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Transition Metal Electrical Connectors Theory and Use

1st Edition - 2025

NiobiCon™

by

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Table of Contents

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Table of Figures

Prologue

This book is a compendium of the present-day knowledge of the physics, electrochemistry, design, and use of connectors with niobium and other transition metal contacts. This is a very early-stage and rapidly evolving field of knowledge and practice. The information presented herein is mostly of an applied nature to enable the reader to gain a working understanding of the principles of niobium and transition metal connectors and then efficiently apply this in practice. Anyone wishing to design and build connectors using this technology should first contact Northrop Grumman Corporation for a license. Non-exclusive licenses are available for (a) manufacturing and (b) development and use.

The fundamental research and data that exists are also presented, and suggestions for areas of further research are provided. As time progresses, more fundamental academic research work is expected, and our intent is to include those results in subsequent editions. We hope that the promise of this technology will intrigue the academic community and spur them to conduct and publish research on the topic of niobium and other transition metal connectors.

The authors wish to acknowledge the funding and support provided by Northrop Grumman Systems Corporation in developing this technology. The vision of the various programs that have funded this work has allowed this technology to advance to this point of application.

Chapter 1 - Introduction

NiobiCon™ is the common law trademark name for the patented transition-metal-based electrical connector technology developed by Northrop Grumman that is the basis of this book. The use of the expression Transition Metal Connector (TMC) will be used throughout to refer to this technology. The term NiobiCon™ will only be used where it is germane to the topic of discussion or as related to patents.

TMCs are a new and unique class of electrical connectors which are intended for use in underwater and wet or corrosive environments. The characteristic that makes TMCs unique is that their electrical contacts are made from transition metals, rather than the copper-alloy contacts used in traditional connectors. Transition metals such as niobium, tantalum, titanium, and other metals and alloys have the property of generating very thin insulating oxides on their surfaces when exposed to water and this film acts an insulative barrier layer for electricity when voltages are applied. This oxide, while very thin, on the order of 100nm, is an excellent insulator and enables these metals to form protective layers by “self-insulating” themselves from a conductive electrolytic environment such as seawater. This oxide is so thin though, that even gentle rubbing will scrape off enough of the film to allow a pair of contacts to achieve direct metal-to-metal contact when mated to allow current to pass between them.

This self-insulating property of these transition metals allows an electrical connector to be produced which can operate underwater without any seals or mechanisms to keep water or other electrolytic liquids away from the contacts. Eliminating the requirement to keep water away from the electrical contacts affords a great deal of freedom in the design of a wet or underwater connector. The self-insulating property also provides intrinsic safety against electrical shock as live contacts can be touched with bare skin underwater without incurring electrical shock.

Analogy Between Capacitors and TMCs

Tantalum and niobium capacitors (a device that stores electrical energy) get their high capacitance by the development of an extremely thin metal oxide film on the outer surface of a metal created by anodizing it in sulfuric acid bath which acts as an electrolyte. Anodization is a process in which a metal such as niobium or tantalum is connected to the positive terminal of a voltage source while in an electrolytic environment with respect to a cathodic electrode in the same environment. This thin oxide film acts as the dielectric (an electrically insulative material that can support an electric field across it) in the capacitor. This same dielectric film is developed on niobium TMCs by immersion and anodization in salt water which also acts as an electrolyte. In the case of transition metal capacitors (e.g. tantalum capacitors), there are three aspects working in conjunction to produce the very high capacitance per unit volume for a given voltage that they are known for. These three aspects are as follows:

- Extreme thinness of the oxide film (2.4nm/V for niobium)
- High dielectric constant of oxide film (~26 for Ta_2O_5)
- The large area of the spongy structure of the sintered tantalum or niobium pellet

In TMCs it is the electrical insulating, or dielectric, property of the film that is relied upon to insulate the contacts from water.

General references on tantalum capacitors and electrolytic capacitors can be found through internet searches. For a more in-depth explanation of the characteristics of tantalum and niobium capacitors, the book “Tantalum and Niobium-Based Capacitors: Science, Technology, and Applications” by Yuri Freeman is available.

Origin of the NiobiCon™ Technology

Harvey Hack, having worked with wet-mate connectors and being frustrated with the expense, complexity, and cost of the then-current wet-mate connectors for high voltages, decided to design a connector that would handle high voltages and allow the contacts to be wet with seawater. His idea was to design a connector with a high seawater path resistance between the positive and negative contacts so that the contacts themselves would be exposed to only a small portion of the applied high voltage, the rest of the voltage being taken up by the IR drop (voltage loss due to electrical resistance in the circuit) through the seawater. To implement this, he needed a corrosion-resistant metal for the contacts, so he chose niobium because in his previous job as a corrosion electrochemist at the Naval Surface Warfare Center he had heard that niobium had the highest passive film breakdown potential (the voltage at which insulation fails and current passes through) of any metal. This was later proved to be incorrect since tantalum has a similar or slightly higher breakdown potential but is more expensive than niobium. In 2009, Harvey convinced Northrop Grumman Corporation (NGC) to fund a $6.8K Engineering Special Project to develop a new concept for high voltage wet-mate connectors. This project resulted in a non-working model of a 12-contact, high voltage connector (shown in Figure 1-1 through Figure 1-5) and a simple working model of a three-contact connector that used niobium contacts (shown in Figure 1-5). The intent was to form a high-resistance electrolyte path between adjacent contacts by putting the contacts at the end of long fingers that fit into holes in the mating side with a very tight clearance. Two O-rings, each with a slot, provided a labyrinthine path for current at the base of each finger, further increasing path length and therefore path resistance. Because of the tight clearance of the fingers to the holes, a hydraulic effect was expected when mating or de-mating, so the female side of the connector had passages to relieve the differential pressure, and the male contacts had a rubber tip that would seal these passages upon full mating. A cam was used to create sufficient mating force to compress the multiple O-rings and contact tip seals. Initial testing of the three-contact model indicated positive results. A Northrop Grumman invention disclosure was written and evaluated, that later resulted in US patent 9,197,006. Since this patent used IR drop to handle the high voltage, it was a different concept from the NiobiCon™ patents that subsequently followed. Harvey stopped testing because despite the long seawater path between the contacts, the contacts still developed a thin oxide film during testing that discolored them. It was later determined that this film was formed early in the exposure and that it allowed so little current to flow that the IR drop that was expected was never realized.

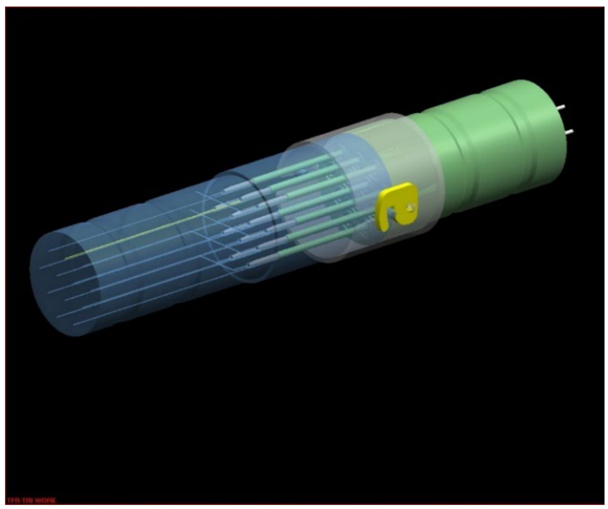

Figure 1-1 - Initial Concept for a 12-Contact IR Drop Connector Using Niobium Contacts

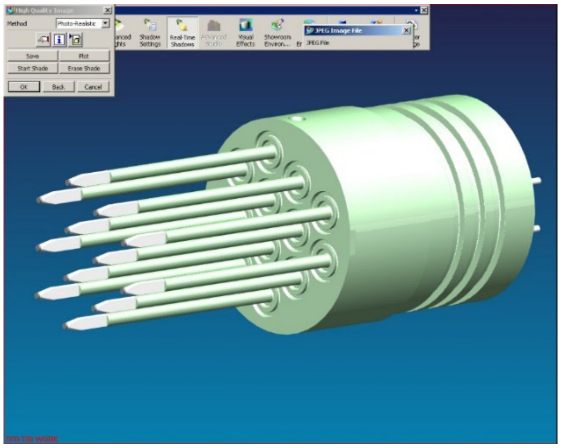

Figure 1-2 - Male Half Showing Fingers and O-Ring Grooves

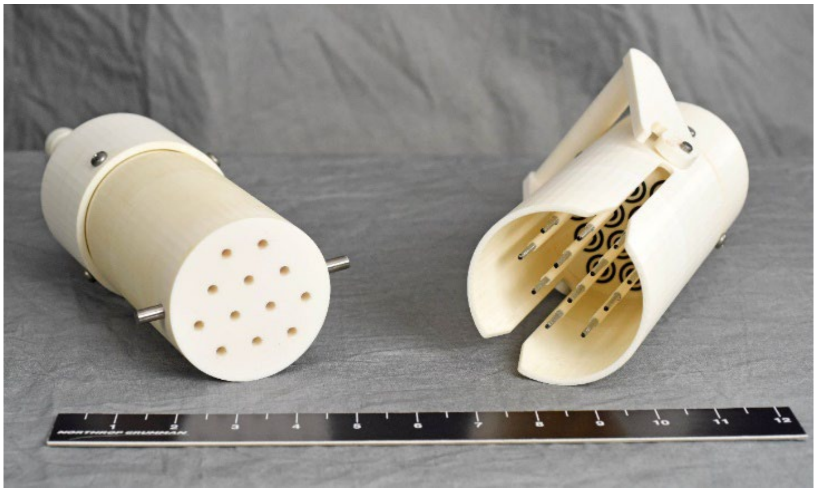

Figure 1-3 - Plastic Model of Initial Concept Unmated Showing Double O-Rings and Niobium Simulated with Paint

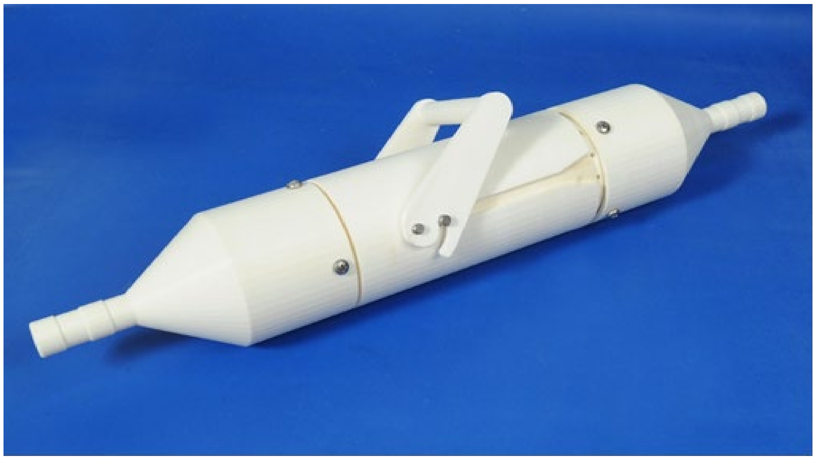

Figure 1-4 - Initial Concept Plastic Model Painted

Figure 1-5 - 3-Contact Working Model of the IR Drop Concept

The idea of TMCs came from a proposal effort that Jim Windgassen was working on in 2011 which involved the problem of how to recharge and perform data transfer from several unmanned underwater vehicles (UUV) repeatedly coming to an underwater docking station. The baseline proposal was to use an inductive charger, but the efficiency was unacceptable to Jim, and the electronics required were sizeable and carried the risks of causing electromagnetic interference with the UUV's other electronics. A simpler and more efficient means to recharge and perform data transfer from UUVs was desired.

Jim, unaware of Harvey's earlier work, had an idea unrelated to TMCs that utilized noble metals such as platinum electrodes running at very low voltages and very high currents with a loose seal to produce a wet underwater connector that would not corrode. Jim described the idea to his Northrop Grumman colleague, Harvey Hack, a metallurgist. As described above, Harvey had previously tried to make an underwater wet-mate electrical connector that relied on long narrow channels to produce high resistance and shared this with Jim. Harvey had used the metal niobium for the contacts in the hope that niobium's naturally high resistance to corrosion would avoid corrosion of the contacts. When Harvey mentioned the use of niobium, Jim thought about how an electrical device called a tantalum wet-slug capacitor operates and that tantalum and niobium are very similar materials. In a tantalum capacitor, the very thin insulating oxide is formed which becomes the dielectric for the capacitor. This same dielectric film is the basis for how TMCs work. Jim proposed that due to the extreme thinness of this oxide, it would likely be quite delicate and susceptible to puncture. Jim's enthusiasm for this idea was the key for further development and, in 2015, he and a colleague, Jeff Matejka built a demonstration unit (shown in Figure 1-6 and Figure 1-7) and US patent 9,893,460, the first NiobiCon™ patent, was issued resulting from this work. That patent had the names of Harvey, Jim, and Jeff as co-inventors. When tested, it was discovered that the concept worked extremely well, and this is what launched the development of TMCs.

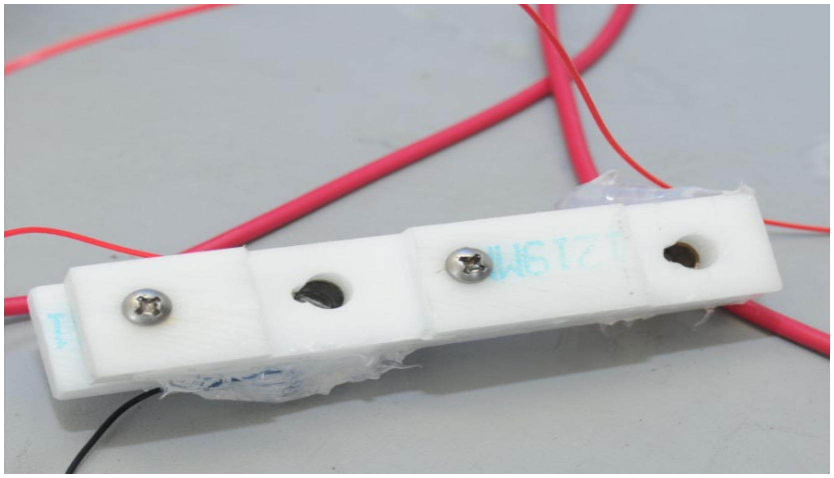

Figure 1-6 - First NiobiCon™ Concept Demonstrator, Female Half

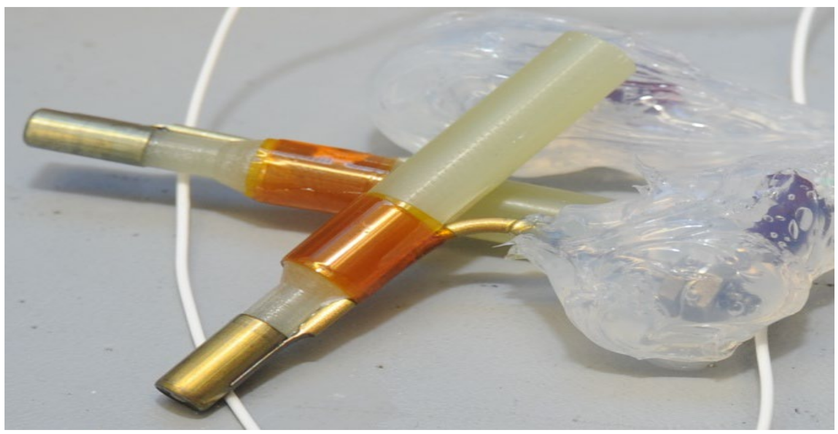

Figure 1-7 - First NiobiCon™ Concept Demonstrator, Male Half

A square connector demonstrator (Figure 1-8) was next built, funded using internal research and development funding. This connector was demonstrated at a Northrop Grumman Technical Expo where it was seen by Keith Johanns who had recently been hired for commercializing intellectual property outside Northrop Grumman.

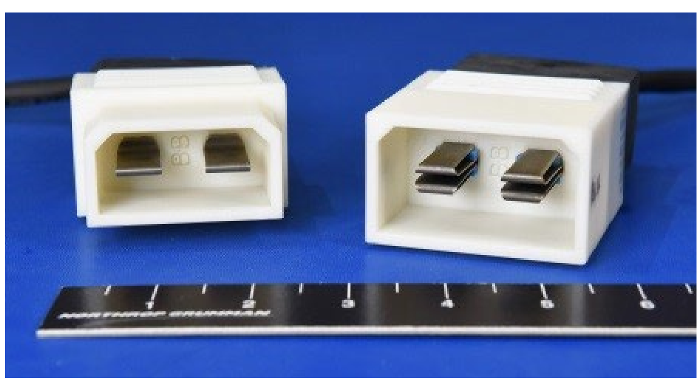

Figure 1-8 - First Demonstration Connector, Square

In 2016, another invention disclosure was written, this time for using niobium wire to transfer power underwater without the need for electrical insulation.

In 2017, an Advanced Technology Study Program was funded to further develop the concept of an underwater wet-mate connector with niobium contacts by performing the necessary electrochemistry to prove out the concept. This work eventually resulted in a niobium electrochemistry white paper and the construction of a high-power coaxial connector demonstrator (Figure 1-9 through Figure 1-11).

This early square prototype demonstration enabled Harvey and Jim to secure funding to produce a higher fidelity prototype which they then took to several internal company events where they met Keith Johanns, a colleague who was in the intellectual property group, and who was tasked with commercializing technologies developed at Northrop Grumman. The commercialization effort for TMCs then began in earnest with Keith's help. The first licensee of the technology was iCONN Systems LLC, a medium sized firm located in Lombard, IL who specializes in custom connector design.

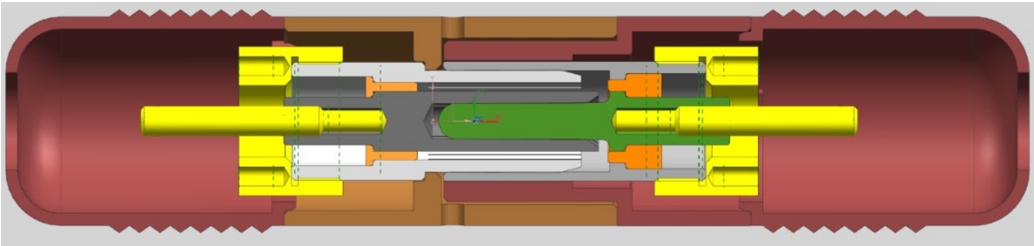

Figure 1-9 - High Power Coaxial Connector Concept Cross-Section

Figure 1-10 - High Power Coaxial Connector Demonstrator, Mated

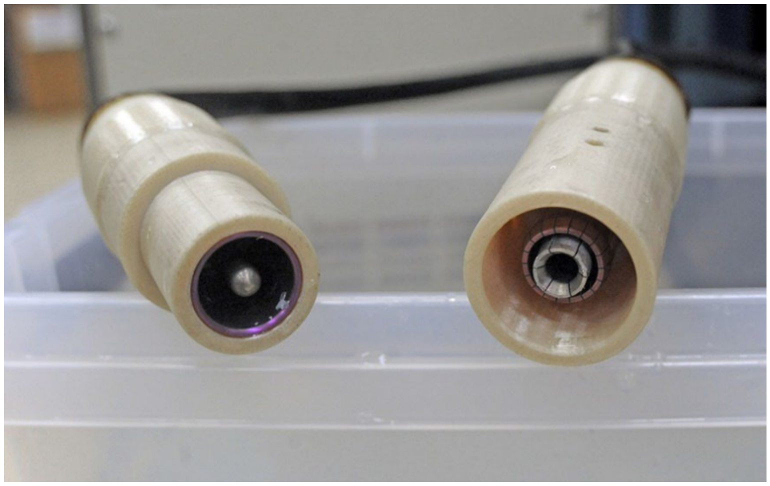

Figure 1-11 - High Power Coaxial Connector Demonstrator, De-Mated

Jim had a great idea for a demonstration using a 48 V power supply to power a light bulb through one of the demonstration connectors while the connector was immersed in a tank full of artificial seawater. This was first done with the low-power square connector and then later with the high-power coaxial connector (see Figure 1-12). Power to the connector remained on throughout the demonstration, and he was even able to touch the live contacts underwater without getting shocked. Later, he added Ethernet data superimposed over the DC power to enhance the demonstration. The details of how data over power is achieved are discussed in Chapter 4. Two portable demonstration kits were then created for traveling demonstrations (Figure 1-13).

Figure 1-12 - Jim Windgassen with NiobiCon™ demonstrator using the high-power connector

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Figure 1-13 – Portable Demonstrator Kit (one of two)

Market Applications

The potential markets for a TMC are nearly endless. The obvious use is for continuous-immersion underwater applications such as underwater electrical connectors for power and signal applications, including underwater vehicle recharging, welding, swappable batteries for diver's equipment (flashlights and electrical tools), power busses, rail-powered systems, etc. Applications in fresh water include pool and fountain motors and lighting. Applications that have intermittent immersion include boat trailer electrical systems, remote-operated vehicle umbilical, lighting sensor, and motor connections, etc. Some applications may just require a highly-corrosion-resistant connector even though they may not be immersed. These include firefighting, agriculture, transportation, external ship and boat connections, wearable fabrics, and more. Industries include offshore oil, shipbuilding, boating, pools, fountains, transportation, defense, clothing, diving, food processing and construction, amongst others.

External Recognition

TMCs are such a unique and disruptive technology in the electrical connector market that they have been recognized for their inventiveness by a variety of sources. In April 2020 the Department of Energy and the National Oceanographic and Atmospheric Administration gave this technology the Powering the Blue Economy™ Ocean Observing Prize. In November of that year SAE International awarded this technology first place in their "Create the Future" contact. In April 2021 NACE International (now the Association for Materials Performance and Protection) Materials Performance Magazine gave this technology an Innovation of the Year award and in May 2022 the Licensing Executives Society International gave the commercialization efforts for this technology their Innovation for Large Enterprises Award.

Chapter 2 - How Niobium TMCs Work

The International Union of Pure and Applied Chemistry (IUPAC) defines a transition metal as "an element whose atom has a partially filled *d* sub-shell (a type of electron configuration related to how elements bond and conduct electricity), or which can give rise to cations with an incomplete *d* sub-shell". From a practical standpoint, this is any element in the d-block of the periodic table (the central section containing transition metals) as shown in Figure 2-1.

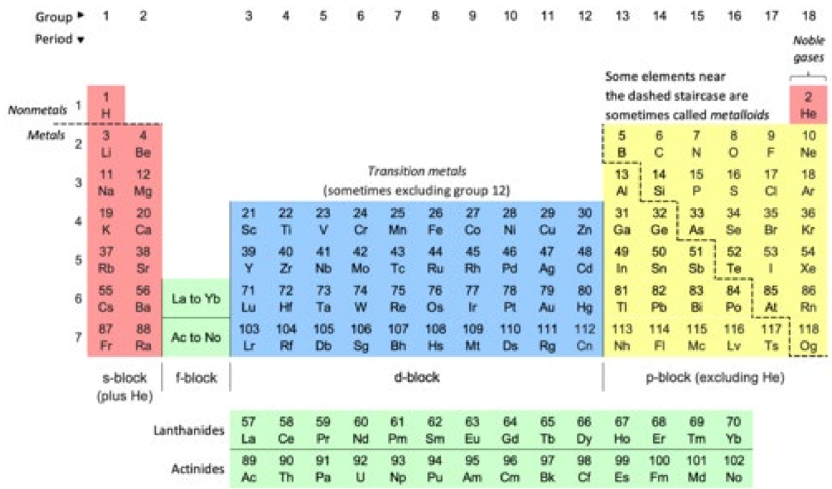

Figure 2-1 - Transition metals in the periodic table

This practical definition is not totally clear since some believe that elements in group 12, which includes zinc, cadmium, and mercury, should not be included in this classification. This is because, although they are in group 12 of the table, they each have a d shell which is completely filled with electrons. For the purposes of this book, transition metals will include any elements in groups 3-11 and not the group 12 elements. Not all transition metals are named specifically in the NiobiCon™ patents. The patents, although stating that all transition metals are covered, only specifically name the following elements as examples: niobium, tantalum, titanium, zirconium, molybdenum, ruthenium, rhodium, palladium, hafnium, tungsten, rhenium, osmium, and iridium. Some of the transition metals were specifically not named because they are not passive-film-forming elements in water or because they are impractical to make contacts out of due to expense or radioactivity. Lanthanides and actinides, although technically transition metals, are not included in this category as well.

Of all the named transition metals niobium and tantalum form passive films (thin, protective oxide layers that prevent corrosion) with the highest breakdown potentials and therefore can be used in connectors with the highest voltage ratings. Niobium is much less expensive than tantalum and so it was chosen for the initial connector designs. It is the element niobium from which the name NiobiCon™, or Niobium Connector, was derived. The name NiobiCon™ was developed by Harvey Hack as well as the logo used.

Historically, niobium and tantalum were originally thought to be a single element called tantalum after the Greek god Tantalus. Charles Hatchett (see Figure 2-2) determined that tantalum really consisted of two separate elements; the second one he named columbium after the ore columbite in which the two elements are found, but others still believed that the two elements were identical. Much later Heinrich Rose determined that tantalum ore did contain two elements, the second which he named niobium after Tantalus' daughter Niobe. Shortly thereafter it was determined that columbium and niobium were the same element. Today, IUPAC recognizes only the name niobium, but until recently metallurgists continued to use the name columbium. Today, the Charles Hatchett Award, given by the Companhia Brasileira de Metalurgia e Mineração, is given for "the best research on the science and technology of niobium and its alloys" and consists of a medal cast from pure niobium. Two minerals found in Australia are named after Hatchett, hatchettolite and hatchettine (or hatchettite).

A quote contributed to Charles Hatchett is, "Considering, therefore, that the metal which has been examined is to [sp] different from those hitherto discovered, it appeared proper that it should be distinguished by a peculiar name; and, having consulted with several of the eminent and ingenious chemists of this country, I have been induced to give it the name of Columbium."

Figure 2-2 - Charles Hatchett

Like many metals, niobium forms a **passivation** layer in water. "Passivation" refers to coating a material so that it becomes less readily affected or corroded by the environment. Many metals that we typically think of as having good corrosion resistance spontaneously grow a passivation layer by reaction with water. Examples include aluminum, stainless steel, titanium, nickel alloys, tantalum, and niobium. Passive films that form in water do so very quickly, typically in milliseconds, and the resulting films are thin enough to see through, i.e., with thicknesses on the order of tens of nanometers or less (see Figure 2-3). These films have extremely good properties as electrical insulators so they effectively insulate the underlying metal from its environment. This is what imparts corrosion resistance to the underlying materials. Passive films typically fail locally which results in corrosion phenomena such as pitting (small holes) and crevice corrosion (localized corrosion in tight gaps). A common example of this is the passive film that protects stainless steels, which can be attacked by chloride ions in saltwater. This means that stainless steels that do not corrode in fresh water can be subject to pitting and crevice corrosion in seawater.

Figure 2-3 – Simulated thickness comparison of human hair with niobium passive film (150 nm thick)

The passive film on niobium and certain other elements (titanium, nickel, etc.) is thin enough that it can be removed by scraping of mating connector contacts, allowing a direct metal-to-metal low-resistance metallic connection to be formed between mating contacts. Only the passive film at the microscopic contact points is disturbed, which is a very small area. Upon de-mating the film will reform in milliseconds. The leakage current into the water after de-mating when voltage is applied has a small peak magnitude (a few milliamps that falls off exponentially towards zero over a period of a few milliseconds as the film re-forms). This timeframe is so small that the spike in current while the film re-forms is typically inconsequential to the electronics attached to the connector. The contacts effectively insulate themselves by growing this film, preventing electrical current from leaving the contacts and going into the seawater or other electrolytic environment (where dissolved salts carry electricity via ionic conduction). This is illustrated in the video in this link: NiobiCon - How it Works - YouTube

Chapter 3 – Properties of TMCs

Voltage and Current Limits

The passive film that insulates niobium from its environment breaks down at applied voltages of somewhat over 120V. This is illustrated in

Figure 3-1. In Figure 3-1, the rapid increase in current at about 140V is due to breakdown of the seal between the niobium specimen and the apparatus (test equipment or setup) holding it, not the breakdown of the passive film (when the protective layer fails and current flows through) on the niobium.

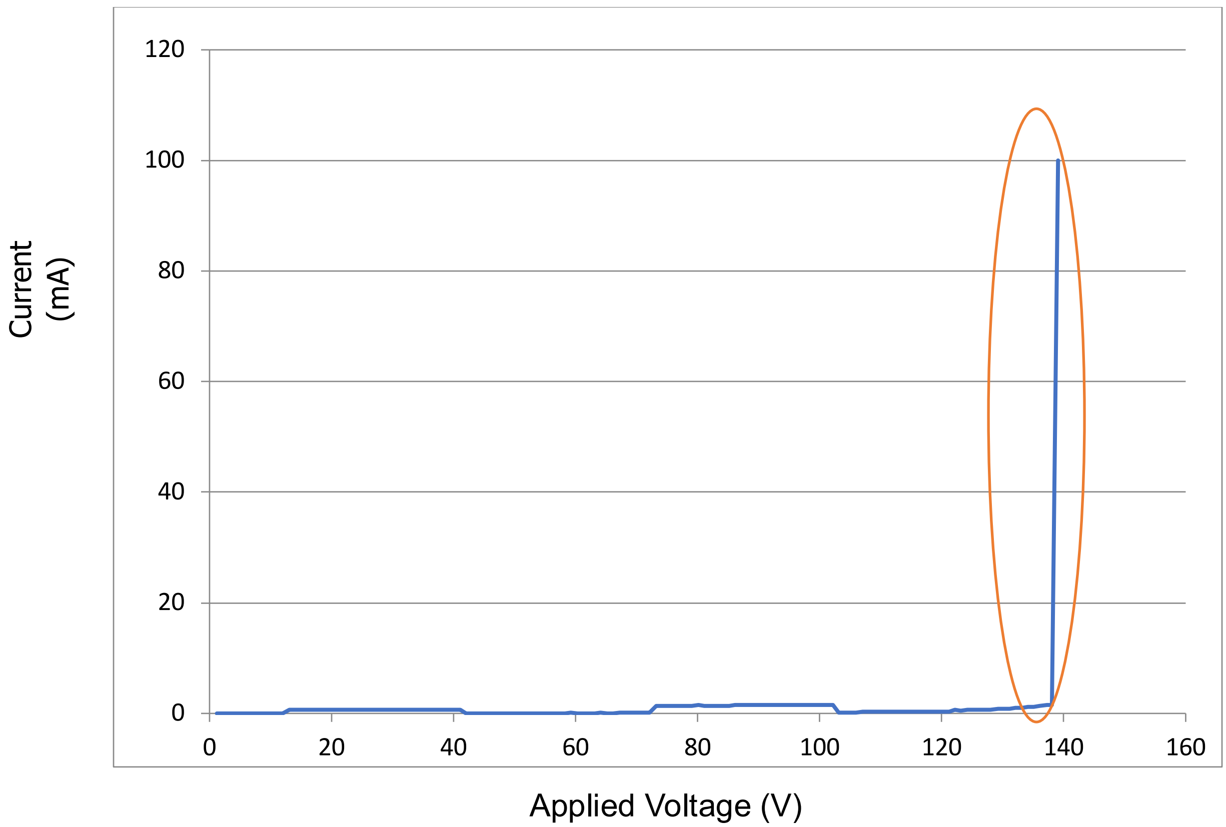

Figure 3-1 - Breakdown of part of the test fixture unrelated to the niobium occurred at about 140 V

A potentiodynamic sweep (a test that gradually increases voltage while measuring current) with greater current resolution shows no film breakdown at over 130V, see Figure 3-2. The scale on the vertical axis of this figure shows how small leakage current (small unintended current that passes through an insulating layer) is.

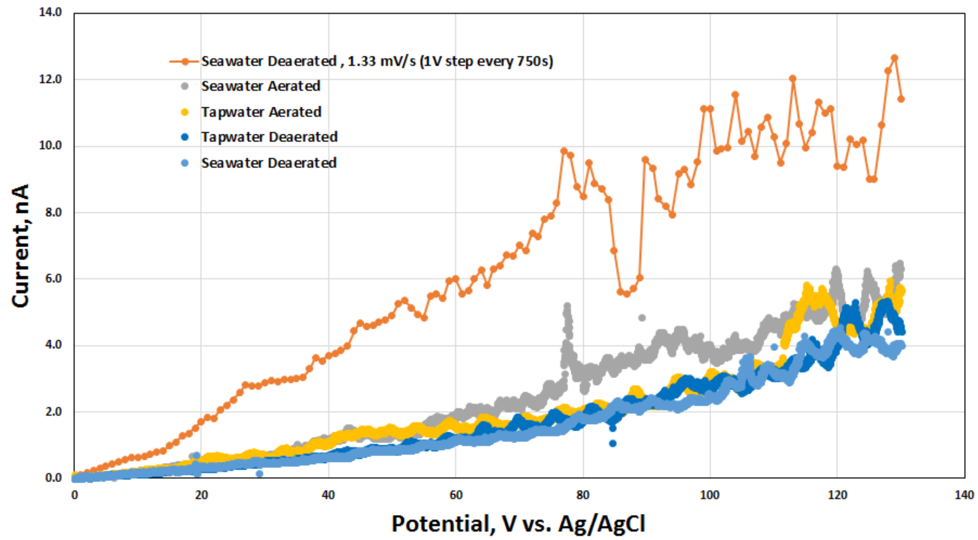

Figure 3-2 - Niobium potentiodynamic sweep at 1.43 mV/s in artificial seawater

If the specimen is held somewhat below this maximum voltage, in the case of the Figure 3-3 at about 100V, the passive film will convert to a thick, hard white oxide.

Figure 3-3 - Hard white deposit formed on niobium with an applied voltage of about 100V in artificial seawater

When voltage is increased this hard white film will eventually break down by creating a series of arcs that travel over the surface without a large current spike; in other words, the coating fails gracefully.

For these reasons and to allow for a margin of safety, the maximum voltage for niobium contacts in water is stated to be 60-75V. The authors have conducted many tests in this voltage range without ever seeing a breakdown in the passive film.

Commercially pure titanium can also be used for TMC contacts. From literature sources, the maximum voltage that can be applied to titanium contacts is around 15V, so allowing for a margin of safety, TMC contacts made from titanium are limited to applied voltages of 5-10V.

How the Film Grows

Electrochemical measurements show that the open-circuit potential of niobium in artificial seawater shifts positive over time, indicating that a protective film is growing even without any applied voltage (See Figure 3-4)

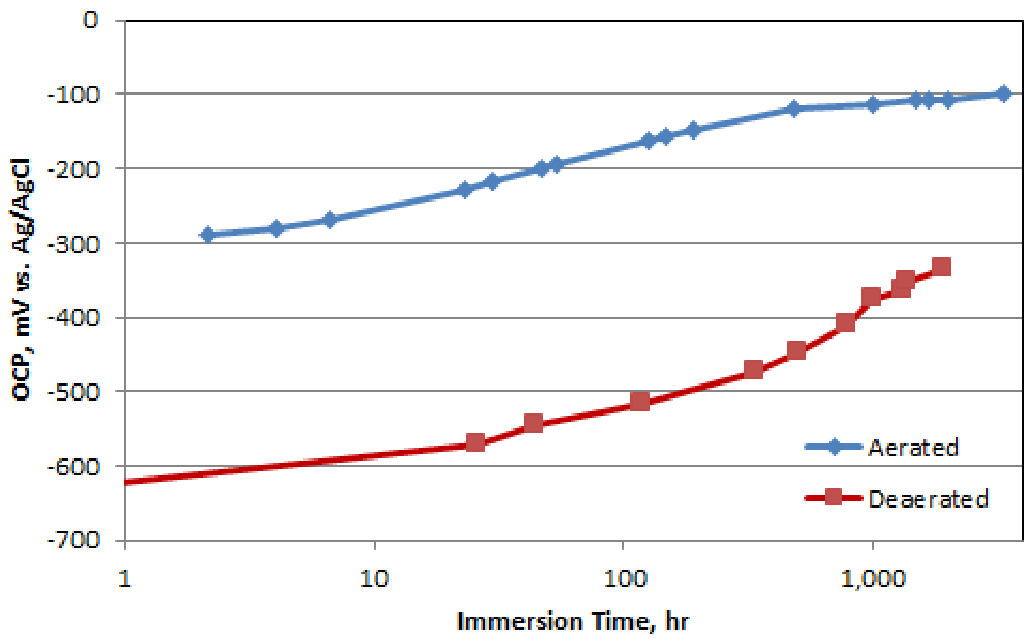

Figure 3-4 - Open-circuit potential of niobium in artificial seawater

Electrochemical Impedance Spectroscopy (EIS) (a method to measure resistance and film thickness overtime) shows that the passive film, even without applied voltage, grows, and continues to grow, over a period of thousands of hours in both aerated (Figure 3-5) and de-aerated (Figure 3-6) artificial seawater. EIS is a technique used to study the electrical properties of materials and electrochemical systems by applying a small AC voltage or current and then measuring the resulting response (current or voltage respectively) over a range of frequencies. EIS allows among other things the measurement and characterization of passivation films that grow on metals which is why it was used to study the films on metals used in TMC connectors.

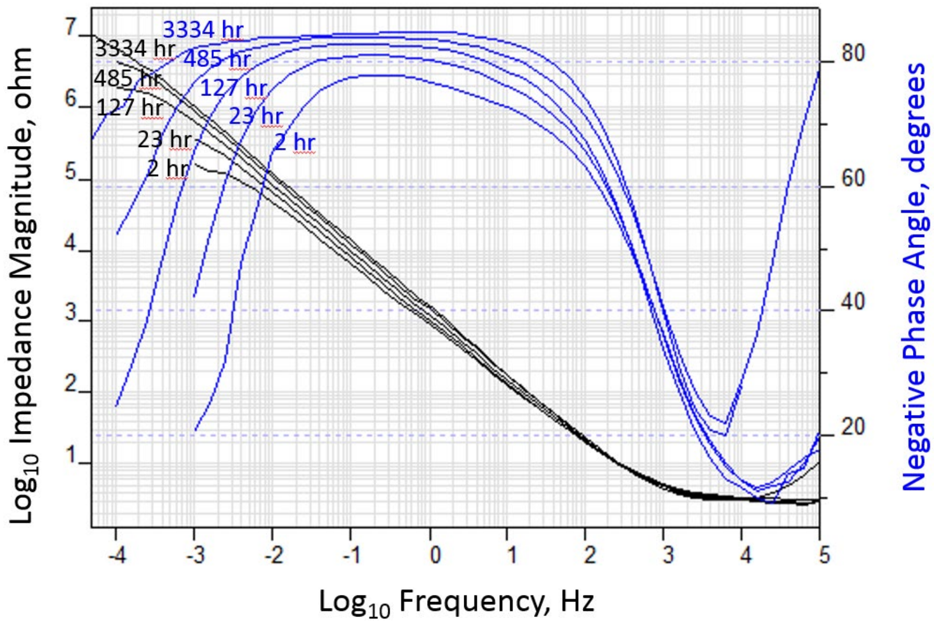

Figure 3-5 - Electrochemical impedance as a function of exposure time for niobium in aerated artificial seawater

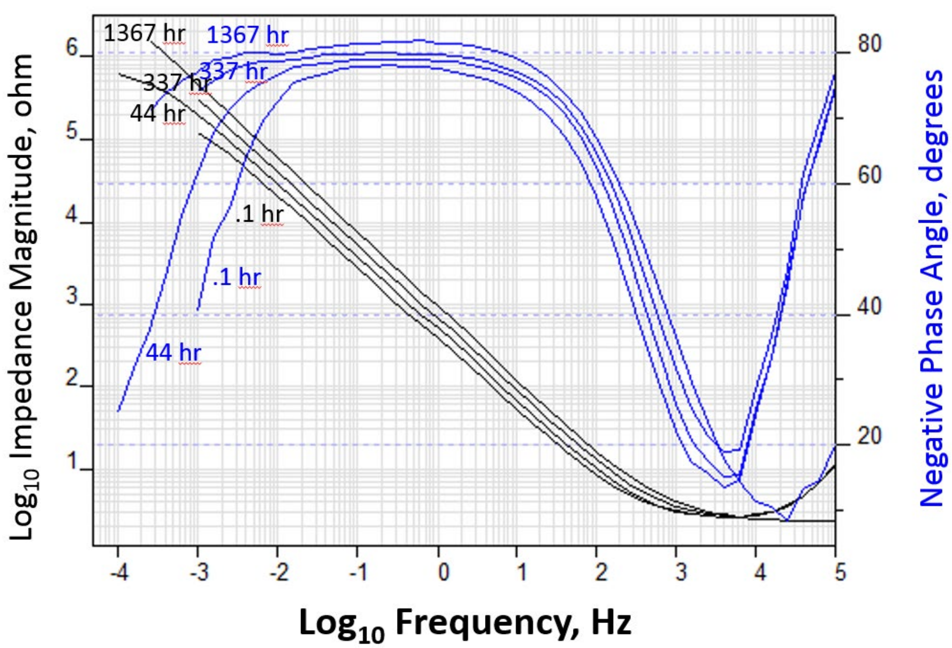

Figure 3-6 - Electrochemical impedance as a function of exposure time for niobium in de-aerated artificial seawater

This is indicated by rising impedance magnitudes at low frequencies as a function of exposure time. This data also shows that the capacitance remains almost constant over time, as indicated by phase angles not changing significantly over time. This means that the passive film does not grow in thickness over time but increases in resistance, indicating that it is becoming denser with increasing exposure time. This resistance increase is best illustrated in Figure 3-7 while the relative constant capacitance is best illustrated in Figure 3-8.

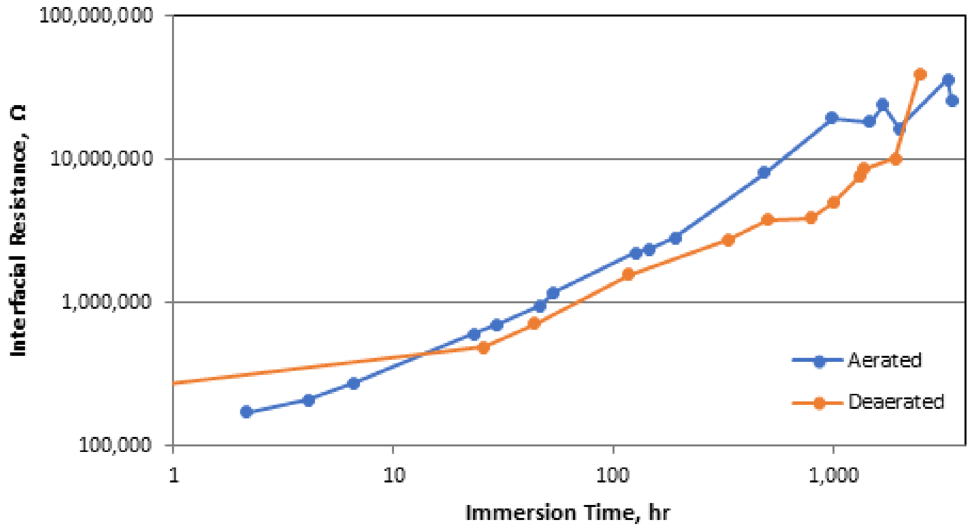

Figure 3-7 - Interfacial resistance of niobium in artificial seawater

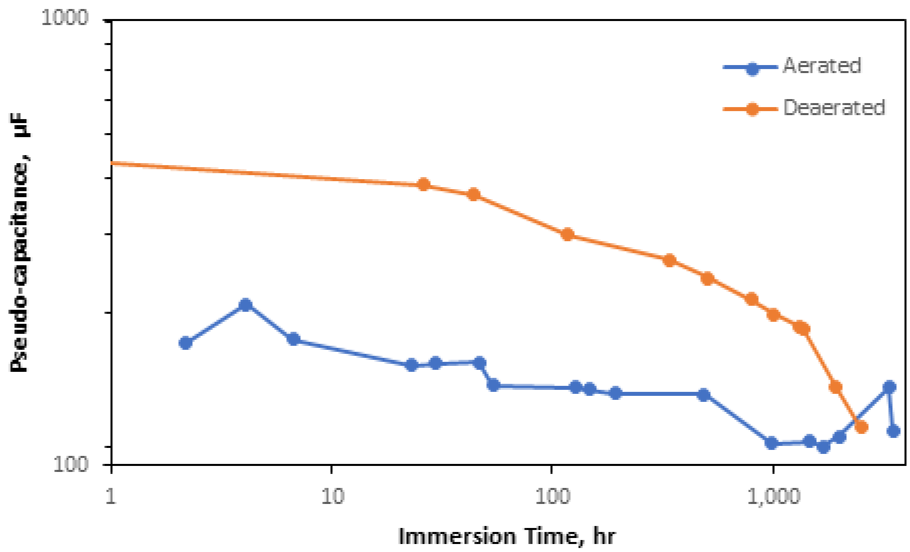

Figure 3-8 - Interfacial pseudo-capacitance for niobium in artificial seawater

Short-term electrochemical tests of niobium 1% zirconium alloy (ASTM B392, grade 3) held at 70V for several days in aerated artificial seawater did not show passive film breakdown, meaning that this alloy is usable for connector contacts in seawater along with pure niobium (grades 1 and 2). The grade 4 alloy, although having some additional impurities, also will likely be suitable for this application. The 1% zirconium alloy has significantly improved mechanical properties as compared to pure niobium. The ultimate tensile strength (maximum stress before breaking) of the 1% Zr alloy is 195MPa vs pure Nb at 125MPa. The yield strength (stress at which the material begins to deform permanently) of 1% Zr alloy is 125MPa vs 73MPa for pure Nb. These enhanced properties of the 1% Zr alloy are particularly helpful when fabricating contacts that are designed to exert spring pressure. Using pure niobium to make small contacts that must exert a spring force (pressure needed to keep two parts in contact) to maintain contact pressure can be challenging.

The Insulating Properties of the Passive Film

The insulating properties of the passive film on niobium are best illustrated by looking at the leakage current that leaves the niobium and goes into artificial seawater when the niobium has 50V applied to it. The currents in Figure 3-9 are for a specimen that is much larger than most connector contacts, about 6 square cm in surface area, and yet the leakage currents are on the order of 10 microamps and falling exponentially with time.

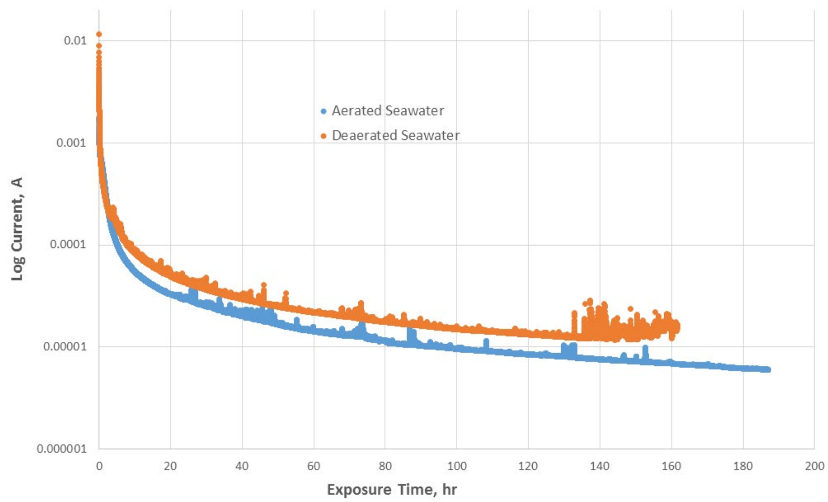

Figure 3-9 - Niobium at 50V applied potential in artificial seawater

Environmental Flexibility

Niobium contacts have been tested in various environments and its passive film will not break down below 120V in the following environments:

- Aerated and de-aerated artificial and natural seawater
- Artificial seawater at temperatures near boiling and near freezing
- Aerated and de-aerated fresh water
- Simulated cattle urine

As stated earlier, wet-slug tantalum and niobium capacitors create a similar passive film on these metals by immersing them in sulfuric acid. For this reason, these metals should self-insulate in strong acids as well. Testing in alkaline environments has not yet been performed, but literature studies lead to the belief that the passive film will break down in strong alkaline environments such as a solution of sodium hydroxide. The pH above which this would occur has not yet been determined, so weak alkaline environments may still allow contacts of these metals to perform their insulating function. Formation of a similar passive film in a capacitor is illustrated in Figure 3-10.

Figure 3-10 - How a passive film is used in a tantalum capacitor to create capacitance (source: Wikipedia)

Design flexibility

Because the contacts of a TMC connector can get wet there is no need to exclude the surrounding environment from the contacts. Therefore, these connectors need no seals (O-rings, gaskets, molded rubber) or dielectric oils (with oil bladders). The only mechanical requirement for these connectors is that the contacts have a slight scraping motion and enough contact pressure to remove the passive film upon mating. This means that tolerances can be much looser on this type of connector than on a traditional connector that may use O-rings or oil bladders. Looser tolerances result in lower production cost. Since the contacts need no protection from the environment there may not even be a need for a connector body or shell; all that is really needed in some cases is the contacts. Since the contacts are made from metal there is nothing compressible in the connector, meaning that for underwater use this technology is essentially independent of depth pressure. Also, only the positive (anodic) contact needs to be made from the transition metal; the negative (cathodic) contact can be made from any conductive material that is corrosion-resistant in the environment. This design flexibility can lead to rather unique geometries which will be discussed later in this book.

High voltage polarization of niobium compared to other transition metals

Electrochemical polarization testing was performed in a Gamry electrochemical cell (a setup for testing electrochemical reactions) using a 1 N Ag/AgCl reference electrode (an electrode used in electrochemistry that has a stable and well known electrode potential), a graphite counter electrode (completes the circuit), and a cylindrical specimen holder. Since standard potentiostats can’t apply more than 10-20 volts and are designed for much lower voltages than this, a Keithley SourceMeter® model 2450 was programmed to act as a high voltage potentiostat using a slightly modified version of Keithley’s electrochemistry software package (2450-EC) that can be run on the unit. The Keithley SourceMeter® 2450 can output up to 200V, which allows for the full range of testing on niobium. The test environment was Instant Ocean® artificial sea salt mixed with tap water according to manufacturer’s recommendations for the niobium and niobium-1% zirconium, and 3.5% NaCl in tap water for the other tests.

The specimens were first prepared with 400-grit abrasive paper, their dimensions measured and then placed in the test cell. They were allowed to equilibrate for 1 -1.5 hours while the test solution was aerated using a fish tank air supply and a bubbler. They were then polarized, starting at 0V vs. the reference cell and ramped anodically (gradually increased voltage in the positive direction) to 150V vs. the reference cell at a ramp rate of 10mV/sec, with a maximum current limit of 100mA. This allowed a test to be completed in less than one day. Testing was performed at room temperature.

The results of the polarization (testing electrical behavior by varying voltage) measurements are shown in Figure 3-11 through Figure 3-17.

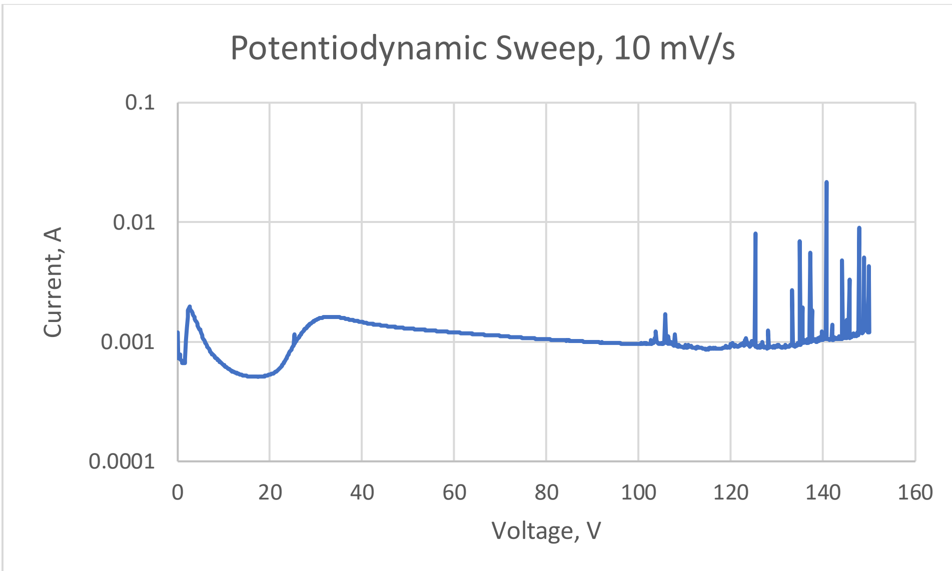

Figure 3-11 – Polarization Data for Nb, First Run

Figure 3-11 shows that the leakage current is well below 1 mA for niobium. The passive film doesn't break down below 110V since the current remains low. The current shows spikes above 110V, indicating that the passive film, although briefly disrupted, reforms and the current returns to low values. There is no sharp current increase as voltage increases, possibly because the scan rate is high enough to give insufficient time for film breakdown to occur. At sufficiently high voltages, the current increase is likely due to oxygen evolution, and gas bubbles were first noted on the surface of the specimen above 110V and covered the surface in a continuous sheath at 140V. Current noise near the end of the test is likely due to these bubbles. In previous studies, the passive film in niobium was shown to continue to increase in resistance over time after it initially forms. The current increase at higher voltages could therefore indicate that the film resistance doesn't have sufficient time to increase enough at the high scan rates used in this test to prevent current leakage and bubble formation. Slower scans may therefore not show this current increase. This is especially true since previous potentiostatic studies do not show this current increase at higher voltages. This provides support for the need to precondition niobium electrical contacts that will be used in corrosive environments.

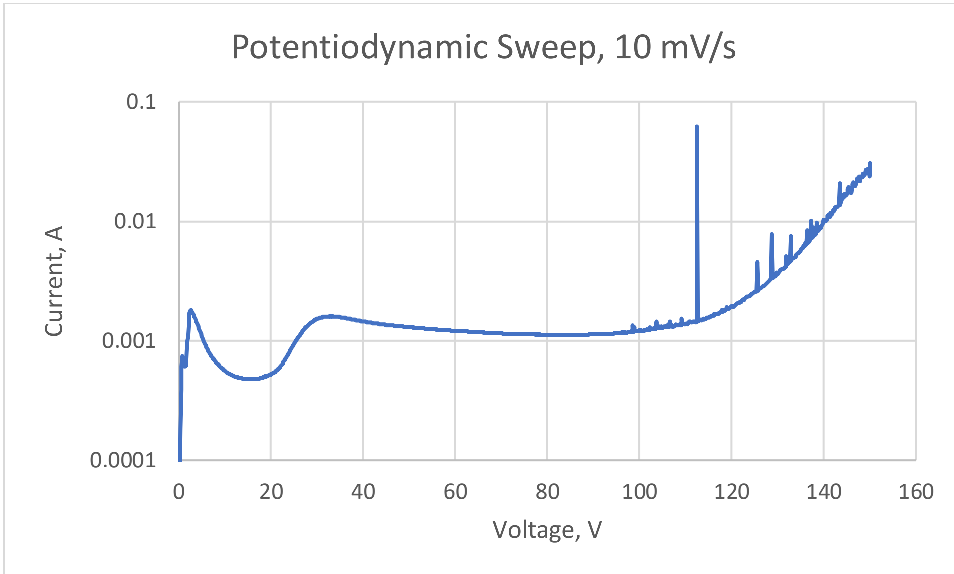

Figure 3-12 – Polarization Data for Nb, Second Run

Figure 3-12 shows a repeat of the first run. Here the passive current is a bit higher, but still at around 1-2 mA. The current spikes begin at a lower voltage than in the first run, 95V, but with the first major spike at around 115V. As in the first run, the current spikes are brief, indicating that the surface re-passivates after the brief corrosion event. Re-passivation is a good thing in that it means that if the passive film is disrupted by mating forces on electrical contacts it will reform quickly at the indicated voltages. Bubbles started forming at around 76V and the current instability at around 140V or above is likely due to these bubbles, as in the first run, however the current plateau at close to 100 mA was never reached, indicating that the film resistance at the higher voltages was higher in this second run.

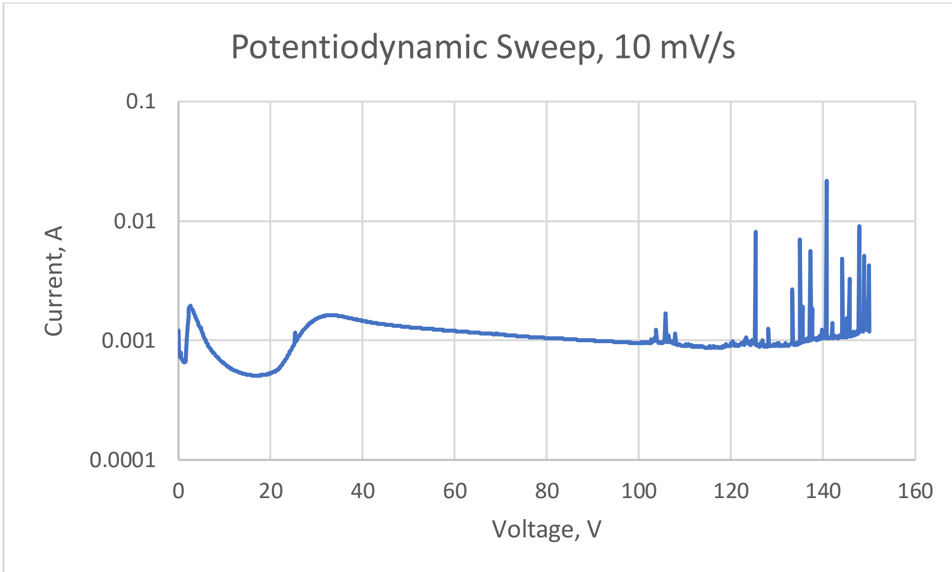

Figure 3-13 – Polarization Data for Nb-1%Zr

Figure 3-13 shows the polarization behavior for the niobium-1% zirconium alloy. Passive current is similar to that of pure niobium at around 1 mA. Current spikes start at about 105V but, as with pure niobium, the surface re-passivates quickly. There is less increase in current at the highest voltages, indicating that the passive film is likely more resistive than that of pure niobium. This could mean that the film develops more quickly than that on pure niobium, in which case slower scans would give more time for the film to develop higher resistance at higher voltages for pure niobium but have no effect on this alloy. Bubbles started streaming from the specimen at around 28V, however bubble generation slowed over the test, with only minor bubbling being evident at 84V and above. It is possible that something caused an area to de-passivate at around 20V and it took some time for the passive film to develop enough resistance to inhibit bubble formation.

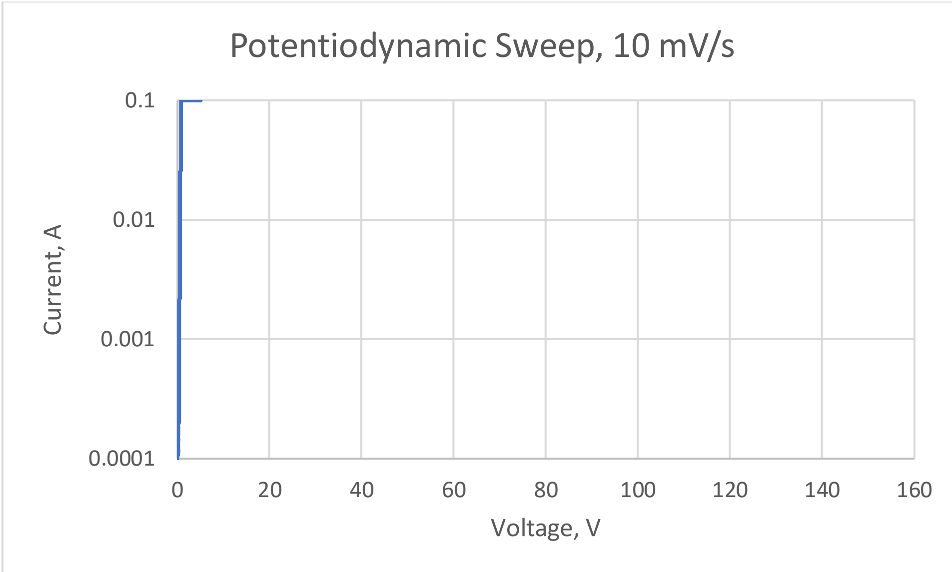

Figure 3-14 – Polarization Data for Zr

Polarization behavior of pure zirconium is shown in Figure 3-14. The current rapidly reached the limiting value set at the potentiostat of 100mA, at a voltage of +900mV. The test was stopped early at 5.0V. The specimen showed significant scattered pitting at the conclusion of the test. This means that the passive film that forms on pure zirconium is not very resistant to applied voltages and this material would not be a good choice for powered contacts in corrosive environments.

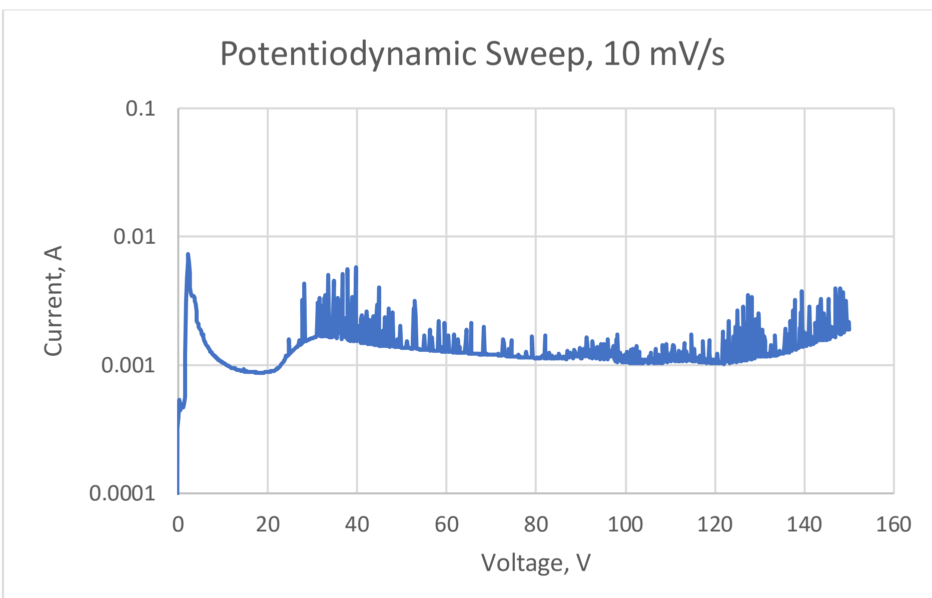

Figure 3-15 – Polarization Data for Ta

Polarization data for pure tantalum is shown in Figure 3-15. Tantalum was expected to behave like niobium due to its similar chemical behavior, and that is what happened in this test. In fact, the leakage current on tantalum at 150V was more than an order of magnitude less than that on niobium at the same voltage, indicating that this is electrochemically a better material to use for underwater contacts than niobium. However, the current was noisier for tantalum than for niobium. The reason for this is unknown, however the noise magnitude is low enough that it should not affect the operation of an underwater connector with tantalum contacts.

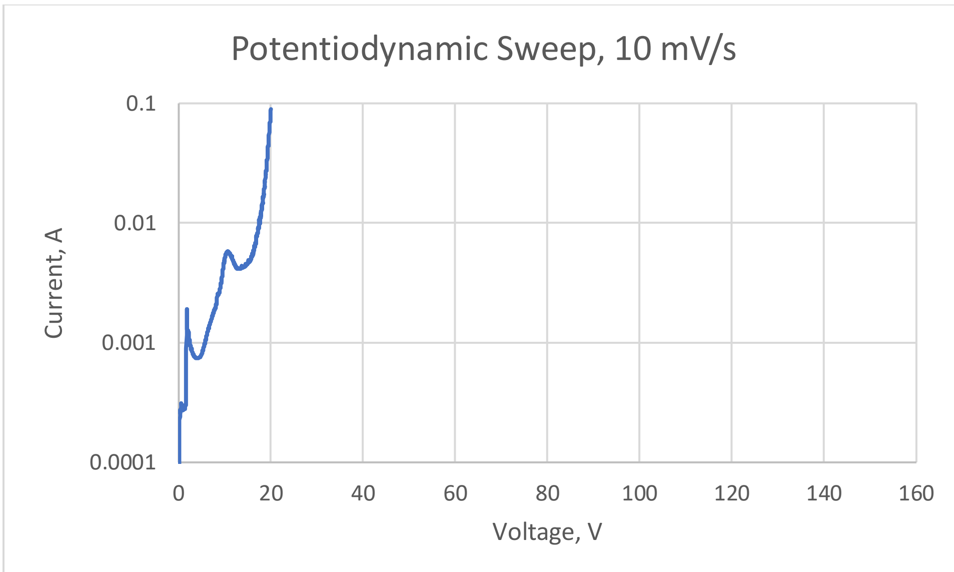

Figure 3-16 – Polarization Data for Ti

Polarization data for commercially pure titanium is shown in Figure 3-16. Titanium experienced several secondary passivation reactions as evidenced by valleys in the curve, however the final breakdown was at around 15V. The test was stopped early at 20V. Titanium can perform well as wetted contacts provided the applied voltages are low, no more than 5-8 V.

Polarization data for pure tungsten is shown in Figure 3-17. The peaks at 30 and 40 V are due to brief test interruptions.

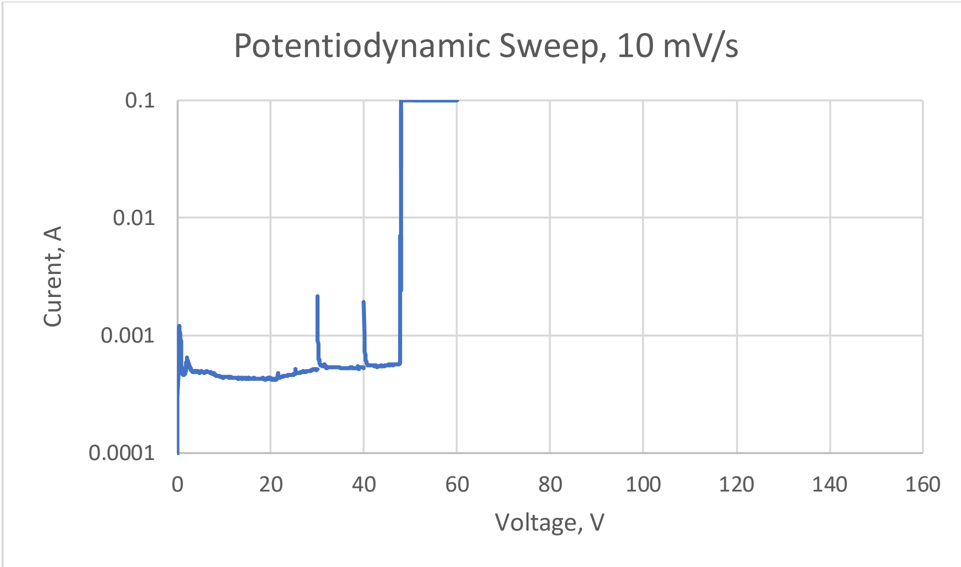

Figure 3-17 – Polarization Data for W

Tungsten was so brittle that it couldn't be threaded without cracking the specimen. As a result, it was tested in rod form with the end of the rod inserted into the solution about the same distance as the height of the specimens of the other materials. This means that the tungsten specimen had a waterline effect but no crevice effect from a mounting gasket as was the case for the other materials. Tungsten experienced a rapid breakdown at 48 V.

The test results support the assumption that the breakdown potential for pure niobium is over 120V in seawater. The tests showed that the niobium-1% zirconium alloy had a breakdown potential similar to, or greater than, pure niobium, making it a good candidate for a connector wet contact material, especially since it has a higher yield strength than pure niobium, making it "springier" than the pure metal. Pure tantalum also had a high breakdown potential, which would be expected given its similar chemical behavior to niobium, and lower currents at the highest voltages. It would make a good, although expensive, wet electrical contact material. Zirconium hit the hardware limiting current early in the scan at well under 1V, making it unsuitable for electrical contacts in seawater. This was a surprise given its position on the Periodic Table close to niobium and its beneficial effect as an alloying element in niobium. Titanium had a breakdown potential of about 15V, as expected based on previous studies in the literature, making it a useful contact material for low-voltage applications. Tungsten had a fast breakdown at 48 V. Given the difficulty in machining tungsten, it is unlikely that it can be used in an underwater connector, although it should perform well at voltages well below its breakdown potential.

Chapter 4 – Power and Data Transmission Across TMCs

Power Transmission

Transmission of low to medium power levels power across TMCs presents little challenge, however as the amount of power increases there are challenges that can be greater than for traditional connectors. The biggest challenges stem from the fact that the materials used for contacts in TMCs have higher resistivities than the copper-based metals traditionally used for connector contacts and have lower thermal conductivities than traditional contact materials. In addition, high power transfer must be achieved using high currents due to the upper voltage limits of TMC's.

The underlying pure metal body of a solid niobium or other transition metal contact conducts less efficiently due to its lower electrical conductivity than traditional contact materials such as copper, and this is exacerbated with the higher surface resistance of a TMC than is present with traditional noble metal gold-plated contact. This results in a higher resistance of the metallic path through a TMC than through a connector using traditional contact materials. In many electronic applications this higher contact resistance creates no issues, however in power transmission this extra resistance creates extra heat. It becomes harder to reject this heat to the surroundings because the thermal conductivity of the contacts is also much lower than traditional copper alloys. To overcome these issues TMC contacts must be larger than traditional contacts and creative methods of removing heat may be required, especially for operation in air. Operation in water may not be as affected by heat generation due to cooling effects of the water. Overcoming thermal issues will be discussed in a later chapter.

DC Power Transmission Methods

Demonstration connectors have been constructed to transfer direct current (DC), including various small connectors which will be illustrated later, a high current coaxial connector which has been operated at up to 55A and 50V for a power level of 2.75kW (shown in Chapter 2), underwater continuously powered open rails, an underwater single contact with a seawater ground return path, and underwater dynamic sliding contacts. These latter three are illustrated in Chapter 9.

AC Power Transmission Methods

The passive film that forms on niobium in water forms only on the positive, or anodic, contact, whereas any film that may be on the negative, or cathodic, contact is reduced and is no longer protective. This means that if the polarity of contacts reverses then it will take a few milliseconds for the previously negative contact to form this insulating film, resulting in a small spike in leakage current. For alternating current (AC), the continual reversal of polarity results in leakage of current through the water. In addition to the electrochemical issues, the capacitance formed across the oxide film allows an AC current to flow through the water via the capacitive reactance. This makes the passage of AC through TMCs not practical. AC can, however, be superimposed on top of direct current (DC) if the magnitude of the AC signal is less than the DC voltage, meaning that the polarity of the contacts will never reverse so the passive film doesn't' need to continuously re-form. When AC is passed through the contacts by superposition over DC, the AC peak-to-peak voltage must not be allowed to exceed the DC voltage and the superposition of the maximum AC peak voltage and the DC voltage must never be greater than what the passive film can handle, typically 60-75V for niobium.

Although alternating current can't be passed directly through niobium contacts, there are methods that can allow AC to pass by turning it into a changing DC signal on one side, sending it through the contacts, then turning it back into AC on the other side. This method is called the "synchronous un-rectifier" and it is the subject of US Patent 11,005,390. There have been no connectors built to date that can pass AC, but the theory on how to do so is sound. The idea behind this patent is to rectify incoming AC voltage using a full wave diode bridge rectifier to turn the AC voltage into a series of pulses at twice the incoming frequency which only go from 0V to Vpk, thus maintaining one TMC contact anodic with respect to another contact which is cathodic. On the receiving side, once past the TMC contacts, a full bridge circuit fed with these pulses comprised of 4 transistors is toggled by a flip-flop circuit. This circuit effectively un-rectifies the pulses back together to form AC again.

Some very limited research has been done by the inventors that indicates that AC power passed over niobium contacts could result in a minor inequality of performance of the two opposite contacts resulting in a form of rectification which could preserve the passive film selectively on one electrode. At this point this is just conjecture, however. The test that was performed was as follows: A pair of bare metal niobium contacts (sanded down to bare metal) were placed into a beaker of salt water and connected to a variable AC source with an incandescent light bulb acting as a current limiter in series. The AC voltage was raised slowly and the amount of current flowing through the niobium contacts was monitored. When the AC voltage source was applied, current would initially flow freely causing the light bulb to light and the current was limited by the increasing resistance of the hot filament. Over a period of a minute or two, the current would begin to drop, and it was noted that one of the two niobium electrodes would begin to take on a color indicating that it was developing an oxide film. After some time had passed, the current would drop precipitously to a low level of some milliamps. The milliamps of leakage currents noted at the end of the experiment is most likely a combination of the reactive current flowing due to the capacitance across the film plus a real component flowing through the passivation film itself as it forms and breaks down with the alternating voltage. Further measurements would be needed to verify and quantify the real and reactive current flows. No corrosion of either of the two niobium electrodes was noted. More research is needed to understand the electrochemical effects being seen, and to determine if there is a way to improve upon them to produce a useful effect that is suitable for making a practical AC power connector.

Another issue with passing AC through TMCs is that the very thin passive film acts like a high-value capacitor; this is very similar to how a wet-slug tantalum capacitor functions. Capacitors offer a low-impedance path for high frequency signals, so at high frequencies any AC signals transmitted through TMCs will be shorted out. Recall that the impedance of a capacitor is:

$$Z = \frac{1}{j\omega C}$$

where

$$\omega = 2\pi f$$

The impedance of a capacitor falls as the inverse of frequency. A method to avoid this by creating electrolyte path resistance between the opposing contacts will be discussed in Chapter 5.

Data Transmission

Data can be transmitted over TMC connectors if they are designed appropriately. RS-422 serial data, ethernet, USB, and RF modulated onto power (powerline data comms) have all been demonstrated on connectors using NiobiCon™ technology. There are however some design considerations and caveats that must be considered to be successful.

Figure 4-1 and Figure 4-2 illustrate construction of a USB-A connector with niobium contacts. This connector will function while flooded underwater in brackish water (up to 50% of the salinity of regular seawater) but will not function in full strength seawater due to the capacitance between the contacts disrupting the controlled impedance required for USB. This connector prototype does not incorporate baffling features to mitigate the capacitive loading effects (discussed later). A purpose-built connector incorporating baffling features would be able to function in full strength seawater.

Figure 4-1 - USB-A NiobiCon™ connector

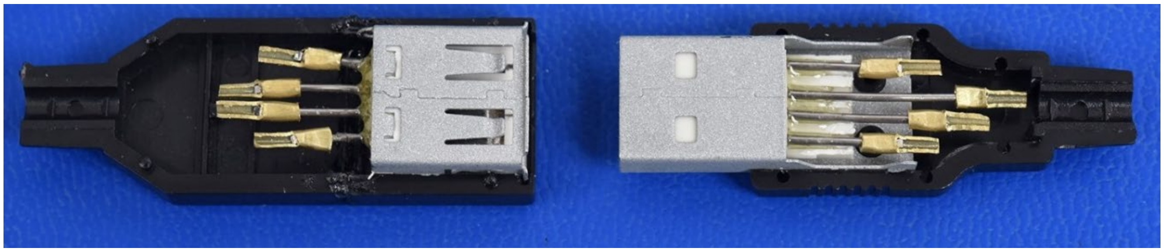

Figure 4-2 - Construction of a USB-A NiobiCon™ connector

Simplified Electrical Model of a TMC Connector in an Electrolyte

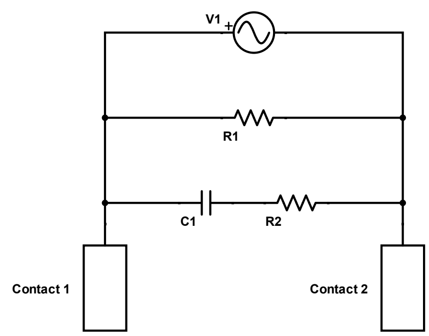

Figure 4-3 - Simplified Electrical Model of a 2 Pin TMC Connector in an Electrolyte

Capacitance Effects

Capacitance increases when the gap between two conductors gets smaller. This means that a TMC contact with a very thin insulating film separating the contact metal from the electrolytic environment will have a high capacitance per unit area. Since capacitors block DC but will pass AC of sufficiently high frequency, high frequencies that are passed through TMCs when immersed in a conductive electrolyte such as seawater can be effectively shorted-out through the film and surrounding electrolyte. This effect can inhibit TMCs from carrying high frequency AC signals.

The frequency where AC shorting will become an issue decreases as the capacitance increases, meaning that at when the film is formed at low applied voltages where it is thin the frequencies of concern will be lower than for contact with a film formed at higher voltages. The frequencies of concern will also decrease as the wetted surface area of the contact increases. This means that to maximize the frequencies below which this becomes a problem contact should be small and the film should form at the highest safe voltage.

Another method of defeating the capacitance effect is by adding electrolyte resistance between contacts carrying opposite sides of the AC. This can be done by increasing resistivity of the electrolyte. That means that this is far less of an issue in pure water than it is in seawater. Path resistance can also be increased by adding non-metallic baffling to increase current path length and decreasing current path cross-sectional area through the electrolyte.

The resistance through the electrolyte path is:

$$R = \rho * L / A$$

Where: R = electrolyte path resistance, ohm

ρ = resistivity of the electrolyte

L = the length of the path that the current travels through

A = the cross-sectional area of the path that the current travels through

This means that the electrolyte path resistance can be increased by making the path that the current must travel between opposite polarity contacts as long and as narrow as possible.

Another way to avoid this issue, especially when frequencies are at or above the limits for copper conduction to be optimal is to use fiber-optic connections in parallel to the TMC power connections. The biggest issue with typical underwater fiber-optic connections is the need for the mating halves of the connector to be in exact alignment so that the fiber ends are perfectly aligned, and there can be no intervening electrolyte which could block the light signal due to turbidity. These issues are overcome by combining TMC power transfer with free-space optical data transfer, as mentioned in US Patent 11,038,594: Self-insulating high bandwidth connector. Such a device has been built using off-the-shelf free-space optical transceivers which have been hardened to withstand high pressures and seawater exposure. The transceivers are powered by the TMC contacts and are only fractions of a cm in size.

To date capacitance has not been an issue in passing video signals over TMCs in seawater, even with large contacts, and RS422 data rates can be achieved in seawater, however passing USB rate signals over USB-A TMCs was not possible in full strength seawater, although it was achieved in 50% brackish water. Modifying the connector housing to add baffles to create a resistive seawater path between the contacts to remove the loading effects of the capacitance would likely resolve this issue and allow the USB connector to function in full strength seawater.

Figure 4-4 - TMC Connector Incorporating Plastic Baffles to Increase AC Impedance

Combination Power and Data Connectors

It is possible to send both power and data across a single pair of TMC contacts simultaneously with ease. In this method, an RF signal is superimposed on top of the DC voltage being used for power. A high-level methodology for how this is accomplished is shown in Figure 4-5 below.

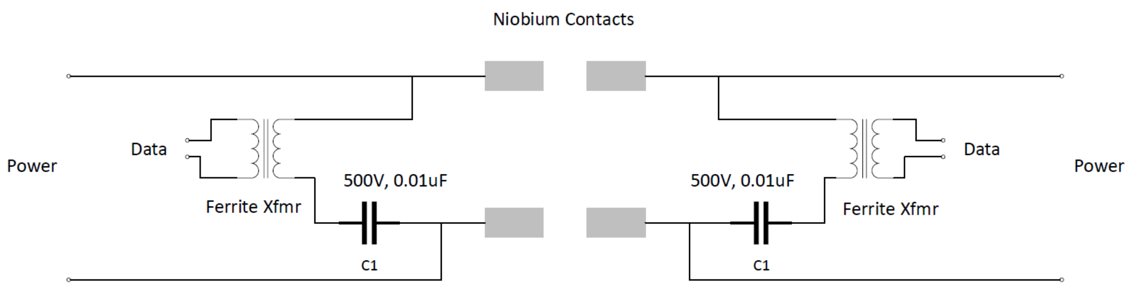

Figure 4-5 – How to Superimpose RF Across a Two-Pin Power Connector Carrying Power

In Figure 4-5 above, a modulated RF signal is differentially injected via a small ferrite cored transformer which is AC coupled through a coupling capacitor. This signal is then stripped off on the receiving side by using the same arrangement in reverse.

Superimposing RF on top of power (either DC or low frequency AC) is a technique that has been used for decades. A contemporary example of this is a powerline ethernet adapter commonly used in homes to send ethernet traffic across a home's mains wiring as an alternative to running a dedicated Ethernet cable. These devices employ IEEE standard 1901 protocol to allow for up to 500 Mbps (as of 2024) speeds over mains wiring. There are many manufacturers of these devices, and they are available for less than $100 per pair. Some exemplar powerline to Ethernet adapters are shown in Figure 4-6.

Figure 4-6 – Example Powerline to Ethernet Adapters Manufactured by TP-Link®

Commercial powerline to Ethernet adapters are designed to run off AC mains voltages (120VAC, 60Hz in the USA, and 220VAC, 50Hz in other parts of the world). A useful discovery about these devices is that all the units that Jim, one of the authors of this book, has tested, work well on as low as 48V DC power with no modifications. The power supplies in these devices are typically a simple full wave bridge rectifier feeding a capacitor which then feeds a flyback type converter. Flyback type power converters can handle very large input voltage ranges. This property of being able to be used directly with lower voltage DC power means that a high-performance data system can be constructed at a very low cost.

There are other devices available that can perform powerline to Ethernet data as well such as boards available from Blue Robotics® and RAK™ Wireless. These devices are shown in Figure 4-7 and Figure 4-8.

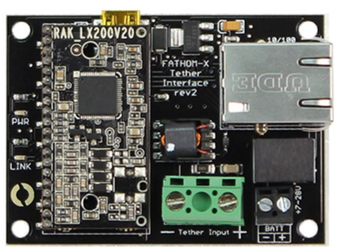

Figure 4-7 - Blue Robotics® Fathom X™ - 65 x 47mm

Figure 4-8 - WisLink PLC™ LX200V50 EVB – 1000 Mbps

When using these devices on a DC power-based system, there are several things to consider in order to maximize their performance. The first thing to consider is that many DC systems appear as an RF short circuit to differential mode signals due to the capacitors used and can also cause unwanted side effects due to the presence of other components across the positive and negative terminals of power supplies and loads. A simple means to mitigate the effects of the tendency of these capacitances to short out or otherwise disrupt the RF signal is to insert an RF choke at the output of the power supply and at the load, as close to the powerline to ethernet converter as possible.

An arrangement showing the two RF chokes inserted in a TMC application using powerline to Ethernet converters is shown in Figure 4-9, *Note that the RF choke is placed as close to the powerline to Ethernet adapters as possible to minimize RF reflective stubs which will be discussed later.*

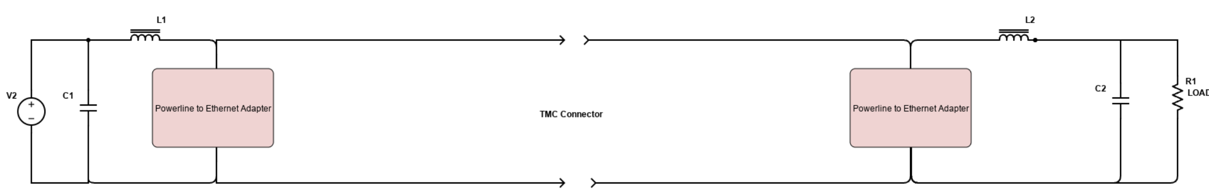

Figure 4-9 - Illustration of Using RF Chokes to Block Disruption of RF Over Power in a TMC System

A suitably sized RF choke will produce a high impedance to the RF signal while allowing the DC power to pass unimpeded. Typical RF frequencies used by powerline to ethernet adapters are 2-30MHz, and a minimum impedance of around 500 ohms at the low band has proven sufficient to provide good RF isolation.

Recall that the impedance of an inductor is:

$$Z = j\omega L$$

where

$$\omega = 2\pi f$$

For a given inductance, L, the impedance Z increases linearly with frequency. An RF choke with an inductance of 40µH has been successfully used to optimize the performance of an off the shelf powerline to Ethernet converter used in a 48VDC power system. A 40µH inductor produces an impedance of 500 ohms at 2MHz.

Note that the inductor used must be able to handle a DC bias current equal to the full current of the system. In addition, the inductor used should have a self-resonant frequency equal to or more than the highest frequencies used by the powerline to Ethernet adapter. The highest impedance that a real-world inductor exhibits is at its self-resonant frequency.

A further consideration of optimizing RF data superimposed over power systems is to avoid stubs to the greatest extent possible. Stubs are a source of reflections which can cause interference which will degrade the maximum achievable data rate.

Niobium TMC Varistor Like Effect, Fritting and Tunneling

Initially it was assumed that the passive film that forms on niobium is completely removed when mating contacts are scraped against each other, but anomalies occurred when trying to measure contact resistance of dry niobium contacts using a standard digital resistance meter. Anomalous high contact resistances were measured whereas when Kelvin sensing (measuring voltage drop across the connector at a constant current) was used for the measurement the measured resistances were much lower. A more detailed set of measurement were then performed to determine the cause for this. Figure 4-10 shows a plot of the first measurement of voltage against current for a set of dry contacts. The beginning of the plot up to about 50mA is far from linear as it should be for a pure ohmic resistance and looks more like the plot that would be obtained when measuring a varistor or a diode. Several discrete drops in measured voltage as the current increases appear to be due to partial deterioration of the oxide film.

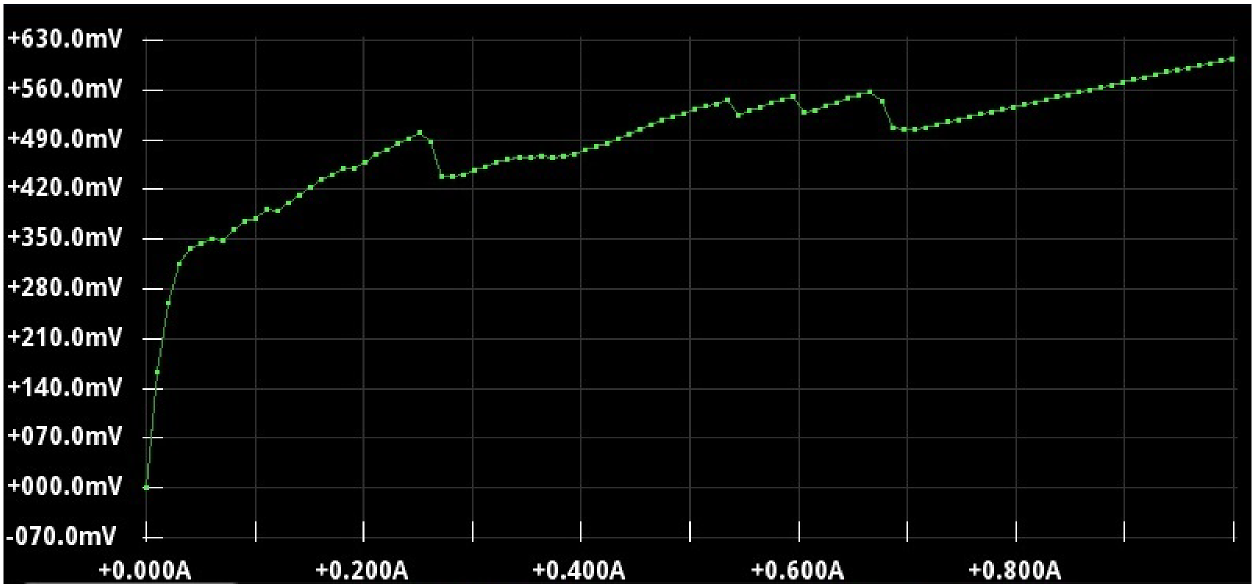

Figure 4-10 – First Measurement of Dry Niobium Contacts

Figure 4-11 shows a plot of a second identical measurement on the same contacts without any changes in setup or configuration and shows dramatically different behavior, i.e. it is linear indicating a pure ohmic resistance. Apparently, the first measurement reached high enough voltages to essentially “burn” or short out the oxide film so that the second measurement just indicated a pure resistance. This effect was repeatable, that is, if the contacts were moved against each other so that different microscopic areas of the contacts were touching and scraping, the first measurement would look like a varistor and the second measurement would look like a resistor.

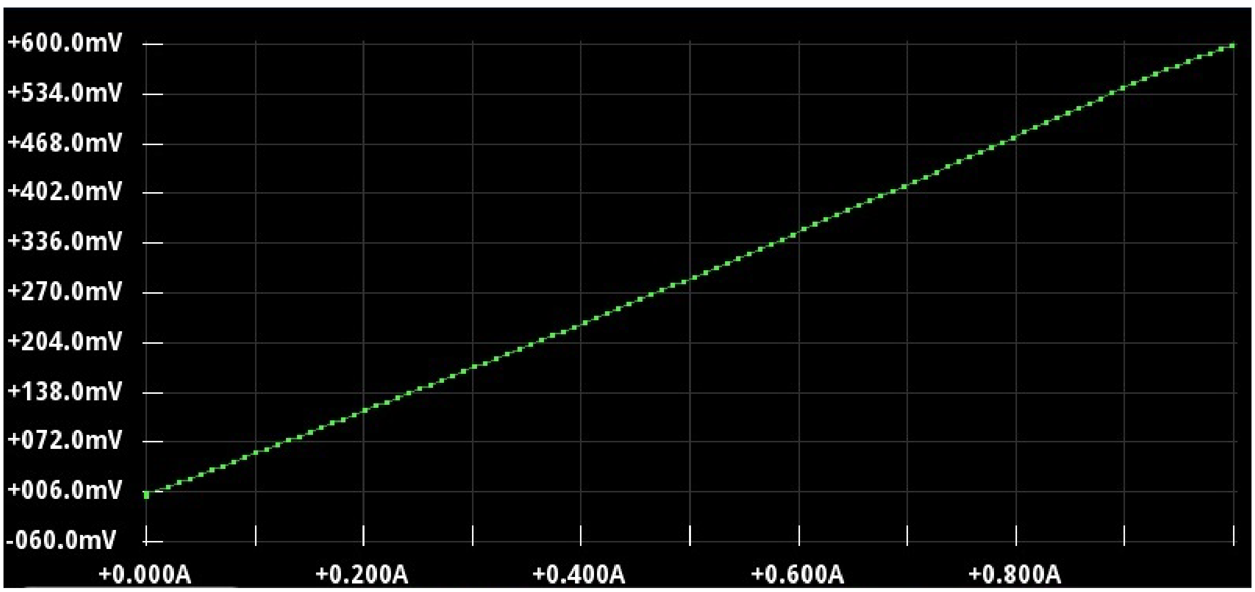

Figure 4-11 - Second Measurement of Dry Niobium Contacts

This phenomenon needs more study to determine what the actual film that remains on the niobium surface is made from and how it “burns” and shorts out when sufficient current or voltage is applied to it. To complicate this, this varistor effect is not found on contacts that are immersed in seawater; the first and all subsequent measurements all show identical pure resistance behavior.

The result of this is that contact resistance for dry niobium contacts cannot be measured using a traditional resistance meter because it doesn't apply enough voltage or current to negate this varistor effect. Instead, Kelvin sensing must be used to measure contact resistance of dry niobium contacts. It is unknown if this same effect occurs with other metals such as titanium.

For power connectors, this effect is negligible and will not likely be noticed. However, for data connectors made with TMCs, this may have an effect when the connectors are dry mated. In data protocols that use low voltage swings such as ethernet, it has been observed that in a dry state, niobium TMCs can exhibit performance degradation of the Ethernet signals due to the varistor-like effect. When the connectors are immersed in water however, the problems disappear, and the connector performs normally. For data protocols such as RS-422 or RS-485 which utilize voltage swings, no performance degradation is noted whether the connector is dry or wet.

In the book "Electric Contacts, Theory and Application" by Ragnar Holm, he discusses several subjects relevant to this varistor like effect seen in dry TMCs. Chapter 26 discusses the Tunneling Effect and Chapter 27 has discussions Fritting. This book is a masterpiece and is an amazing reference on electrical contacts.

The subject of fritting discussed in the book above is of relevance to the dry mated characteristics of TMCs. Consider two metallic contacts separated by a high resistivity thin film perhaps 100 to 500 angstroms thick. A low voltage is first applied, and gradually increased. At the initial low applied voltage, a very small current flows due to the high resistivity of the film. However, once a potential gradient, typically on the order of 10^8 volts per meter is developed across the film, a sudden increase in the current and a sharp decrease in the voltage across the contacts occurs. This voltage potential is called the fritting voltage. A spot on the contacts called an a-spot develops, and this spot is able to carry the current at a contact voltage below the melting voltage but above the softening voltage of the contact metal. The voltage that remains across the contacts after the fritting voltage has broken down the film is called the cessation voltage.

The first stage of a high resistivity film breakdown is the injection of electrons into the film by a kind of field emission or Zener effect. The strong electric field makes the boundary barrier steeper and thinner, and electrons begin tunneling through the hill. The injection of electrons will happen at some preferred point in the film where it is weaker. The injection of electrons produces a strongly enhanced current flow in a very narrow channel which produces a number of effects. The material within the path is strongly heated by the current, and as a result, the cohesion of the film is disrupted and as a result a conductive channel is formed through the film. In addition, it is possible that the underlying metal may reach its softening point at which time the material plastically deforms at a microscopic scale and further widens the channel.

The subject of tunneling and fritting in TMC connectors needs to be studied in further detail. TMCs rely on a relatively thick oxide layer for their self-insulating characteristic in an electrolyte. Remember that the oxide thickness is 24 angstroms per volt for niobium, so 1440 angstroms of oxide for a niobium connector anodized to 60V. In addition, many of the transition metals used to make TMC contacts such as niobium are refractory metals with melting points far above most commonly used contact materials such as silver alloys.

Most of these tunneling and fritting behaviors seem to be negated when operating TMCs in electrolytic environments such as seawater, but it would still be very helpful to understand these behaviors in more detail as the operation of TMCs in dry environments could likely be enhanced if the physics of fritting and tunneling in TMCs was thoroughly understood.

The dry mating fritting and tunneling behavior of various transition metals such as titanium, tantalum and niobium has not been fully characterized. It is likely that some materials may be better when dry mating fritting behavior is of importance as it may be for certain types of data connectors. This is also an area for further research.

It is strongly suggested by the authors of this book to consult Ragnar Holms' book as a starting point for further research and understanding of the tunneling and fritting behaviors summarized in this section.

Chapter 5 – Application Notes for TMCs

Polarity

As stated earlier, the polarity of the applied signals on TMCs is important since the dielectric film forms primarily on the positive, or anodic, contacts. If the polarity reverses, then this will cause current to leak from the contacts to the external environment, creating the possibility of short circuiting or electrical shock. When designing the application which uses a TMC then it must be assured that positive contacts always remain positive.

Peak Voltage

Peak voltages must remain well below the breakdown voltage of the dielectric passive film. For niobium the applied voltage should not exceed 60 V continuous, or if a varying voltage is used such as superimposed AC over DC then the peak should still be below 60 V, although it may be possible to “get away” with peak voltages of up to 75V, however this should be tested to ensure that the resultant film will still scape off readily when mating.

Multiple Sets of Contacts

Since all contacts in multiple-contact TMCs will exist in the same electrolyte when immersed, polarity and maximum voltage can experience interactions unless the power supplies to the various contacts are fully isolated from each other, which means also isolating them from any common ground. If this isolation is not done, then unexpected crosstalk can occur which could affect polarity and peak voltages as well.

TMCs in a Common Electrolyte

When multiple TMCs are immersed in a common conductive electrolyte or when multiple contact pairs are used in a single TMC they will interact in a way that doesn’t occur in air. The electrolyte into which they are immersed can be thought of as a conductive universe, just like immersion in liquid mercury. Therefore, the various contact pairs can interact through the electrolyte. This is illustrated in Figure 5-1 where the relative polarity of contacts in the first connector can change when a second connector of greater voltage is placed in the same electrolyte.

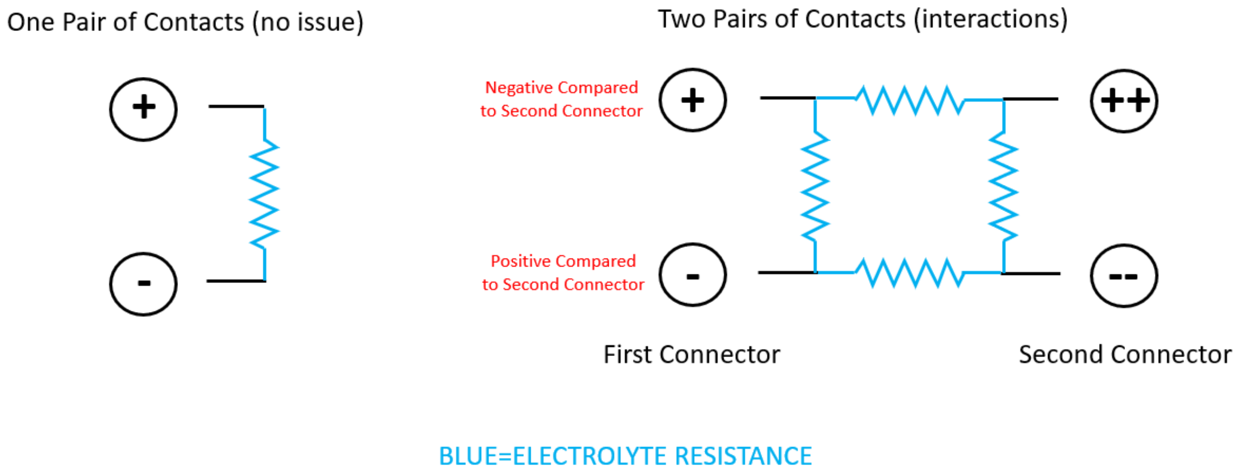

Figure 5-1 – Interaction Between Two Connectors

The interaction described above can be mitigated by increasing electrolyte path resistance as described above for minimizing capacitance effects, but the easiest way to prevent this is for each contact pair to be used with its own isolated power supply. As long as no common ground exists, the various contact pairs cannot interact.

Leakage Currents of TMCs and Ground Fault Detectors in Underwater Vehicles

Many underwater vehicles employ the use of ground fault detectors which can be sensitive to microamps of current flow. By their nature, TMCs will leak tiny amounts (microamps) of current, and this must be considered at the system level when using them as they may cause a ground fault to appear. The absolute amount of leakage current will depend on the design of the TMC and the size of the contacts. One possible solution to solving the ground fault trip problem may be to use an isolated power converter to feed and / or to receive power from TMCs in systems employing a ground fault detector. The use of an isolated power supply will maintain the galvanic isolation to the hull of the vehicle.

Another potentially viable method may be to separately measure the leakage current of the TMC connector and subtract that from the overall leakage current as the leakage current in the TMC connector is not a fault.

Chapter 6 – Physical Properties of Niobium and Other TMC Metals

Niobium & Niobium Alloys

Niobium is a soft, malleable, ductile, gray-white metal. It has a body-centered cubic crystalline structure and in its physical and chemical properties it resembles tantalum. The three largest mines of pyrochlore which is a source of niobium are in Brazil and Canada. There is also a small mine in Nigeria. It is used as a microalloying element in some steels and in superalloys and becomes superconducting at sufficiently low temperatures. Since it is a hypoallergenic material, it is used for human implants and high-quality earrings. Niobium dust is a mild irritant to skin and eyes. Since it can be anodized to various bright colors it also is used in various pieces of jewelry, as shown in Figure 6-1. Since it is also a high-temperature refractory material which melts at 2477 C it has been used for rocket nozzles.

Figure 6-1 - Niobium Jewelry (source: Angelwear Creations, used with permission)

The artist in Figure 6-1 is Angelwear Creations who sells their beautiful work on an Etsy store which can be found here: https://www.etsy.com/shop/AngelwearCreations?ref=shop_sugg_market The artist was kind enough to allow us to use their work in our book.

Physical properties

Symbol Nb
Atomic number 41
Atomic weight 92.91 g/mol
Crystal structure body centered cubic
Density 8.57 g/cm^3
Melting point 2477°C, 4491°F
Boiling point 4744°C, 8571°F

Mechanical properties

Reported mechanical properties of niobium and its alloys vary somewhat because they are significantly influenced by minor impurities. Table 8-1 gives a general idea of typical properties for the various alloys. These typical properties will exceed the guaranteed minimum mechanical properties listed in standards for some of these alloys but are useful for forming and other mechanical operations.

Alloy	Yield Strength, ksi (MPa)	Ultimate Strength, ksi (MPa)	Elongation, %	Elastic Modulus, Msi (GPa)	Thermal Conductivity at 800C, W/mC
C-103	42.9 (296)	60.9 (420)	26	13 (90)	37.4
Nb-1Zr	21.8 (150)	39.9 (275)	40	12 (80)	59
PWC-11	25.4 (175)	46.4 (320)	26	12 (80)	
WC-3009	109 (752)	125 (862)	24	17.9 (123)	
FS-85	67.0 (462)	82.7 (570)	23	20.4 (140)	52.8

Modulus of elasticity 15250 ksi (105 GPa)
Shear modulus 5511 ksi (38 GPa)
Poissons ratio 0.4
Harness, Brinell 736
Hardness, Vickers 1320
Hardness, Mohs 6

Electrical properties

Electrical resistivity at 0°C 152 nohm-m

Thermal properties

Thermal conductivity at 300K 53.7 W/m-K
Thermal expansion 4.1 µin/in-F (7.3 µm/m-K)

Specifications

ASTM B391, ASTM B392, ASTM B393, ASTM B394
SAE AMS 7850 (extremely pure)
CAS 7440-03-01 (composition only)

Machining notes

Use high speed tooling with good lubrication
High galling tendency
Easily formed, stamped, and spun due to low work hardening rate

Welding

TIG with covering gas
Spot welding

Forging

Good cold working characteristics

Heat treatment

Annealing 2192°F (1200°C) in vacuum or inert gas
Stress relieving 1472°F (800°C)

Grades in ASTM B391, ASTM B392, ASTM B393, and ASTM B394

R04200-Type 1 – Reactor grade unalloyed niobium
R04210-Type 2 – Commercial grade unalloyed niobium
R04251-Type 3 – Reactor grade niobium 1% zirconium
R04261-Type 4 – Commercial grade niobium 1% zirconium

ASTM B394 also lists R04220-Type 5 – RRR grade pure niobium (extremely pure for superconducting applications only, poor mechanical properties due to large grain size. This extremely pure alloy is also the one specified in SAE AMS 7850.)

The differences in grades, besides the zirconium additions, include the following impurities:

Reactor grades: .0250 max oxygen, .0100 max carbon
Commercial grades: .0400 max oxygen, .0150 max carbon

Mechanical properties of annealed and 90% minimum recrystallized rod in this specification are:

Types 1 and 2: Ultimate 18ksi (125 MPa), Yield 10.5ksi (73MPa), elongation 25%
Types 3 and 4: Ultimate 28ksi (195 MPa), Yield 18ksi (125MPa), elongation 20%

Other Metals for TMCs

Commercially pure titanium: Pure titanium can be used for lower voltage applications since it has a much lower breakdown potential for its passive film than niobium, on the order of 15V. Its use should be limited to applied voltages less than 10V, and preferably less than 8V. It has the advantage of making a better spring material than niobium, so more resilient contacts can be manufactured from it. Standards for unalloyed titanium include ASTM B265 (grade 2), ASTM B348 (grade 2), ASTM B863 (grade 1), and AMS4902 (grade 2). Although ASTM B265 lists grades 1-4 (including grade 2H) with varying purity, grade 2 is relatively easy to obtain and works fine for TMC contacts. Grade 2 mechanical properties are: Ultimate 50 ksi (345 MPa), Yield 40 ksi (275 MPa) and elongation 20%.

Tantalum has almost identical properties to niobium and could be used instead, however it is far more expensive than niobium and offers no advantages except for perhaps a slightly higher breakdown potential for its passive film.

Platinum doesn't form a passive film and instead delivers current very efficiently into surrounding electrolytes like water without corroding. Platinum therefore cannot be used in the same fashion as other TMC contact materials mentioned to date. Its use so far in TMCs has been limited to demonstration connectors that operate on the principle of using high IR drop to overcome high voltages since it is easy to generate current in the surrounding electrolyte using platinum.

Chapter 7 – Design of TMCs

Designing TMCs is radically different from designing connectors with contacts made from traditional materials. While traditional connectors are designed to minimize contact resistance, exclude water (if used in severe environments), and to be produced cheaply in large quantities, these considerations are much lower in priority when designing TMCs. It is likely not possible to use an existing connector design and just replace the contacts with a TMC material due to the mechanical, electrical, and thermal properties of most metals used for TMC contacts being different from these properties for traditional metal contacts.

Requirements

Material for positive contacts: The positive contacts, or anodes, in a TMC must be made from a material that forms a dielectric film quickly when exposed to the corrosive environment. Tantalum or niobium are good choices since the dielectric films that forms on them in seawater, called passive films, have the largest breakdown voltage of any known metals, over 120V. Since niobium is cheaper than tantalum it has, to date, been the primary choice for anode contacts for connectors that can be used underwater. ASTM Standard B391, Standard Specification for Niobium and Niobium Alloy Ingots lists several grades of unalloyed and alloyed niobium. Both reactor grade (R04200, type 1) and commercial grade (RO4210, type 2) pure niobium have been used successfully. This standard also lists two alloys containing 1% zirconium: reactor grade (R04251, type 3) and commercial grade (R04261, type 4). Preliminary tests indicate that these alloys should probably work in connectors as well, although they have not been made into connectors as of this writing. The alloys have the advantage of having higher mechanical properties which would make them into better springs than pure niobium.

Commercially pure titanium (ASTM B265 grades 1-4 or AMS4902) can be used for anode contacts, although its breakdown voltage of around 15V limits the maximum applied voltage on such contacts to around 5-8V. There are many other metals besides niobium, tantalum and titanium listed as potential contact materials in the NiobiCon™ patents: zirconium, molybdenum, ruthenium, rhodium, palladium, hafnium, tungsten, rhenium, osmium, and iridium. Most have not yet been explored in detail. Contacts that mate should be made from the same material, or at a minimum from materials close together in a galvanic series in the environment of interest to prevent galvanic corrosion. For example, a low-voltage banana-plug contact was constructed where the female side of the contact was made from niobium and the male side from titanium to take advantage of the spring-like characteristics of titanium while avoiding galling that can occur when scraping titanium against itself. These two metals both have similar potentials on the galvanic series in seawater.

Material for negative contacts: The negative contacts, or cathodes, in a TMC can be made from a variety of materials if they have sufficient corrosion resistance in the environment of interest. These contacts, if immersed in conductive electrolytes such as water, will receive cathodic protection for as long as voltage is applied, therefore preventing them from corroding, however continuous power cannot always be guaranteed so the cathodic protection effect cannot normally be relied on. Therefore, the cathode contacts must be made from a material that resists corrosion in the environment of interest. A logical choice is to use the same material as for the anode contact so that the same analyses as used for the anode contacts can be used for the cathode contacts. In critical applications where heat generation must be minimized more electrically or thermally conductive materials may need to be used for these cathode contacts, provided that the materials chosen have sufficient inherent corrosion resistance. Copper-alloy contacts may be used if they have sufficient corrosion resistance in the environment of interest. Graphite or carbon-fiber contacts may be used if their mechanical characteristics are adequate. Contacts that mate should be made from the same material, or at a minimum from materials close together in a galvanic series in the environment of interest to prevent galvanic corrosion. For example, a titanium contact which acts as a spring can be mated against a rigid graphite contact for use underwater.

The use of something other than niobium or another transition metal for the negative contact may be driven by one or more of the following considerations:

- Lower cost materials
- Lower contact resistance is possible with other materials
- Better mechanical properties
- Better thermal performance

Baseline requirements for designing TMCs are as follows:

1) Contact materials must not corrode in the environment of interest
2) Contacts must have a slight scraping action parallel to the surfaces when mating to effectively scrape off the film. This scraping can be microscopic but contact travel that is purely normal to the contact surfaces may not provide adequate removal of the passive film during mating. Examples are in Figure 7-1 through Figure 7-7.

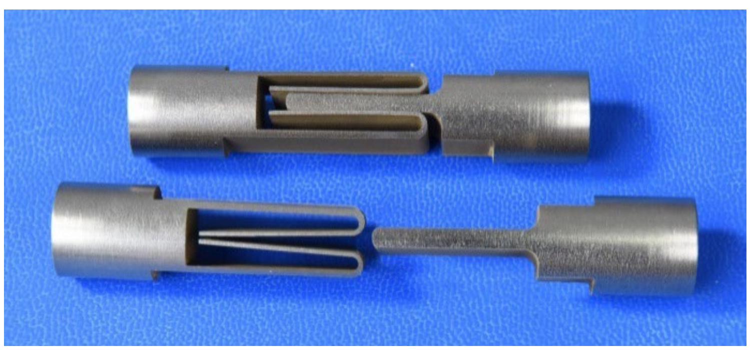

Figure 7-1 - Sliding contacts from early connector design

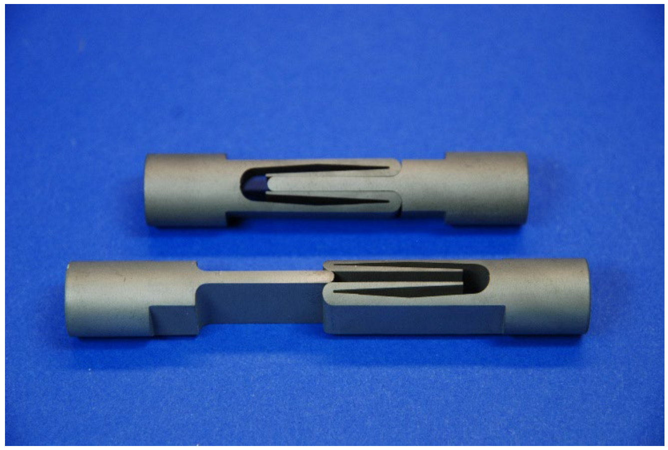

Figure 7-2 - Sliding contacts from later connector design

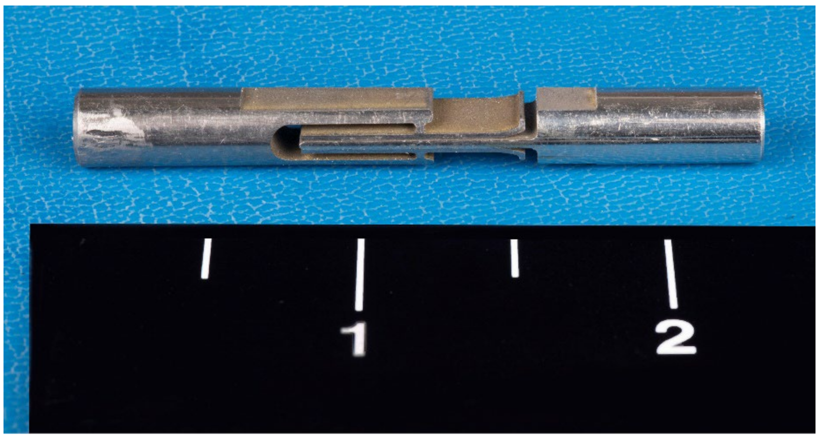

Figure 7-3 – Small 6.4mm (0.25") diameter sliding contacts for long-term immersion connectors

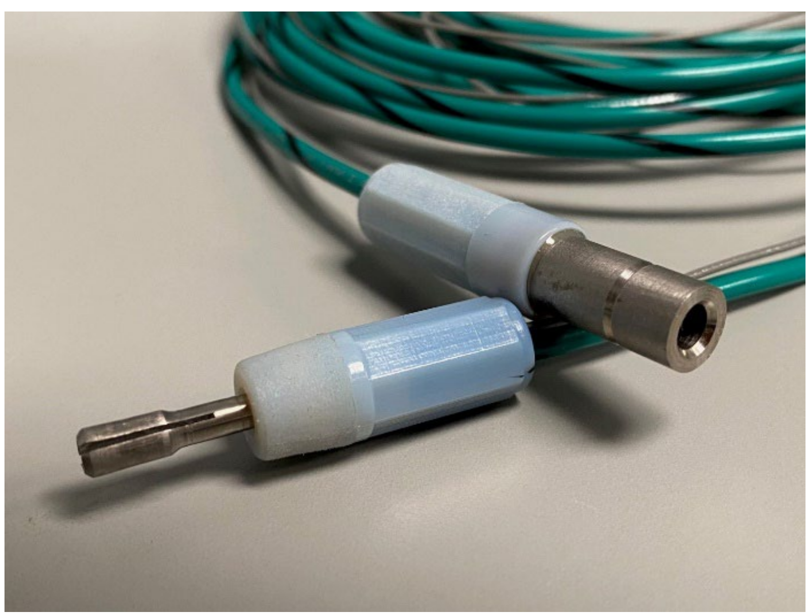

Figure 7-4 - Sliding contacts from banana plug demonstrator (male contact is titanium)

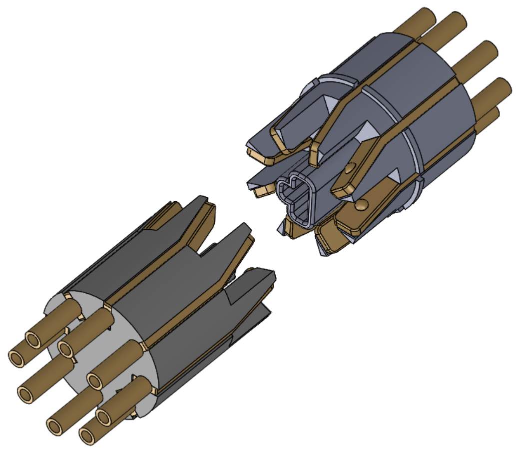

Figure 7-5 - Wedge contacts from patented OctiConn™ connector; unmated

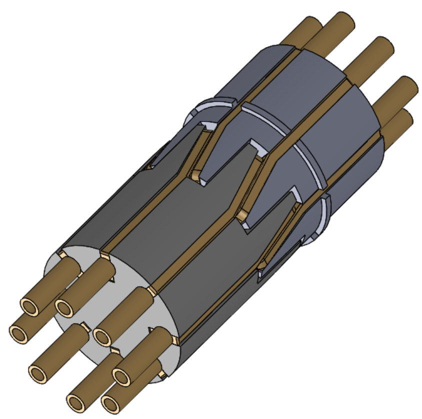

Figure 7-6 - Wedge contacts from patented OctiConn™ connector; mated

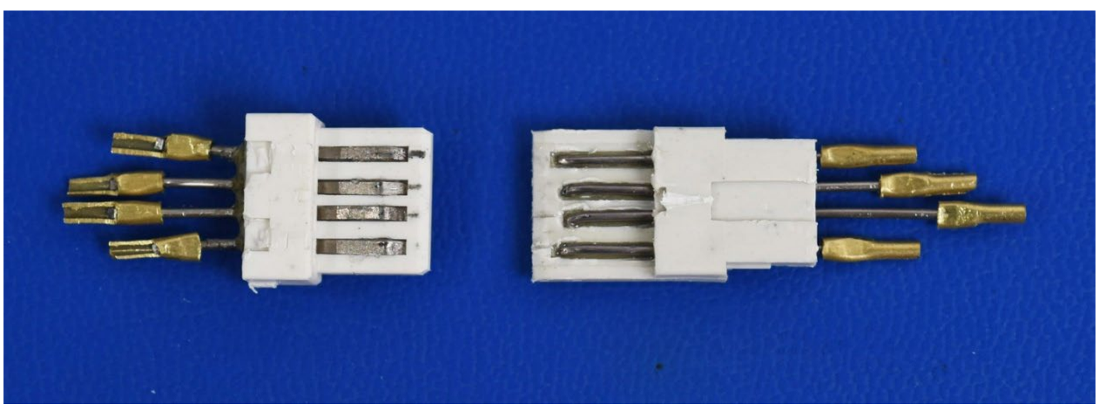

Figure 7-7 - Contacts from NiobiCon™ USB connector demonstrator

3) Electrical connection to the contacts must be solid and low resistance. Attachment of wires to many TMC contact materials, for example tantalum, niobium, and titanium, cannot be done by using traditional 63Pb/37Sn or SAC alloy (96.5%Sn/3%Ag/0.5%Cu) solders. There are however solders containing titanium which can disrupt the passive film on these materials sufficiently to allow them to be soldered, although the procedure to do this without an ultrasonic soldering iron must be carefully worked out or unreliable electrical connections may result. One solder alloy that has been used to successfully join copper wires to niobium is S-Bond 220 which is a solder with a Sn/Ti/Ag composition. To be successful using this solder, you must follow the directions carefully as it is quite different from using a traditional solder. No flux is used, and it is critical to agitate the niobium surface solder joint during the soldering process either by brushing the surface with a stainless-steel brush or the tip of an iron while the solder is molten or by using an ultrasonic soldering iron. The agitation is needed to allow the titanium in the solder to react with and remove the oxides on the surface of the niobium. A successful technique that Jim has used is to tin the surface of the niobium with the S-Bond 220 solder while agitating the niobium surface with either a small stainless-steel brush or the tip of the iron and then to tin the copper wire to be attached. With both sides tinned and a bit of excess solder applied to the copper wire, a secondary soldering step is then employed to join the wire to the niobium.

   Solder joint reliability using the S-Bond 220 solder has been mixed, but the need for agitation of the niobium surface during the soldering step is critical. One frustrating failure mechanism observed with niobium to copper wire solder joints performed with S-Bond 220 is that the joints will sometimes appear solid and strong immediately after soldering, but after a week or two, a gentle tug will cause a complete disbondment (loss of adhesion) of the solder from the niobium surface with the solder remaining attached to the copper wire. Other times, the solder joint will remain strong and intact as expected. The reason for this variability in performance is unknown, but it may be related to the amount of agitation and solder liquidus dwell time as it is critical for the titanium in the solder to have time to react with the surface of the niobium. Further research and process optimization is required before counting on the reliability of soldered joints on niobium.

   Crimping is not reliable for tantalum and niobium because these metals are soft, and crimps may not generate sufficient force for reliable connections. The most reliable connections to these materials are mechanical such as using screws and lugs, although these types of connections are quite bulky, or by spot welding (see Figure 7-8). To minimize resistance at the connection points surfaces must be clean and connections must be tight and of large surface area.

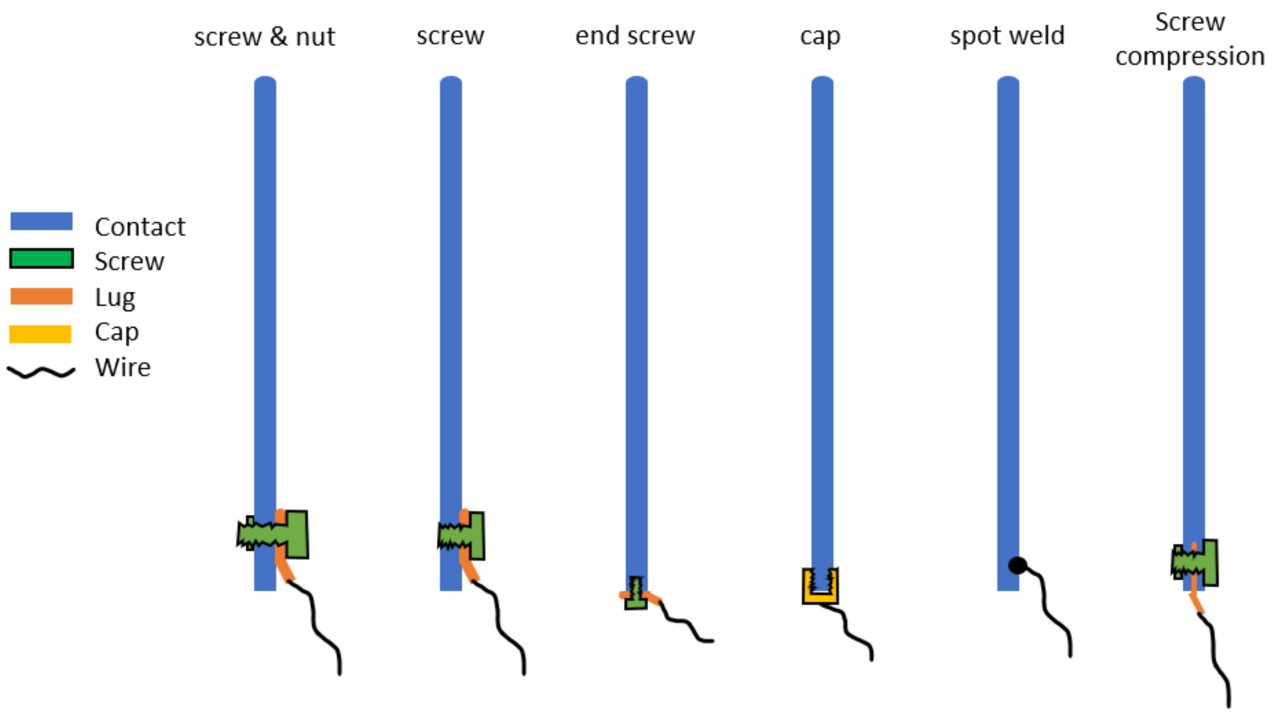

Figure 7-8 – Example methods of electrical connection to contacts (contact area must be potted)

4) There must be sufficient contact force. Since many TMC contact metals do not have good mechanical properties to act as springs, it can be a significant effort to get sufficient contact pressure. Too little contact pressure will not properly scrape off the dielectric film to get good metal-to-metal electrical contact whereas too high contact pressures could lead to galling upon repeated mate/de-mate. To ensure a proper mating pressure, finite element analysis of the contact geometry may be required. For niobium contacts, an initial goal of about 140kPa (20 psi) is a good starting point in designing contacts, although this value may need to be adjusted depending on the amount of scraping, number of mate/de-mate cycles desired, the environment of use, etc. Alternative methods for applying sufficient contact pressure include the use of non-metallic materials to act as springs, or the use of corrosion-resistant metals such as titanium to act as springs which are then electrically isolated from the contacts, for example with dielectric spacers such as plastics or ceramics. Examples are shown in Figure 7-9. Since niobium is relatively low-strength and has a low modulus, cold-worked material may be stronger and springier and could make a better contact material in some designs. All demonstrator contacts were successfully designed without need for an elastomer except for the USB connector, which used RTV rubber behind the contacts to get sufficient contact pressure.

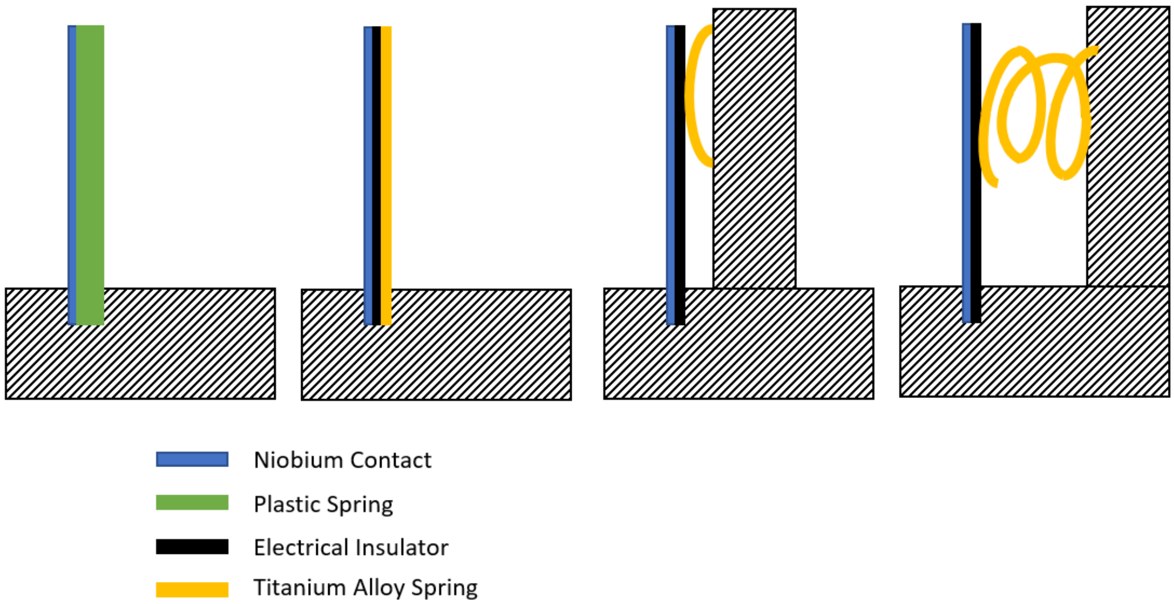

Figure 7-9 – Example methods of creating contact force

5) Electrical resistance of the current path through the contacts must be minimized. This means that TMC contacts will typically be larger than traditional metal contacts since most potential contact metals have much higher resistivities than the copper alloys currently used for contacts. It is unlikely that TMC contacts will ever achieve the low resistances of gold-plated copper-alloy contacts but contact resistances of well under 1 ohm should be achievable with proper design.
6) Rejection of heat generated in the contacts must be considered, especially if the contacts are to be operated in air. This becomes important since most metals used for TMC contacts will have much lower thermal conductivity than traditional metal contacts. An example design for rejecting heat is shown in Figure 7-10.

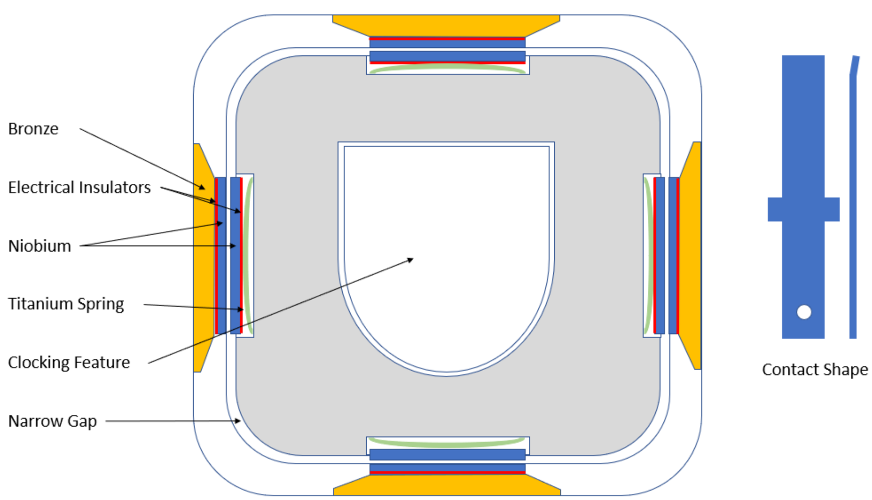

Figure 7-10 - Cross-section of example design to improve thermal rejection

7) The previous three items may be addressed for large contacts by cladding, which means covering one metal with a protective outer layer of another metal. Traditional electroplating is not an option for niobium since such coatings are difficult to apply for niobium and since all electroplated coatings have porosity, which cannot be tolerated as this would cause the underlying material to corrode. Cladding must be done in a fashion that is defect-free in areas where contacts are exposed to corrosive environments. Possible methods for cladding include explosion bonding, casting into a niobium shell, roll-bonding, co-drawing, press-fit, shrink fit, plasma spray, cold spray, etc. Copper has a coefficient of thermal expansion of 16-17 ppm/°C and niobium's is 7.07, so if a copper core is press fitted into a niobium shell, the joint will always remain in compression.

8) Electrical connections from copper wire to niobium that could get wet must be sealed to prevent water from touching this area. Good sealing materials include underwater-rated epoxies and polyurethanes. Follow manufacturer's recommendations for cleaning and priming surfaces before potting. Examples before potting are shown in Figure 7-11, Figure 7-12, and Figure 7-13. Our demonstration connectors used neoprene jacketed cable that was roughened and degreased. Primer used was PPG® Aerospace PR-1523M for plastics and neoprene and PPG® Aerospace PR420 for metal surfaces and the potting material used was PPG® Aerospace PR1592.

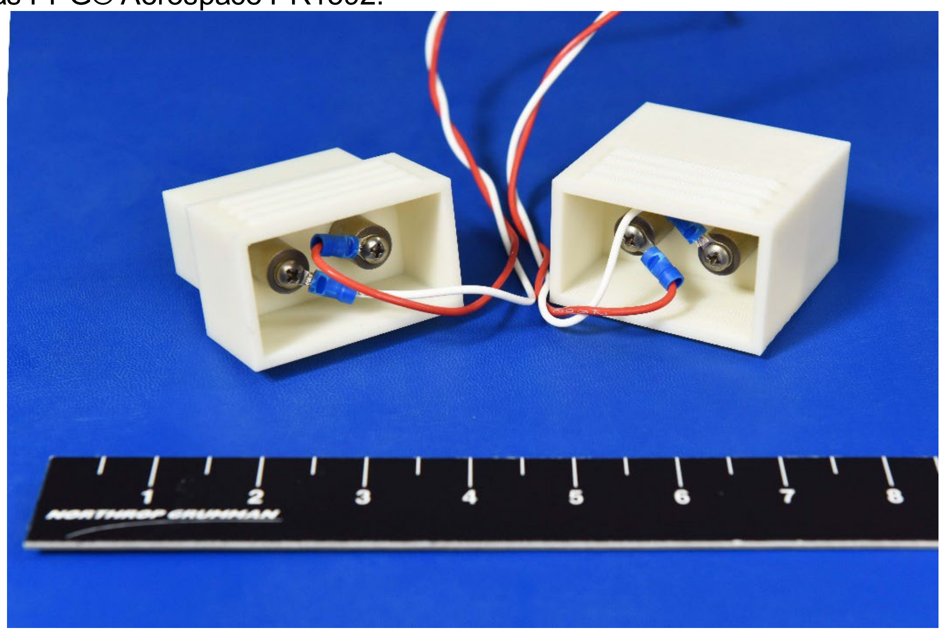

Figure 7-11 - Mechanical screwed contacts in the back of a connector before potting

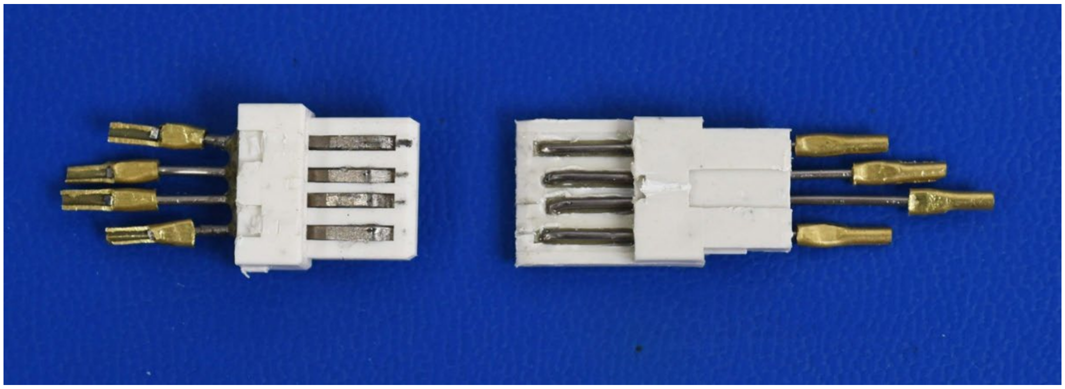

Figure 7-12 Brass tubing crimped onto niobium contacts with solder cups in area to be potted

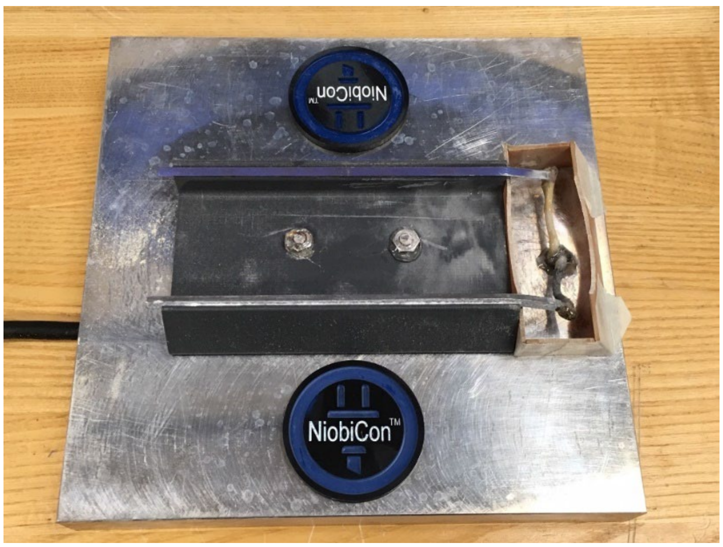

Figure 7-13 - Niobium rods crimped to copper wire before potting (potting volume is on the right)

Another method of keeping the wire connections dry is to use glass-metal sealing technology. This has the additional advantage of allowing the manufacture of high-pressure penetrators. Initial discussions with glass-metal sealing manufacturers indicate that niobium should be easy to seal against glass, although to date no glass-metal seals with niobium have been manufactured.

9) If high frequency signals are to be passed through the connector, impedance matching must be considered, and baffles may be required between contacts to increase electrolyte path resistance.

Since TMCs don't require a connector shell or any means of preventing the environment from reaching the contacts, many non-traditional connector geometries can be envisioned. Underwater charging of vehicles has been demonstrated by having two niobium continuously powered open rails connected to a power source. These rails will not leak significant current into the surrounding water so they can remain powered. A vehicle with niobium shoes can then set down on the rails to receive power. This is shown in Figure 7-14, Figure 7-15, Figure 7-16, and Figure 7-17.

Figure 7-14 - Base with powered parallel niobium rails

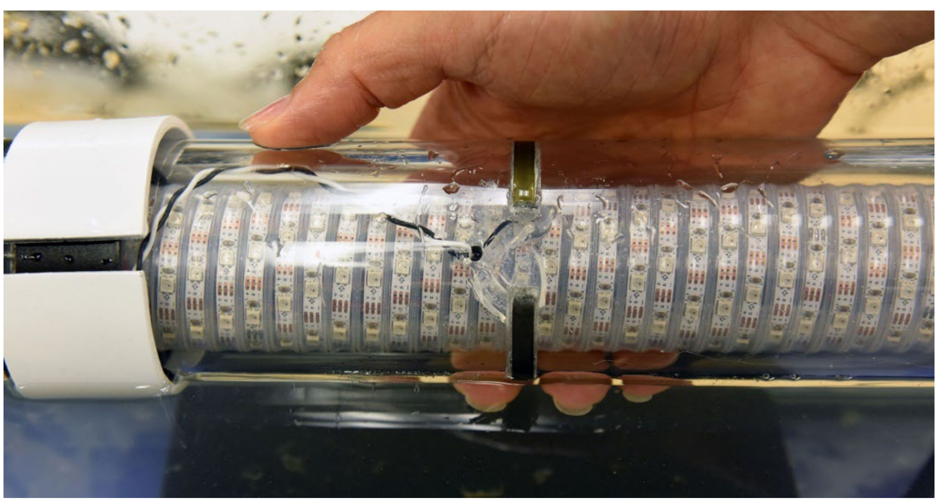

Figure 7-15 - Niobium shoes on proxy underwater vehicle

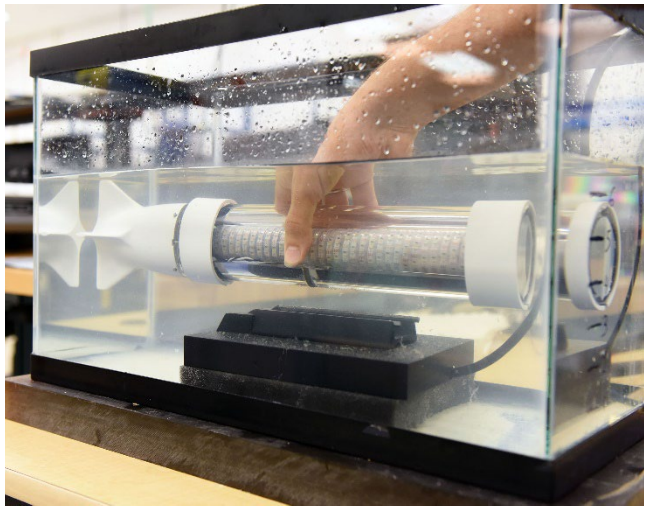

Figure 7-16 - Proxy vehicle unpowered above base

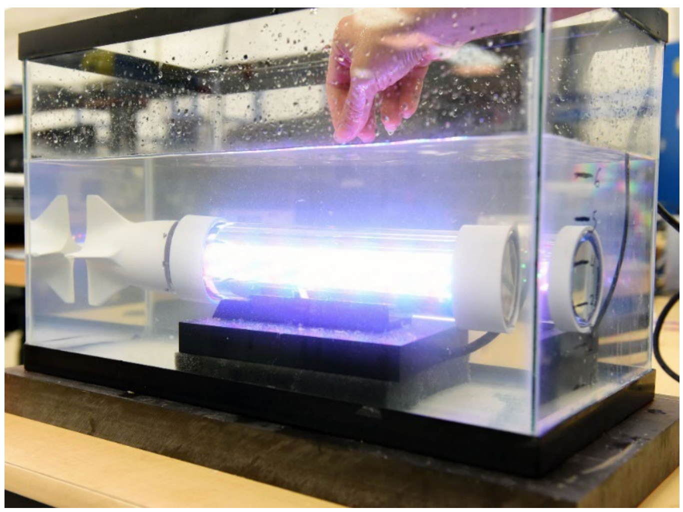

Figure 7-17 - Proxy vehicle powered setting on base

A system has been demonstrated where the negative power return is accomplished through a seawater ground system instead of a second contact, thus allowing power to be delivered underwater with only a single point of contact. This is shown in Figure 7-18, Figure 7-19, Figure 7-20, and Figure 7-21.

Figure 7-18 - Proxy underwater vehicle with niobium contact and graphite electrode

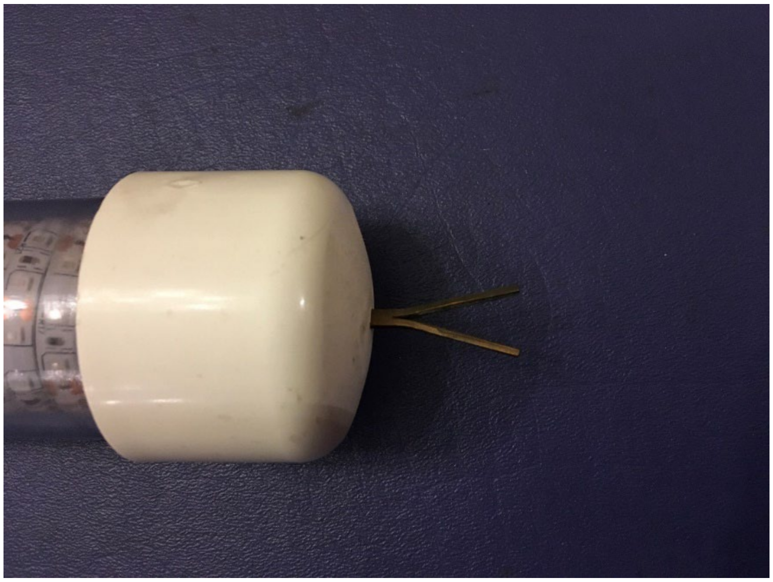

Figure 7-19 - Niobium forked contact on front of proxy vehicle

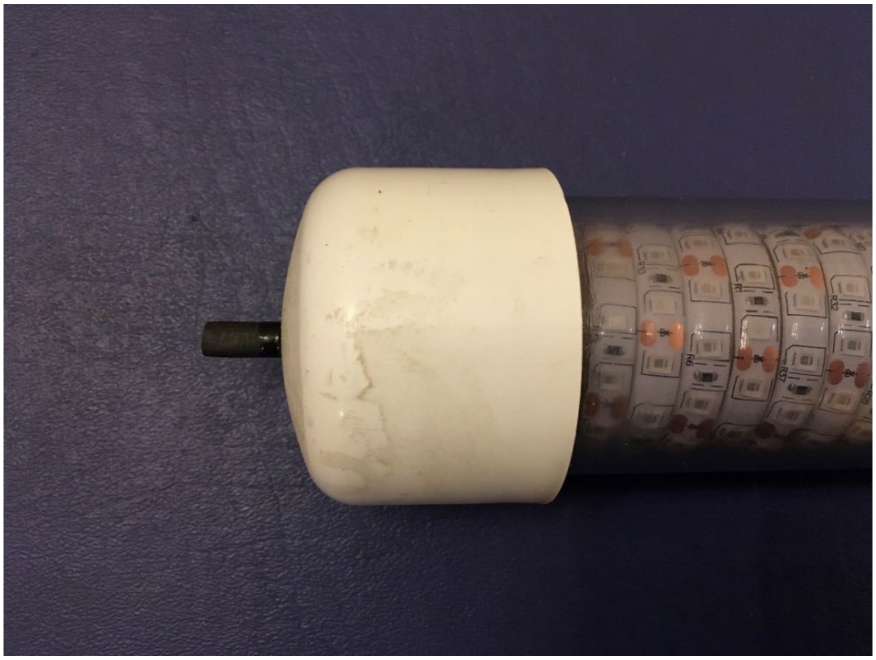

Figure 7-20 - Graphite seawater ground return electrode on back of proxy underwater vehicle

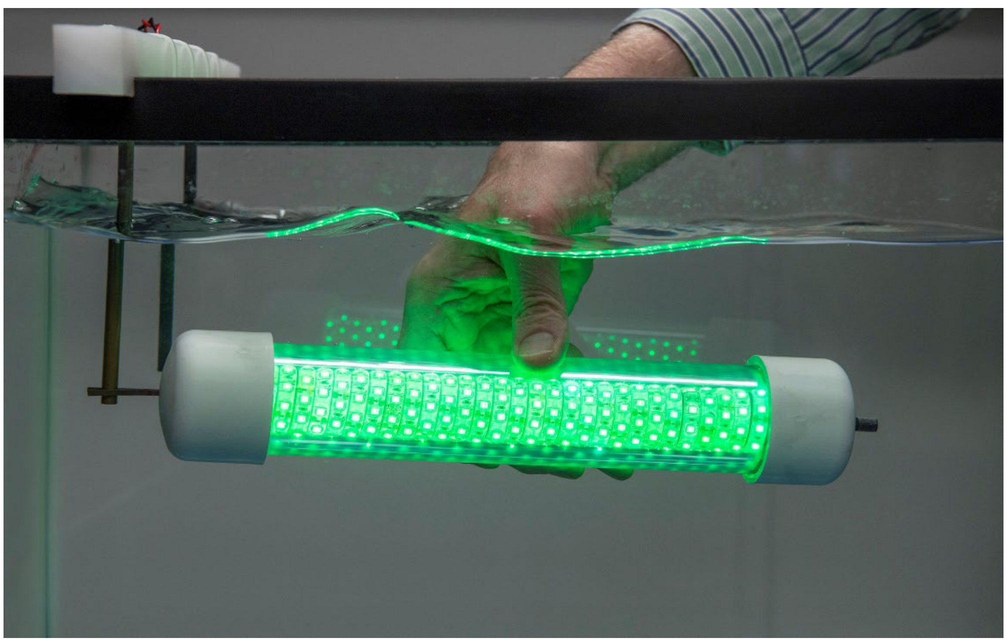

Figure 7-21 - Power supplied to proxy vehicle through contact and electrode

Sliding contacts for underwater vehicle charging from a buoy have been designed, a patent for this configuration has been granted (US Patent 12,195,153) and this system has been used to recharge vehicles underwater (Figure 7-22).

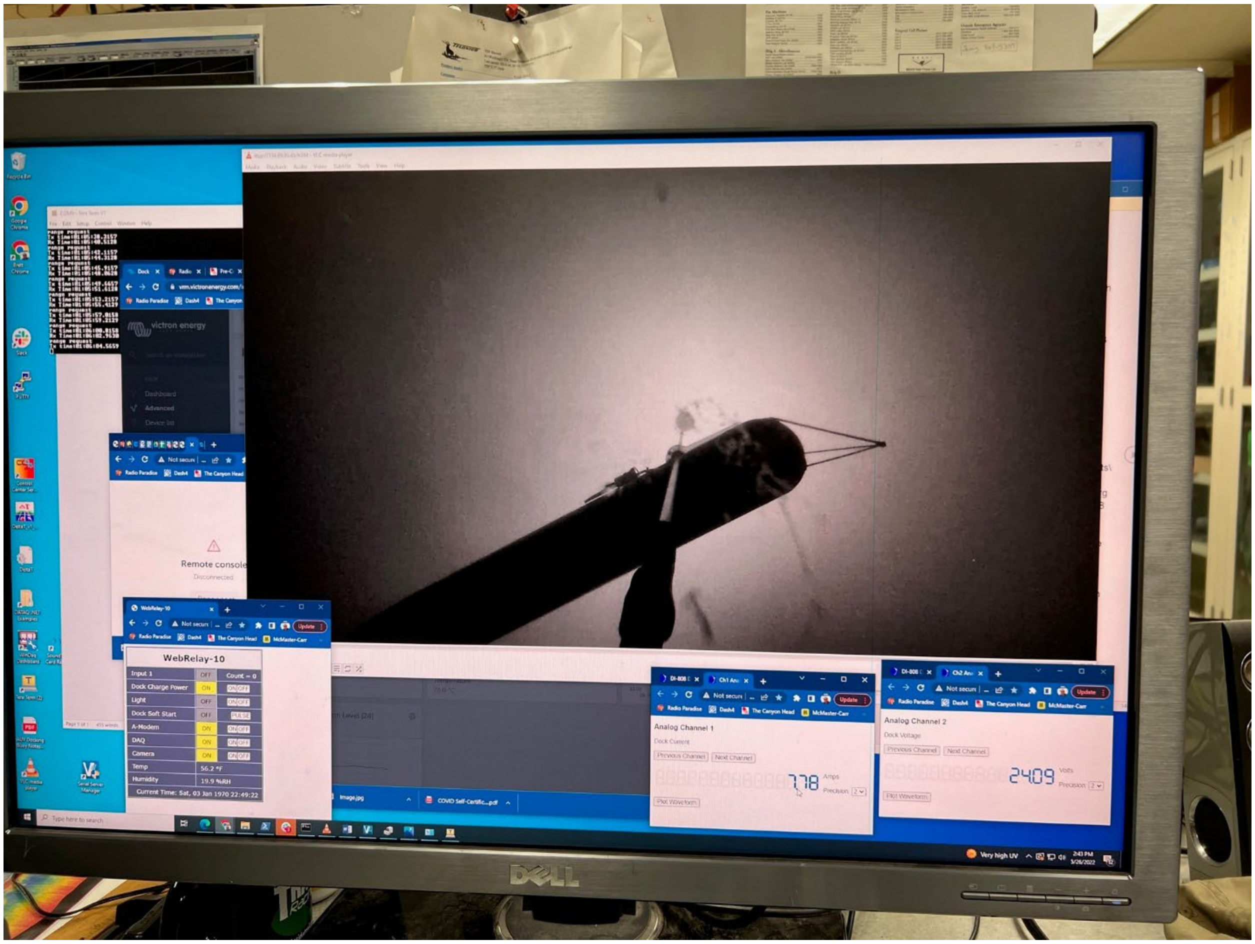

Figure 7-22 - Underwater charging of vehicle, looking up from anchor

A demonstration of an underwater switch was designed and constructed as well. A schematic for this design is shown in Figure 7-23 and the working demonstrator is shown in Figure 7-24.

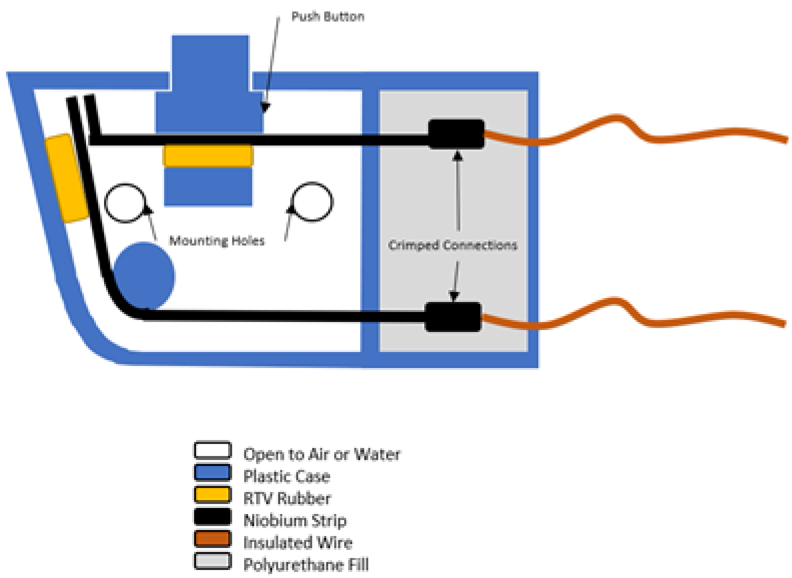

Figure 7-23 – NiobiCon™ push-button switch schematic

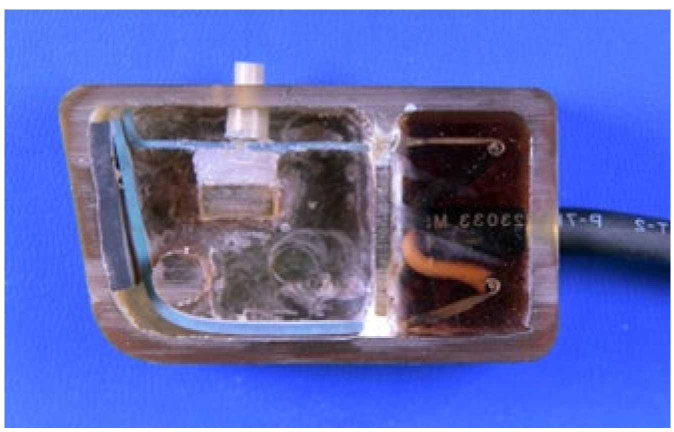

Figure 7-24 – NiobiCon™ underwater switch demonstrator

Demonstrations of rotating contacts have also been constructed, however niobium is unlikely to withstand high speed or long-duration rotation, so it may not be able to be used for motors but should be acceptable for limited duty rotations such as low-speed swivel joints. A demonstration of this concept is shown in Figure 7-25 and Figure 7-26.

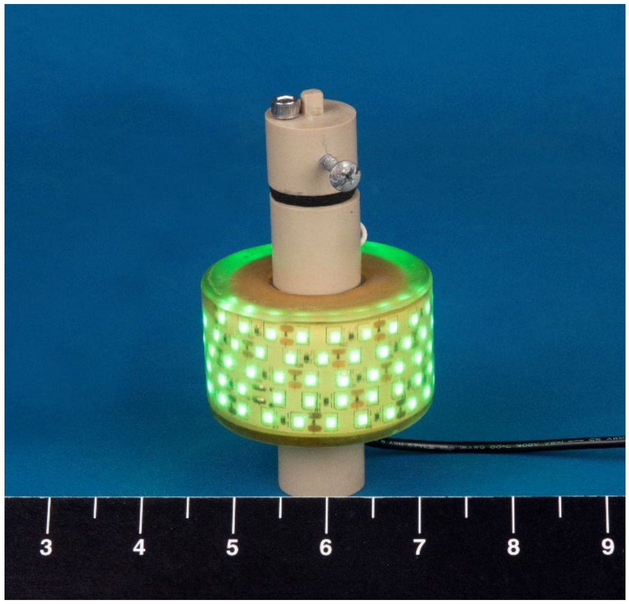

Figure 7-25 - Rotating contact demonstrator with scale (inches)

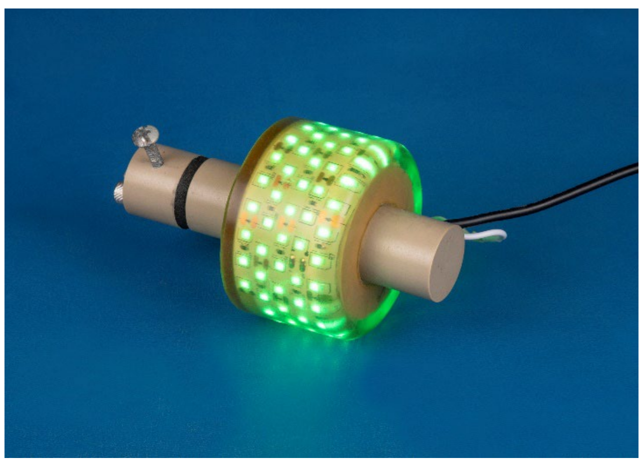

Figure 7-26 - Rotating contact demonstrator side view

The possible connector geometries are limited only by the imagination.

Since the environment doesn't need to be excluded in a TMC, manufacturing tolerances do not have to be as tight as would be required for O-ring seals or rubber gaskets. With no moving parts required and nothing compressible in the connector design except the potting, this also leads to less tight tolerances. Opening manufacturing tolerances can significantly reduce the expense of making the non-contact portions of the connector. If fiber-optic data throughput is required, the use of free-space-optical communication boards powered by TMCs can eliminate the need for fiber end matching connections, which opens manufacturing tolerances for power/fiber optic hybrid connectors (this concept has also been patented).

Preconditioning – After construction, connector contacts should be preconditioned to prevent initial high leakage currents when in use. Preconditioning is an anodizing process that is preferably performed in DI water with 3.5% N_aC_l by applying the same polarity as will be used in the application. The use of DI water and pure N_aC_l for the anodizing process avoids the issue of forming calcareous deposits on the cathodic electrodes as would happen with artificial seawater and / or tap water with dissolved minerals. The negative contacts can be used as the cathodes in the preconditioning process, or a separate noble cathode (graphite or platinum) can be used, and all contacts preconditioned as anodes; this is best if the final polarity of the connector is not known. Current density/voltage should be controlled to avoid visible bubbles. This can be achieved using a laboratory power supply with controlled constant voltage and current limiting capability. Set the power supply for a peak output voltage equal to the maximum voltage that the connector will see in service, but not to exceed 60-75V, and set the current limit to a level which controls bubbling. As the film builds at constant current the voltage will rise with time until it reaches the maximum that has been set, after which current will start to decrease at constant voltage until it reaches low levels (micro-amps), at which time preconditioning is done. A typical total preconditioning time in saltwater at 60V can be as high as 12-15 hours, but in some cases, it can take far less time than this; an hour or two. The total time is dependent on the contact design and the current level used for anodization.

Chapter 8 – Manufacturing of TMCs

Machining niobium

Niobium is relatively soft and gummy to machine. Tapping is difficult unless roll-form taps are used. Machining guidance is provided below. Electric discharge machining (EDM) was used for initial demonstrator contacts except the USB connector, where the contacts were shaped by pressing and hand filing. Machining should be done using cutting fluid and tool speeds should be kept slow. When tapping threads, it is easy for taps to jam and break off, especially for smaller thread sizes. Using roll taps has been found to work better than using cutting taps.

For later connectors, attempts were made to precondition EDM-produced niobium electrical contacts. The preconditioning was attempted by applying a constant current and allowing the voltage to gradually increase until 60 volts (applied versus a platinum cathode) was reached. The machined contacts did not passivate as expected. At an applied current density of roughly 5 mA/cm^2, a raw bar of niobium passivated to 60 V in a few hours. Contacts machined from this same bar were found to deliver excessive current into the saltwater, producing a green scum on the surface of the water, and in some cases never reaching 60 V applied. Preconditioning proceeded normally until 20 V was reached, after which voltage became erratic and failed to increase for a several hours. Extensive bubbling was noted on the contacts at this point. White precipitates also were visible in the saltwater after several hours above 20 V. When preconditioning was shut down due to failure to exceed 25 V, localized corrosion was found on the machined surfaces.

Since the original niobium rod from which the contacts were machined was able to be preconditioned normally, failure to precondition properly must have been due to something in the EDM process. EDM vaporizes the copper-base wire that is used at about the same rate as it vaporizes the niobium, therefore it is logical to assume that some copper is deposited onto the machined surface of the niobium. This assumption is supported by the green scum that was generated during the preconditioning process. Copper chloride corrosion products are green whereas no form of niobium corrosion product is green.

It is unknown why the copper didn't dissolve first under the applied voltage, eventually leaving a pure niobium surface which would then precondition properly, at least during the initial attempts. Somehow the copper on the surface was preventing proper niobium passivation. In later attempts using lower current densities of roughly 1 mA/cm^2, the niobium was eventually able to be preconditioned after passing through the 20-25 V plateau, however this process took over 10 hours.

The presence of bubbles on the contacts would also act as disrupters to any passive film that does try to form. At lower current densities, bubble formation would be reduced with less disruption of the niobium passive film. Also, the Equilibrium Potential, also called the oxidation/reduction potential, of copper is more active than that of niobium. Although this should cause bare copper to dissolve first before bare niobium under applied voltage, it would also mean that the copper could prevent formation of the niobium passive film while it is being dissolved since the niobium would not be able to dissolve to form its film until all the copper was gone. Without its passive film, niobium will corrode rapidly, just as any passive-forming metal such as titanium or aluminum would. Until the copper totally dissolves, the niobium would therefore not be able to form its passive film and would corrode rapidly.

There is additional anecdotal evidence that bubbles could play a key role. If the current is turned off for a minute or two during an erratic voltage event at 20-25 V, thus allowing the bubbles to dissipate, then when current is restored not only is the voltage more constant, but the stable voltage is higher than the previous unstable voltage by 5-10 V. After a minute or two the voltage will again become unstable and drop to its previous level as bubbles once again form.

The above is pure supposition. It is one explanation for the observed phenomenon and it the only one that is obvious to the authors, however there could be a different explanation.

The lessons learned from this are: 1) avoid EDM for manufacturing niobium contacts and, 2) if EDM must be used then use very low current densities to precondition the contacts, carefully monitoring bubble formation and copper precipitation.

Making a TMC connector using solid niobium contacts

1) Machine or stamp out the niobium contacts (avoid using EDM machining unless characterization is done first)
2) Terminate the contacts to copper wires
3) Insert contacts into a plastic, non-conductive housing
4) Pot the area around where the copper wire and niobium connect to keep water away using urethane, epoxy etc.
5) Precondition the contacts by immersing the connector into a sodium chloride / distilled water bath. Using pure NaCl and DI water prevents calcareous deposits from forming at the cathode, but this has also been done using an artificial seawater mix such as Instant Ocean® in tap water. The use of pure NaCl dissolved in DI water is the recommended method. A concentration of 35g NaCl per liter of DI water similar to seawater is typically used, but the absolute concentration of NaCl in the water is not that critical. A saltwater aquarium hydrometer can be used to measure the salinity of the anodization bath. A specific gravity of 1.0264 at 25C corresponds to a salinity of 35g NaCl/L.
6) Precondition (anodize) the contact which will be the positive in the application. It is sometimes more convenient to anodize all contacts at once negative as well as positive, and this will work fine. Preconditioning is done as follows:
    a. Configure a DC power supply to output a constant voltage which is in excess of the working voltage of the connector and set it to have a current limit that is appropriate to the size of the contact being anodized. A small contact might anodize at ~25-50mA, and a larger contact might anodize at 100mA – 0.5A. Avoid generating too many bubbles at once as they can push the solution away. For a connector that is going to be used at 48VDC, 60V has been successfully used for preconditioning.
    b. Connect the negative output of the power supply to a cathode which is also in the bath. A graphite rod makes a convenient cathode as it will not corrode or contaminate the bath, but almost any metal will work since a cathode won't corrode because it is galvanically protected by the current.
    c. Connect the connector contacts to be anodized together in parallel and connect to the positive terminal of the power supply.
    d. Turn on the power supply. The voltage will start out low, and the power supply will run at its current limit. As time goes by, the voltage will gradually increase until it hits the peak voltage the power supply was set for. Then, the current will fall off over time until it is down to only a few microamps. At this point, the contacts are preconditioned.
    e. Rinse and dry…you now have a TMC connector.

If the water starts to turn dark or if the voltage does not increase with time, you may have a leak in the potting and the water has gotten to the copper / niobium junction and the copper is corroding. This will usually require that the connector be re-built from scratch. Details of some of the above steps are described below.

Pre-anodization

Pre-anodization allows for the magic of TMCs to be realized as soon as they are put into use.

The last step in manufacturing a TMC is pre-anodization of the positive contacts; anodization of the negative contacts also can be done, especially if the final polarity of a contact pair will not be determined until final connections are made. Connectors will work if the contacts are not pre-anodized, however initial performance could be erratic, with high leakage currents causing problems with connected electronics. In this case it is better to be safe than sorry and to pre-anodize the contacts. If the contacts are pre-anodized before being assembled into the connector this creates a risk that bonds between the contacts and potting materials that isolate the points where contacts are connected to wiring could be weakened, increasing the possibility that the environment could find its way to the connection points and corrode them. For this reason, it is best to fully assemble the connector before pre-anodizing. In other words, pre-anodizing should be the last step in connector construction.

Pre-anodization can be done in most tap water that has sufficient ionic conductivity to allow a current to flow, although it could require longer times. Anodization can also be done in seawater; however, this introduces the possibility of getting calcareous deposits on the electrode used as the cathode. Capacitors anodize tantalum or niobium in sulfuric acid, although this has not been explored for connectors where the ultimate application is in water. A simple, non-hazardous environment in which to pre-anodize without creating calcareous deposits is to use saltwater such as 3.5% NaCl in distilled water. This has been found to be a very effective environment for pre-anodization, and it is the standard process used.

Pre-anodization can use the negative TMC contact as the negative electrode (cathode) in the process, however it can instead use a separate cathode made from a material that readily passes current into the environment such as graphite or platinum. The disadvantage of using niobium or another TMC contact material as the cathode is that the process will be slower since some of the applied voltage is lost at the cathode. If all TMC contacts, both positive and negative, are pre-anodized together then this makes the process simpler, allows a separate cathode to be used, and doesn't limit the initial polarity of the connector contacts.

The rate of the anodization reaction should be controlled to minimize bubble formation at the anode as this slows down the reaction by partially isolating the contact from the environment. Agitation may help to minimize formation of large bubbles. Anodization can be facilitated by using a power supply that can transition from constant voltage to constant current operation. This power supply is first set for a maximum voltage similar to, or greater than, the operating voltage of the contacts. The maximum current is then adjusted to barely prevent bubble formation. This has the result of causing the anodization to occur at constant current with the voltage rising over time. When the voltage hits the maximum set point then the current will decrease asymptotically with time. Anodization can be stopped when the current reaches a value that is close enough to zero to be nominal for the intended use.

Chapter 9 – Future Research Topics

A long-term seawater exposure of TMCs with niobium contacts is currently in test. This test uses specially designed, ultra-reliable small two-contact connectors that stay powered at 48V and are unplugged and reconnected quarterly. Contact resistance is being monitored as a function of time. In addition, some commercial OctiConn™ connectors are being tested. Data transmission is also being periodically measured during this test. Finally, strips of niobium are under test to determine the effect on biofouling of applied voltage and a mitigation strategy of covering the contacts to minimize light exposure and nutrient availability.

Other potential topics for future research include:

1. Determining how the passing of alternating current through the contacts affects leakage rates over time as a function of applied voltage
2. Verifying the breakdown potential of the passive film on tantalum and tungsten
3. Determining the best method for cladding niobium over other materials such as copper alloys to take advantage of the bulk electrical, thermal, and mechanical properties of these alloys while retaining the electrochemical properties of niobium
4. Determining the best way to make glass-metal seals around niobium pins so that high-pressure feedthroughs can be produced that use this technology
5. The varistor-like fritting effects that is experienced on niobium contacts when used in a dry state needs to be further studied to determine its origin and methods of mitigation in order to increase the applicability of TMCs with niobium contacts in air. There is a good discussion of this in Chapter 4.

Chapter 10 – Patents and Other Intellectual Property

United States Patents:

9,197,006: Electrical connector having male and female contacts in contact with a fluid in fully mated condition, 11/24/2015

This is the first patent that uses niobium as a contact material. It references titanium alloys, graphite, stainless steel, beryllium copper, platinum, alloys of platinum and iridium, niobium and nickel-base super alloys as potential contact materials. The essence of this patent is that narrow electrolyte path channels between opposite electrodes provide sufficient IR drop to allow high voltages applied to the contacts to be mostly mitigated. It requires some current to flow between the contacts, which niobium is unable to provide, however.

9,893,460: Underwater electrical contact mating system, 02/13/2018

This is the first official patent granted to NiobiCon™. It specifically calls out contact materials of niobium, tantalum, titanium, zirconium, molybdenum, ruthenium, rhodium, palladium, hafnium, tungsten, rhenium, osmium, and iridium. It is for a two-contact connector.

10,868,384: Self-insulating contacts for use in electrolytic environments, 12/15/2020

This patent covers connectors with contacts which are coated or plated in order to take advantage of mechanical, electrical, or thermal properties of a substrate while still using the electrochemical properties of a transition-metal surface.

10,985,495: High voltage connector with wet contacts, 04/20/2021

This patent combines the concept of IR drop from 9,197,006 that uses transition metal contacts but overcomes the limitation of insufficient current to create IR drop by adding an additional electrode such as platinum to deliver the current, tied to the transition metal electrode with a Zener diode. The platinum contact therefore allows the IR drop to occur while the Zener diode fixes the voltage that the transition metal contact sees to a low enough value so that the passive film will not break down.

11,005,390: AC power transfer over self-passivating connectors, 05/11/2021

This patent, which we call the “synchronous un-rectifier”, allows alternating current/voltage to pass through NiobiCon™ contacts by using a full-wave bridge rectifier on the supply side to prevent voltage reversal at the contacts and an electrical circuit on the other side to re-construct the alternating signal synchronously with the input signal.

11,038,594: Self-insulating high bandwidth connector, 06/15/2021

This patent combines NiobiCon™ power transfer with a free-space optical transceiver so that high-bandwidth signals such as those from fiber-optics can pass through the connector. The NiobiCon™ contacts transfer power necessary to power the transceivers as well as any other electronics while the optical transceivers convert fiber optic signals into a form that is unaffected by environmental turbidity or debris and allows for less-restrictive mating tolerances than would be used for a typical fiber-optic connector.

11,069,995: Single self-insulating contact for wet electrical connector, 07/20/2021

This patent describes the use of a transition metal for the positive side of a connector and any other material for the negative side. It therefore covers situations such as using a seawater ground return or using more traditional, but less corrosion-resistant, materials for the negative side.

11,075,486: Signal connector system, 07/27/2021

This patent is for a specific contact geometry developed jointly by iCONN Systems LLC and Northrop Grumman. This system uses flat contacts for both the male and female sides and a wedge geometry with plastic backing up the contacts to provide the necessary contact force.

11,569,608: Electrical connector system, 01/31/2023

This patent is for another specific contact geometry developed by iCONN Systems LLC. This system also uses flat contacts for both the male and female sides and a wedge geometry with plastic backing up the contacts to provide the necessary contact force. It also uses contact guides to maintain contact pressure.

Joint Patent, Northop Grumman and Monterey Bay Aquarium Research Institute

12,195,153: Underwater Vehicle Docking System, 01/14/2025

This patent covers a system for docking an underwater vehicle to an energized buoy anchor line using a unique arrangement of brushes.

Northrop Grumman disclosures not filed for a patent:

This disclosure was for transition-metals for water-wetted electrical contacts and was the first attempt to patent NiobiCon™. It was deemed to be a trade secret but was essentially duplicated later by US Patent 9,893,460.

Foreign Filings:

Patent filings for NiobiCon™ have been submitted to multiple countries outside of the United States.

Chapter 11 – Author Biographies

Harvey P. Hack, PhD

Figure 11-1 - Harvey P. Hack, PhD

Dr. Hack is a Northrop Grumman Fellow who has worked at Northrop Grumman Corporation Undersea Systems for 27 years preventing corrosion of their underwater systems. He spent the previous 25 years working for the Naval Surface Warfare Center in the Marine Corrosion Branch, where he did marine corrosion research, electrochemical research, and failure analyses, as well as being Acting Head of the Branch. He has been Chairman of the Board of ASTM International, President of NACE International, and President of the Council of Engineering and Scientific Specialty Boards. Harvey is a Fellow of ASTM International, NACE International (now the Association for Materials Protection and Performance), the Institute for Corrosion (in the UK) and the Washington Academy of Sciences. He is a NACE Certified Corrosion Specialist, Cathodic Protection Specialist, and Coating Inspector Level III. He is one of the inventors of NiobiCon™.

He received a BS in Physics and an MS in Metallurgy and Materials Science from Carnegie-Mellon University and a PhD in Metallurgy from the Pennsylvania State University. Harvey has published over 100 papers in peer-reviewed scientific journals on corrosion and corrosion electrochemistry topics, holds nine patents, and has been an active participant in technical societies, including being Chairman of ASTM Committee G01 on Corrosion of Metals, Chairman of the ASTM Committee on Standards, Chairman of the NACE Committee on Marine Corrosion, Chairman of the NACE Certification Committee, Chairman of the NACE Student Poster Session, and has authored, edited or provided chapters for 7 books.

Harvey received the following awards: the ASTM International Frank W. Reinhart Award for outstanding work on a corrosion publication, the ASTM William T. Cavanaugh Award, the ASTM Award of Merit, the ASTM Award of Appreciation for being an Associate Editor of the Journal of ASTM International, the Dr. Robert Baboian Memorial Lifetime Achievement Award from ASTM Committee G01 on Corrosion of Metals, the Francis L. LaQue Memorial Award from ASTM Committee G01 on Corrosion of Metals, the NACE International T. J. Hull Award for outstanding work on a corrosion publication, the NACE International Distinguished Service Award, the

McFarland Award as an Outstanding Graduate from the Pennsylvania State University Materials Department & ASM, the Francis LaQue Award from the Sea Horse Institute, and the Outstanding Achievement in Engineering Science Award from the Washington Academy of Sciences.

He currently teaches a course on Corrosion Electrochemistry for ASTM International, taught a corrosion course at the US Naval Academy, spent 12 years as the Chairman of the USA Task Advisory Group and head of the USA delegation to ISO Technical Committee 156 on Corrosion of Metals, and was a feature writer for Corrosion Protection in Underwater Magazine for 5 years.

Keith Johanns

Figure 11-2 - Keith Johanns

Keith Johanns leads the Northrop Grumman Mission Systems (NGMS) Intellectual Property & Strategic Technology Agreements (IP&STA) organization. He provides strategic leadership and direction for the identification, protection, commercialization, licensing, and compliance of the NGMS IP portfolio encompassing trade secrets and patents. He leads by example as an inventor with 3 U.S. patents and 4 trade secrets. Keith received degrees in chemical engineering from The Ohio State University and University of Dayton.

James R. Windgassen

Figure 11-3 - James Windgassen

James Windgassen is a multidisciplinary Consulting Engineer at Northrop Grumman Undersea Systems in Annapolis, MD. He is one of the inventors of NiobiCon™. As an electrical engineer, he has worked on analog, power, RF, and embedded designs and has designed many varied electronics systems. His mechanical engineering focus has been in electronics packaging, and he has a wide range of experience ranging from die level packaging to chassis level design.

Jim is one of the founders of the PWB / CCA Community of Practice which seeks to harmonize how Northrop Grumman designs and documents its circuit card assemblies across the entire company and provides a hub for designers across the company to communicate and collaborate.

Jim has been with Northrop Grumman since 2001 when he started his career at Northrop Grumman Xetron Applied Technology Center in Palm Harbor, FL. In 2003 he transferred to Northrop Grumman Undersea Systems Division in Annapolis, MD where he works today. He previously worked at Honeywell in Clearwater, FL where he was involved in the design of inertial navigation systems.

Jim is a passionate engineer and is eternally curious about how things work across a very broad range of subjects. He is an active engineering hobbyist and loves to work on a wide variety of personal projects. In addition, Jim loves to work with children and volunteers his time towards STEM education and more recently, financial literacy for children.

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Figure 2-1 – Color-coded Periodic Table

Source: Wikimedia Commons

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Figure 2-2– Portrait of Charles Hatchett

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Figure 3-10– Tantalum Capacitor Diagrams

Source: Wikipedia

- Wet Slug Ta Capacitor
- Tantalum sintered body
- Dry Slug Ta Capacitor

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Figure 4-7– Fathom-X™ Tether Interface Board

Source: Blue Robotics

Link: https://bluerobotics.com/store/comm-control-power/tether-interface/fathom-x-tether-interface-board-set-copy/

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Figure 4-8– Power Line Communication PLC Module

Source: RAK Wireless

Link: https://store.rakwireless.com/products/lx200v50-evb-power-line-communicationplc-module

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Figure 6-1 – Niobium Jewelry

Source: Angelwear Creations

Link: https://www.etsy.com/shop/AngelwearCreations

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Figure 7-5– I/O Connector Assembly

Source: ICONN Systems

Used with permission from ICONN Systems

Figure 7-6 – I/O Connector Assembly (Alternate View)

Source: ICONN Systems

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Trademarks

- NiobiCon™
  Trademark of Northrop Grumman Systems Corporation

- Powering the Blue Economy™
  Trademark of U.S. Department of Energy's (DOE's) Water Power Technologies Office (WPTO)

- SourceMeter®
  Registered trademark of Keithley Instruments Inc.

- Instant Ocean®
  Registered trademark of Spectrum Brands LLC

- TP-Link®
  Registered trademark of TP-Link Systems Inc.

- Blue Robotics®
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- Fathom-X™
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- RAK®
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- WisLink PLC™
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