailed examination of the material was not made since air had not been carefully excluded.

The electrolysis of a eutectic melt containing cuprous chloride yielded dendrites of copper. Some special precautions had to be taken before a successful experiment was performed. In the first experiments a cupric chloride-potassium chloride eutectic was used, but no copper dendrites were obtained. It seemed probable that the cupric ion had been reduced to cuprous, instead of metal deposition occurring, and this was qualitatively verified by the turbidity of the resulting solution of the electrolyzed melt.

Experiments were then performed with cuprous chloride-potassium chloride eutectic. Again satisfactory results were not obtained. This was attributed to the presence of some cupric ion in the melt. In the successful experiment, copper turnings were introduced into the melt B to prevent the formation of cupric ion. The turnings could not enter the cathode compartment A because of the presence of the filter frit. This experiment yielded about 60% efficiency production of copper dendrites.

III. FUTURE WORK

The electrolysis of the fused salts with the glow discharge shows that true electrolysis can be brought about without the contact of any solid electronic conductor with the electrolyte. Since the electrolysis of fused salts has advantages over that of solid materials, both with respect to the range of materials that can be electrolyzed and the ease of collection of the product, we intend to continue with this process until the end of the project. One objective will be to determine to how many electrolytes the procedure can be extended. For example, can active metals, such as sodium, aluminum, or beryllium be produced by this means? In an experiment soon to be made we will attempt to deposit gadollinium, one of the rare earths. Since the metal is magnetic, we would easily be able to determine whether any of it had been formed.

At the moment we do not envision any practical applications of glow discharge electrolysis of molten salts. The one obvious

advantage is that the deposited metal would not be contaminated by contact with an electrode. On the other hand, if the electro-deposited metal reacted with the melt or dissolved in it to form a solution, the isolation of the product would be vitiated.

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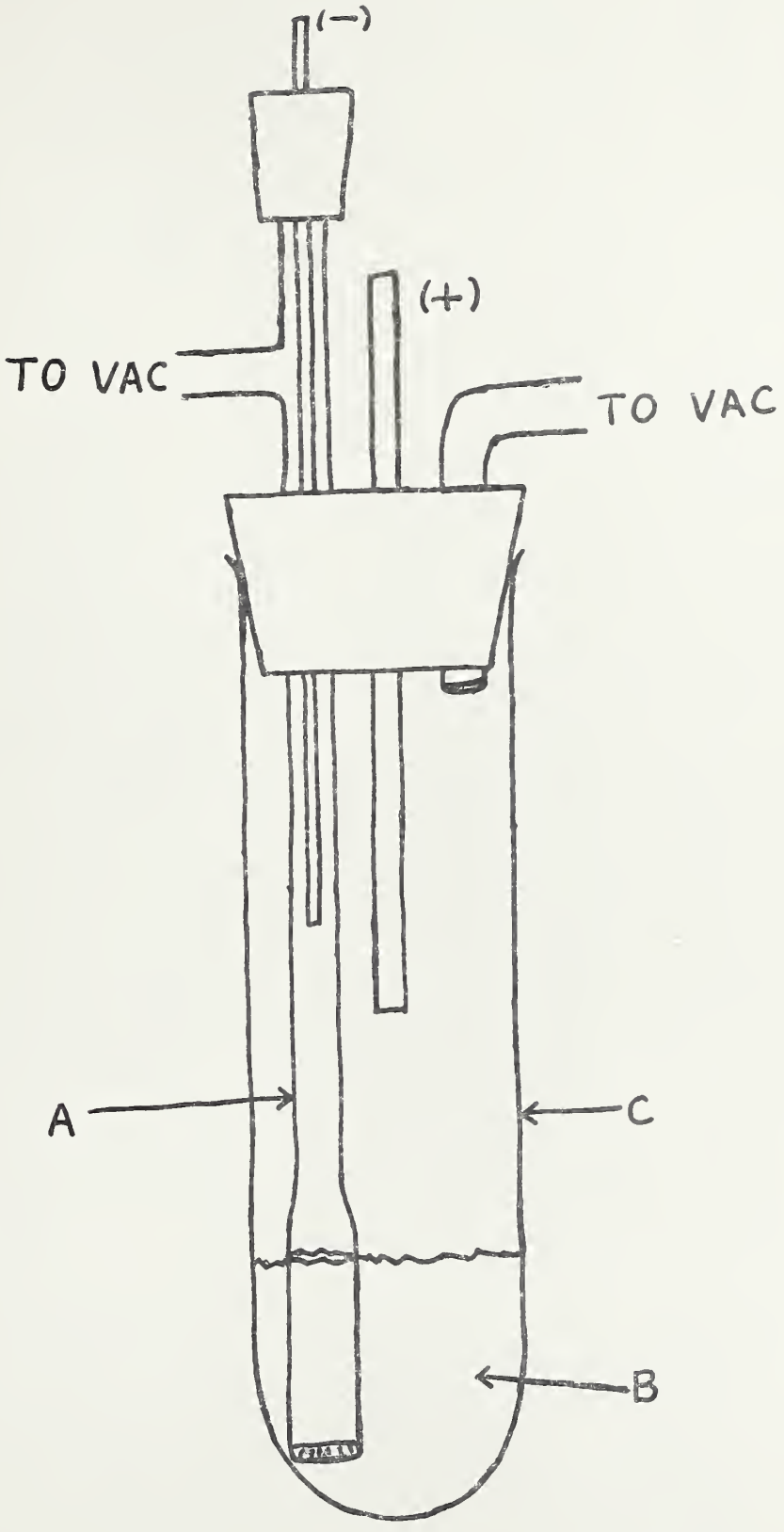

Glow Discharge Cell

Figure 1


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