Nickel Cadmium Batteries: A Medium for the Study of Metal Whiskers and Dendrites

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Abstract

The first documented discovery of metal whiskers creating electrical system failures – specifically, due to whiskers of cadmium – took place in 1946. Subsequently, most studies have focused on tin and zinc whiskers. This research addresses the possibility of whisker-induced failure in nickel cadmium cells, thereby renewing interest in cadmium metal formations as a cause of electrical system failures.

Introduction

Metal whiskers are tiny crystal filaments[1] that form from film deposits of mostly pure metals such as tin, zinc, and cadmium **(see Figure 1)**. Because they are electrically conductive, metal whiskers can pose serious reliability threats to electronics that use tin plated components or tin-based solder. Shorting can occur if a whisker bridges the gap between traces or other components – especially in circuits with low voltage and high impedance. This danger has been known since at least 1946 when H.L. Cobb (Aircraft Radio Corp.) first described how cadmium whiskers forming on an air capacitor had been observed to produce electrical shorts between the plates, rendering many radio sets inoperable **(see Figure 2)**. Subsequently, alternative materials such as tin and zinc were also found to be susceptible to metal whisker formation.

The European RoHS/WEEE legislation, which bans the use of lead (Pb) in electronics, went into effect in July of 2006. In response, manufacturers of all types of electronic components and systems are turning to pure tin component finishes as a replacement for tin-lead (Pb)

[1] They have very uniform cross sectionals, and are generally observed to grow to lengths up to 10 millimeters and diameters of only a few microns.

coatings and solders. This switch to tin has only worsened the potential exposure to the tin whisker problem. [2]

Metal whiskers have been attributed to complete system failures in commercial satellites, nuclear reactors, missile systems, and pacemakers, among others. In March 2006, the Space Shuttle Discovery was impacted when an astonishing number of tin whisker formations were observed in many of the flight avionics systems, which are over fifteen years old **(see Figure 3)**. Until the growth mechanisms behind metal whisker growth are better understood, any electronic devices – particularly those used in aerospace, which have high importance and long projected life-spans – are at risk.

My initial assignments were to conduct literature research for cadmium whisker references, in order to determine if cadmium whiskers have been the focus of recent research, and if they continued to be documented as a cause of electrical systems failures. I also obtained samples of Cd-plated components (e.g., electrical connector shells) to conduct direct examination for cadmium whiskers. During this time, I found that nickel cadmium battery cells have been supposed to fail prematurely due to metal crystal "growths", which short out the cell. Several specialized battery chargers exist – they use revival techniques designed to temporarily "fuse out" the growths, which would otherwise internally short the cell. Manufacturers of these chargers do not readily provide scientific literature about the topic, and terms such as "whiskers", "dendrites", and "crystals" are used interchangeably to refer to these growths.

The purpose of the research was to determine whether these metal formations actually exist. If cadmium whiskers were found, nickel cadmium battery cells could potentially become a new medium for the study of metal whisker growth. If another type of metallic formation was

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[2] The Pb in these tin alloys has been well-established as an effective quencher of tin whisker formation even at levels approaching only 0.5% by weight.

observed instead (e.g., dendrites), it would clarify the ambiguous terminology found in both scientific and non-scientific texts and usage.

Basic construction and operation of a nickel cadmium cell

The basic construction of a nickel cadmium cell is depicted in **Figure 4**. Through my preliminary research, I found that the cells contain a positive nickel hydroxide electrode and a negative cadmium hydroxide electrode. The electrodes are electrically insulated by a separator, and potassium hydroxide (KOH) acts as the electrolyte. These components are reeled into a jelly roll structure, and housed in a case.

The chemical reaction of a nickel cadmium battery cell is described in the equation below:

$$2\ NiO(OH) + Cd + 2\ H_2O \leftrightarrow 2\ Ni(OH)_2 + Cd(OH)_2$$

When the cell is being discharged, the reaction takes place from left to right. When it is being recharged, the reaction occurs from right to left.

Disassembly of a nickel cadmium cell

In order to search for traces of metallic formations, I disassembled an approximately 10-year-old Sanyo Cadnica KR-1300 SC (1.2 V, 1300 mAh) nickel cadmium cell. Using hand tools such as a vise, a hacksaw, and a rotary cutter tool, I made a transverse cut through the cell, separating it into two equal pieces. Then, I made a lateral cut through one of the cell halves in order to better observe the jelly roll structure **(see Figure 5)**.

I examined the disassembled cell under a Leitz optical microscope with a magnification in the range of 3x to 25x, focusing primarily on the separator lining, where the metal formations (if any) would have to pass in order to present electrical shorting problems to the battery cell. The jelly roll structure of the cell was packed tightly and impregnated with the KOH electrolyte in a powdery black solid form instead of a liquid as I had expected. The separator linings were made of transparent polypropylene/polyamide (i.e., nylon) fibers that were woven together compactly. No apparent metal formations were found during this inspection.

From examining the dense structure of the separator, my mentors and I came to believe that it would be highly unlikely for metal whiskers to penetrate the nylon barrier in a manner that would create electrical shorting problems within the cell. Because whiskers are filaments that commonly project as long, straight crystals, it would be difficult for a single whisker to successfully navigate through the complicated weavings of the nylon separator, which is nominally about 0.4 mm thick. Instead, due to the high aspect ratio (length to width), whiskers would have a tendency to bend or stop growing as they attempted to penetrate the densely fibrous nylon separator.

Consideration of metal dendrite formation within a nickel cadmium cell

After finding it highly improbable that metal whiskers could produce damaging shorts within the nickel cadmium cell, my mentors suggested that I focus on metal dendrites – a formation that is often thought to be analogous to whisker growth, but is in fact completely different and better understood **(see Figure 6)**. Metal dendrites form as a result of an electrochemical process in which a solid metal is dissolved by a solvent into a solution of metal ions **(see equation 1)**. These charged metal ions can migrate in the presence of an electric field **(see equation 2)**. The ions then precipitate as solid metal structures with fern-like branches**.** Because the nylon separator is by design porous to liquid penetration, it would be more feasible for a solution of metal ions to navigate the weave and then precipitate into a solid metal dendrite by the electromigration process described by equations 1 through 3. If the metal dendrite were to completely bridge between the cathode and anode, this would create an electrically conductive path with the battery cell capable of depleting the battery life.

Eq. (1) $M + 2H^+ \rightarrow M^+ + H_2\,(gas)$

Eq. (2) M^+ + E moves M^+ to the cathode

Eq. (3) at the cathode $M^+ + e^- \rightarrow M$

(where M = solid metal, H^+ = Hydrogen ions from solvent,

M^+ = metal ions, E = electric field, e^- = electrons)

Running an electrochemical cell

The purpose of my next experiment was to examine the workings of an electrochemical cell, and to watch for metal growths, particularly dendrites **(see Figure 7)**. Two pieces of copper tape served as the positive and negative electrodes – they were placed approximately 1-mm apart on a glass slide. The electrodes were connected to two AA 1.5 V batteries in series (creating a total of 3V), and an ammeter in series. A solution of citric acid and detergent acted as the electrolyte – a few drops were added to the gap between the electrodes, and a bubbling reaction began to take place. This reaction is represented by the following equation using Eq. (1):

$$Cu + 2H^+ \rightarrow Cu^+ + H_2\,(gas)$$

I observed the reaction under a Leitz optical microscope equipped with a Nikon digital video camera, and took time-lapse photos every two minutes to record its progress. A fern-like metal growth began to form from the negative electrode towards the positive electrode **(see**

Figure 8). Within 45 minutes, the copper dendrite had completely bridged the 1-mm gap between the positive and negative electrodes, thereby electrically shorting the circuit. This is represented by the following equations using equations (2) and (3), where E is the electric field between the anode and the cathode:

$$Cu^{+} \quad + \quad \text{E moves } Cu^{+} \text{ to the cathode}$$

$$\text{at the cathode} \quad Cu^{+} + e^{-} \rightarrow Cu$$

Using the time-lapse images, I created movies to illustrate the growth process. This experiment demonstrated that the conditions in an electrochemical cell – and therefore, a battery cell as well – are capable of producing metal dendrites.

Simulating nickel cadmium dendrites

After watching dendrites grow from copper electrodes, I decided to create a scenario in which metal growths would form in an environment similar to that of a nickel cadmium cell. I harvested pieces of the nickel hydroxide and cadmium hydroxide electrodes from the previously disassembled cell, and used epoxy to secure them onto a glass slide, again separating the electrodes approximately 1-mm apart **(see Figure 9)**. The electrodes were then connected to a 9V battery and an ammeter, and the same citric acid/detergent solution was applied as the electrolyte.

I observed the reaction under a microscope, and a large dendrite grew from the negative electrode to the positive electrode within minutes **(see Figure 10)**. The composition of this dendrite was deemed to be cadmium based on its similar appearance in color to the cadmium electrode material.

Conclusions and summary

For the particular construction examined in this research, it is plausible for nickel cadmium battery cells – as electrochemical cells – to form metal growths, and in particular, cadmium dendrites. These experiments do not prove the absence of cadmium whiskers in nickel cadmium cells. However, examination of the cell construction makes it highly unlikely that metal whiskers could produce damage because the nylon separator provides a nearly impenetrable barrier to these types of metal filaments.

Area for future work may include developing improved inspection techniques for finding whiskers as well as dendrites – for example, metal whiskers may have been dislodged from the separator during cell disassembly. Techniques such as X-ray inspection or CT-Scan may have promise as these are nondestructive; however, the extremely narrow dimensions of metal whiskers and the compact nature of nickel cadmium cell construction may make imaging of these filaments a complex process if approached using traditional methods.

The data collected from this project can be used to clearly distinguish between metal whiskers and metal dendrites – though they are often thought as being one in the same, they are in fact very different phenomena. Understanding their differences may aid in the prevention of whisker and dendrite-related failures in aerospace electronics.

Author's final comments

Two weeks after concluding my internship, my mentors ironically encountered cadmium whiskers growing from a Cd-plated steel housing of a battery switch intended for use in a NASA mission **(see Figures 11, 12)**. This observation is a reminder that cadmium finishes should still be considered a risk for the formation of cadmium whiskers and as such, their use should be prohibited in applications which cannot tolerate electrical shorting as a result of their growth.

In addition, both of my mentors informed me that each have been independently approached by professors seeking advice for short term experiments to grow metal whiskers appropriate for a high school science curriculum. Rather than advise them to attempt to grow metal whiskers (a process that is unpredictable and may take months or years to achieve), they provided them with copies of my videos illustrating the process of metal dendrite formation along with a discussion of the work I performed on nickel cadmium cells during my internship.

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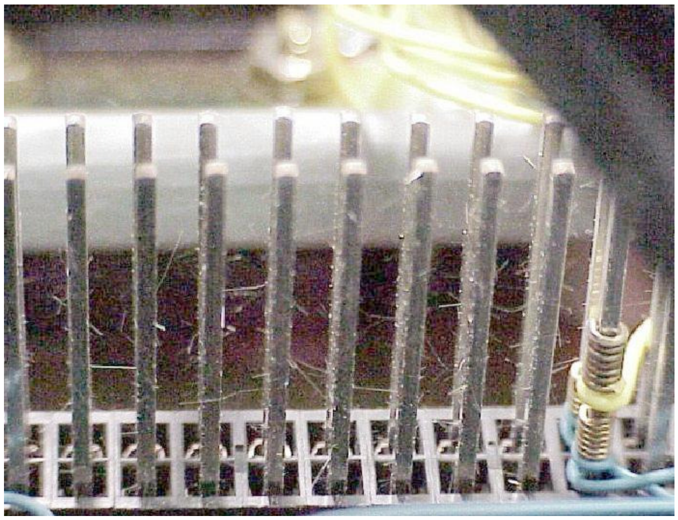
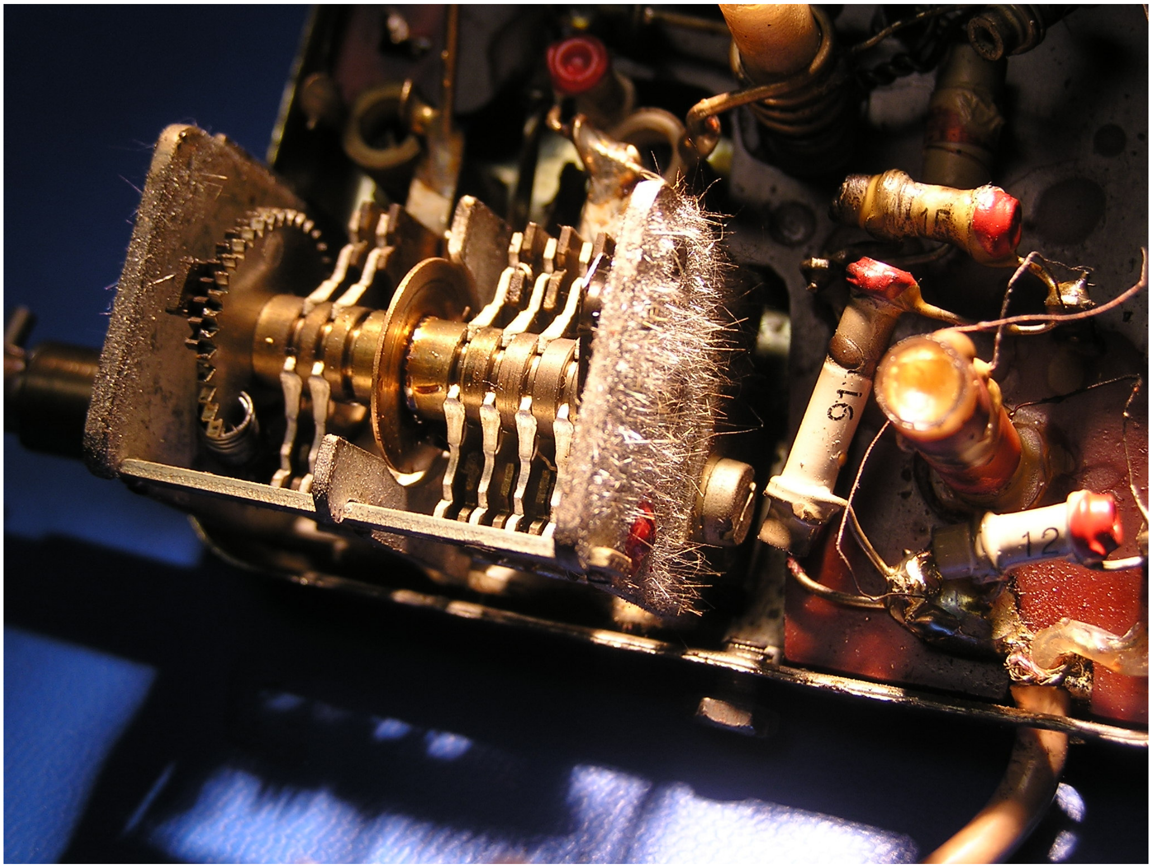
Appendix

Figure 1:



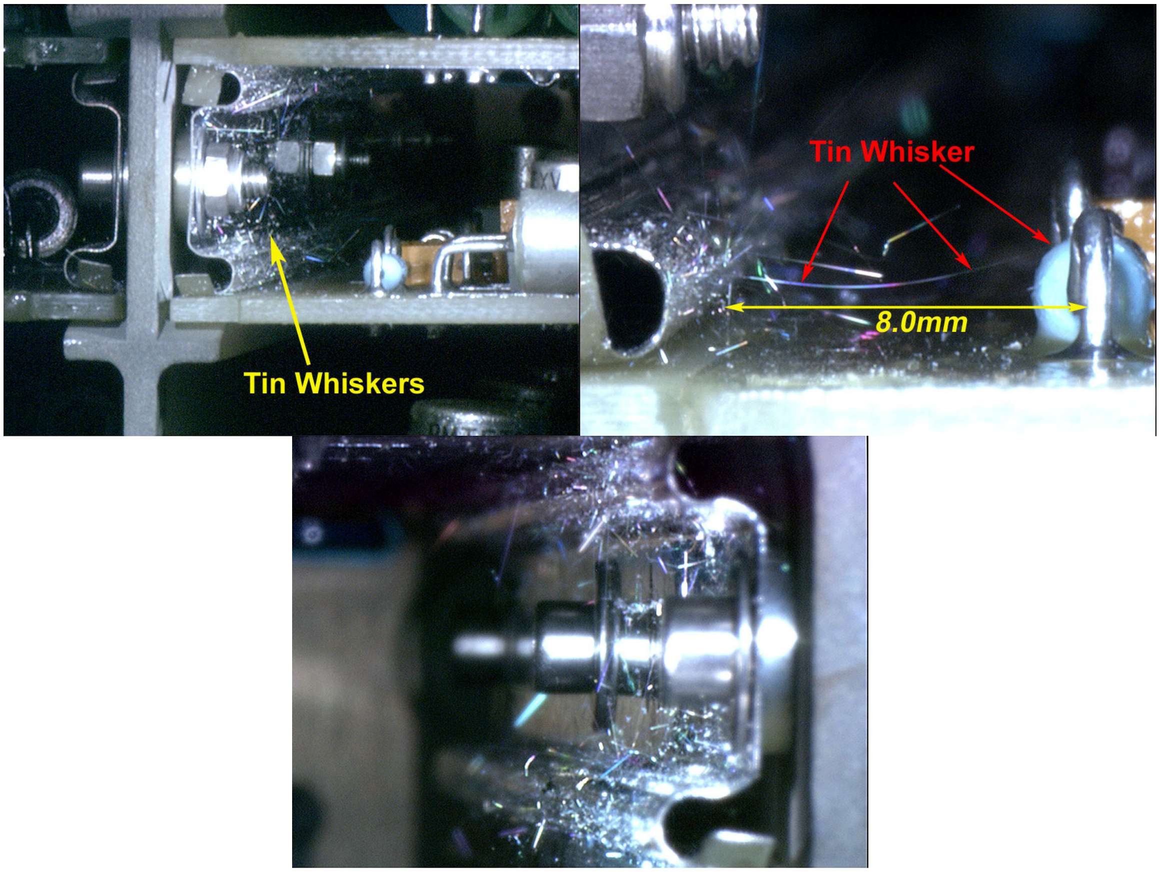
Tin whisker infestation on connector pins producing electrical shorts in an industrial application, (Courtesy of NASA GSFC)

Figure 2:



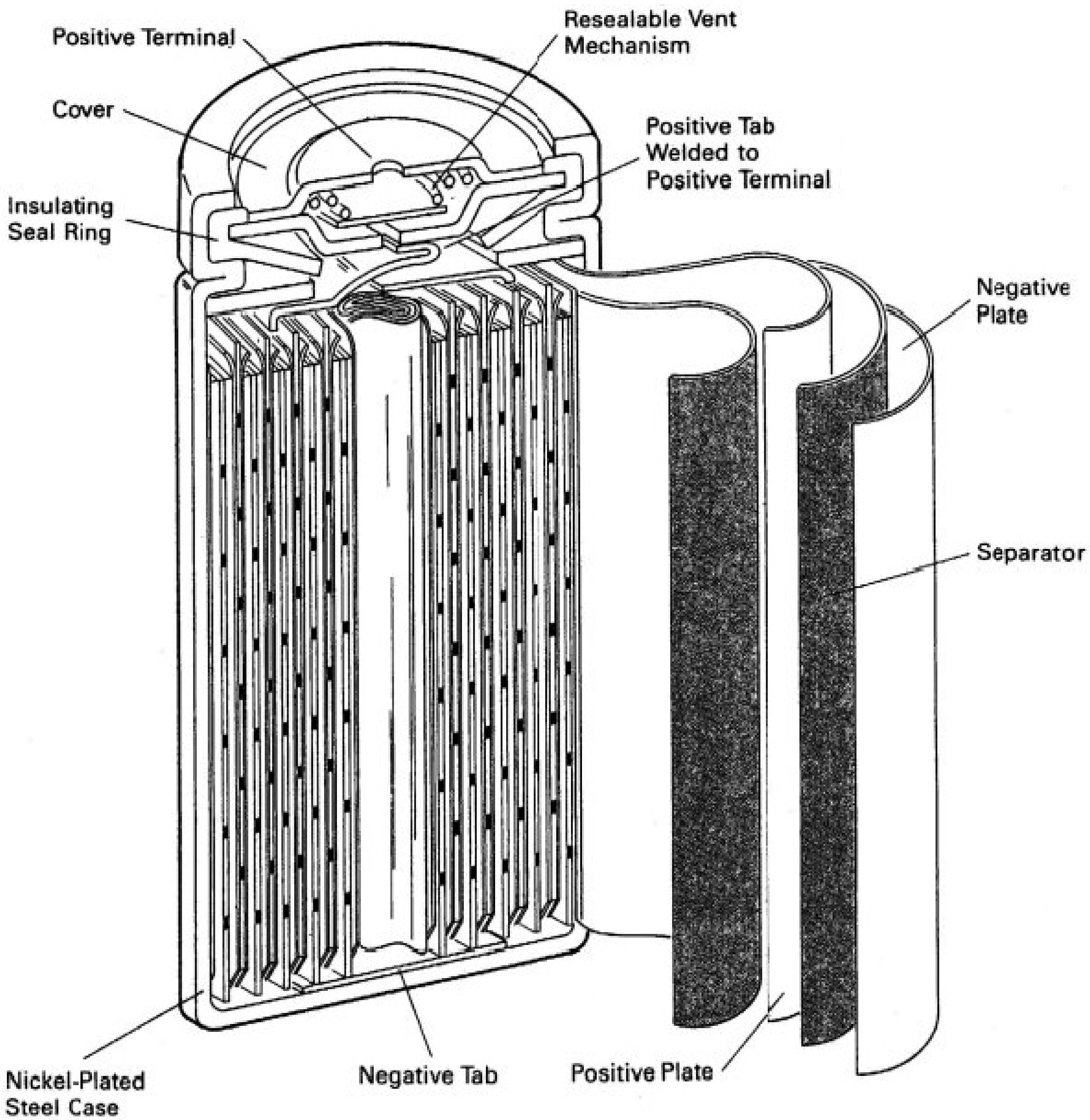
Tin whiskers from a 1960s era variable air capacitor (Courtesy of NASA GSFC)

Figure 3:



Tin whiskers on printed circuit card guides from Space Shuttle – tin plating over beryllium-copper (Be-Cu) (Courtesy of NASA GSFC)

Figure 4:

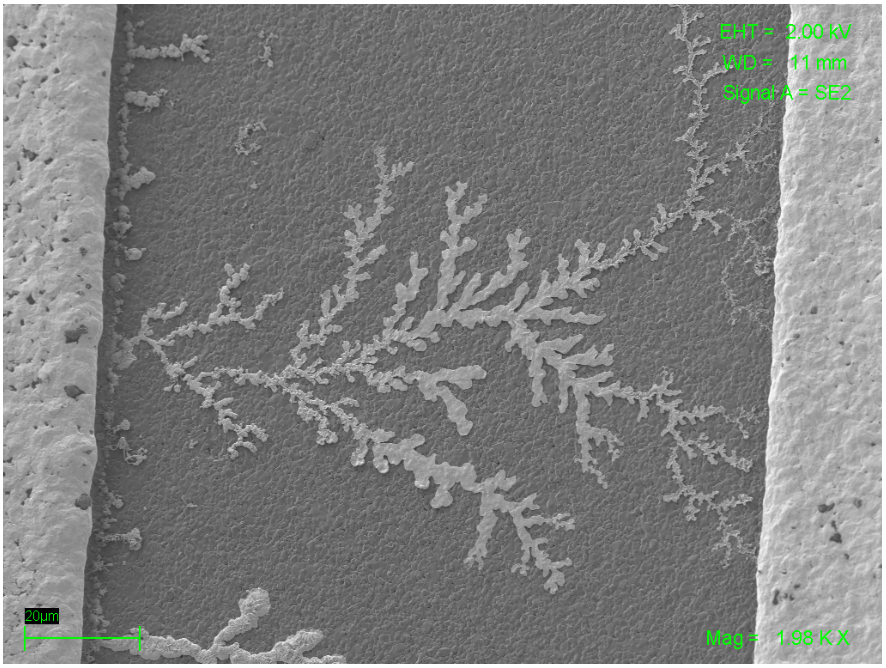


Nickel cadmium battery diagram (courtesy of Radio Shack)

Figure 5:

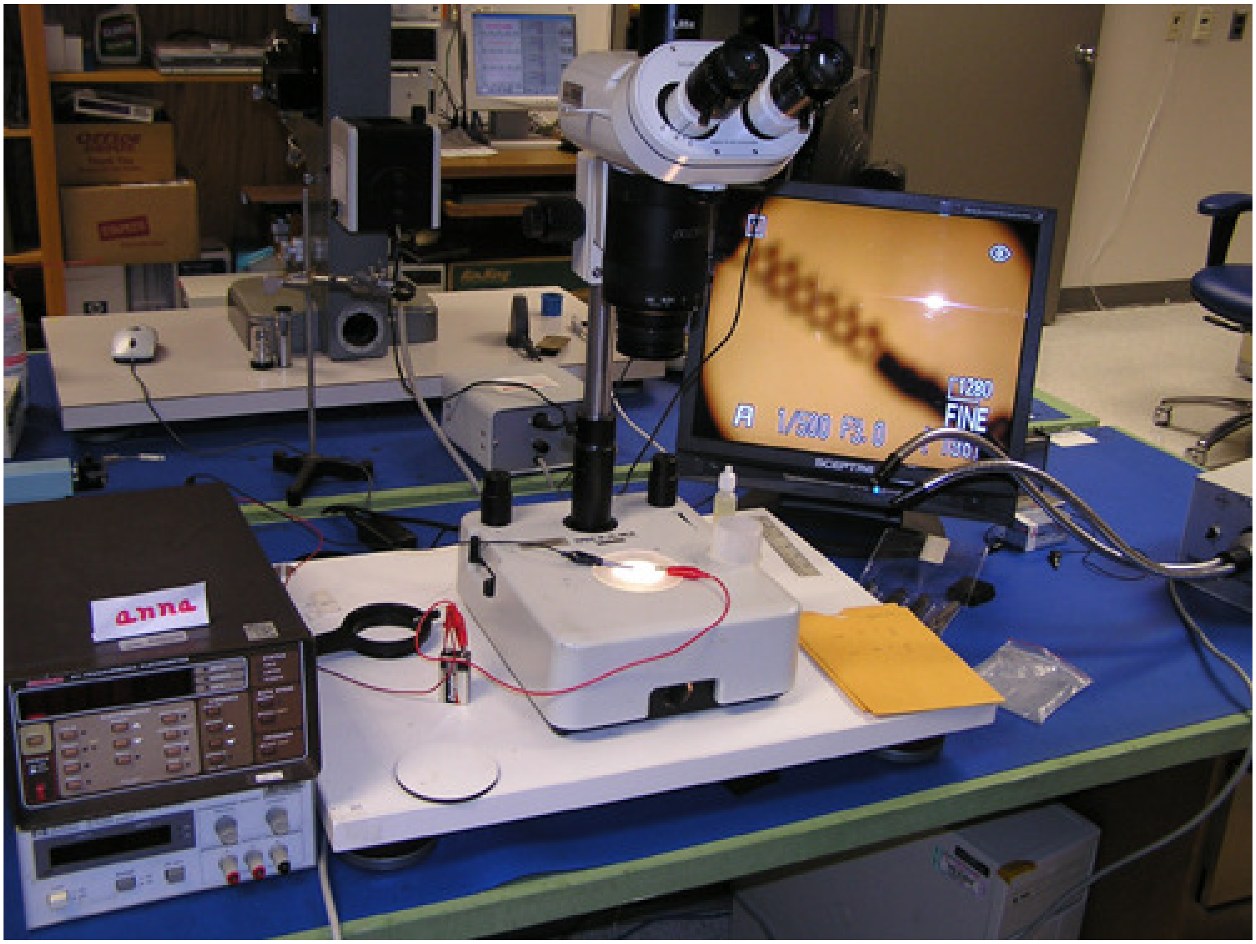
Disassembled Sanyo Cadnica nickel cadmium cell

Figure 6:



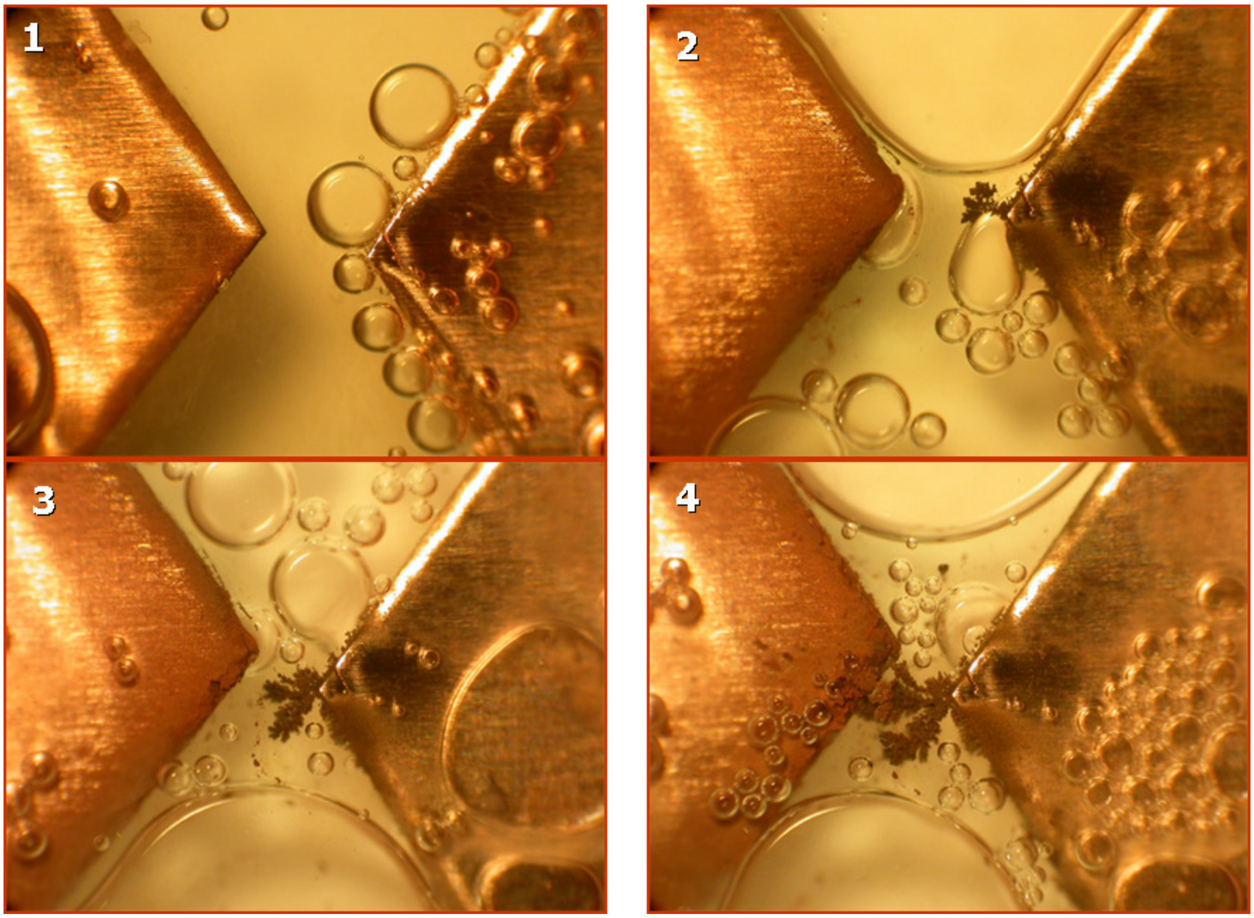
Silver dendrites creating an electrical short inside of a microcircuit (Courtesy of NASA GSFC)

Figure 7:



Laboratory set-up using a Leitz optical microscope equipped with a Nikon digital video camera

Figure 8:

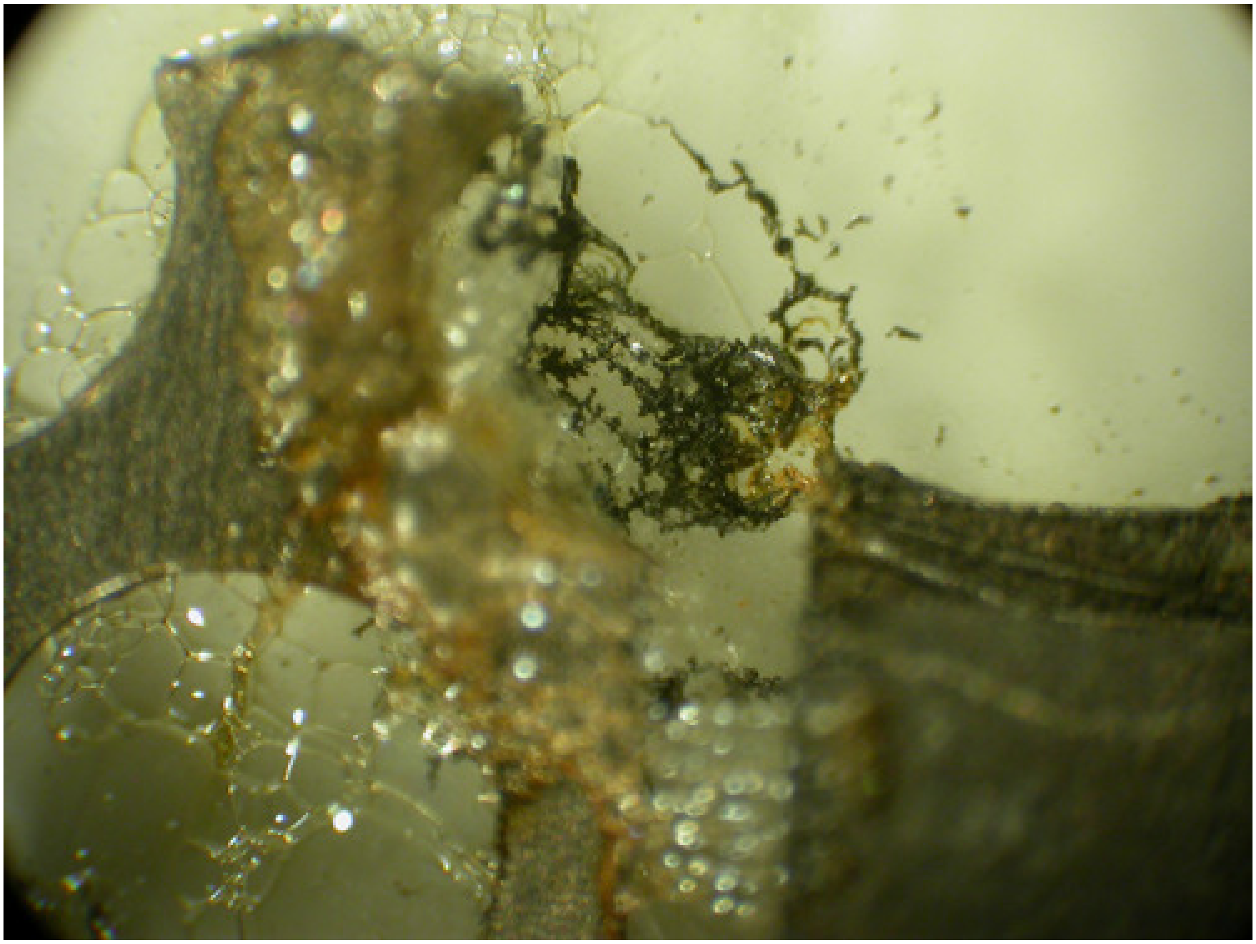


Sequence of time-lapse images of copper dendrite growth

Figure 9:

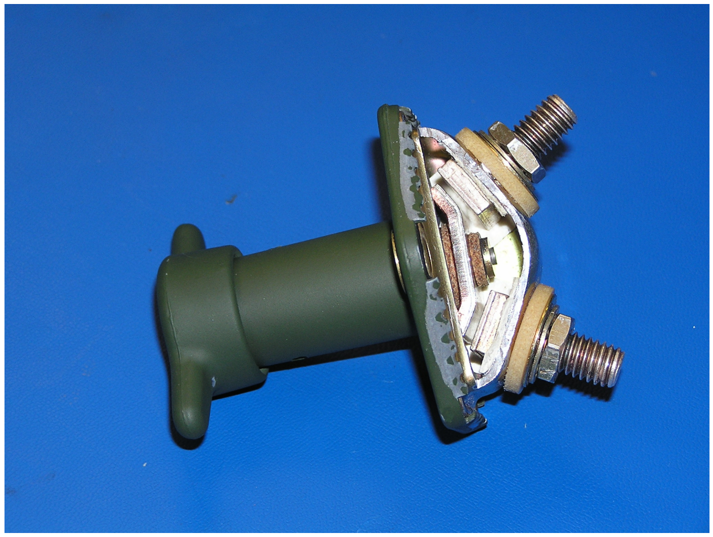
Harvested electrodes from a nickel cadmium cell, secured to a glass slide with epoxy

Figure 10:



Suspected cadmium dendrite growing from the negative electrode, and touching the positive electrode

Figure 11:



Engineering sample battery Switch with Cd-plated (yellow) metal surfaces prone to whisker formation (Courtesy of NASA GSFC)

Figure 12:

Scanning electron microscope image of a Cd whisker in battery switch (Courtesy of NASA GSFC)

Works referenced

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4. Zimmerman, A.H. (1982). *Short-circuit formation during NiCd cell reversal*.