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Background

I wanted to clean some badly rusted plane irons. I used the electrolysis procedure employing a battery charger and a solution of washing soda (sodium carbonate) (see <http://Rusty2L.com> [obsolete link]). I was astounded by the favorable results. I am an electrochemist, yet I didn't know what was happening to the rust. Neither did any of my colleagues. This was too much for my curiosity, so I went to the chemistry literature to see what was happening. Much of what I found was incorrect electrochemistry and a lot was speculation. In fact, it was not until 1996 that the chemistry was figured out. I thought others might also want to know what was happening in this process so I wrote up the results.

The Chemistry of Cleaning Rusted Iron by Electrolysis

by Spencer Hochstetler and Bill Tindall

The cleaning process has 4 components- a battery charger, the water with sodium carbonate (washing soda) dissolved in it, an anode (stainless steel object such as a spoon) and the cathode (the rusty iron).

The solution

The solution of sodium carbonate has two purposes. First, sodium carbonate is basic. The electrochemical reactions that occur at the rusted iron work best in a basic solution. Lye (sodium hydroxide) would work as well but it is less safe to use. Sodium bicarbonate, baking soda, may

not work as well as sodium carbonate because it is less basic. The other purpose for the sodium carbonate is to make the water conduct electricity. When the salt, sodium carbonate, is dissolved in water it becomes sodium ions, Na^+ , and carbonate ions CO_3^{-2} . These positive and negative charged ions carry the current in solution. Carbonate moves to the positive wire from the battery charger and sodium moves to the negative wire. This movement of ions through the solution results in a current, just like electrons moving in a wire results in a current. Pure water has a high resistance, about 20 million ohms per centimeter, and negligible current would pass without the sodium carbonate ions.

The battery charger

is a source of electrical current and voltage. Current is the flow of electrons in a wire. Voltage is a measure of the electron energy. So, the battery charger provides electrons with an energy of 12 volts at its negative lead and accepts electrons at its positive lead. The current indicated by the meter provides a measure of how many electrons are flowing. Current can also flow through water, if the water has ions dissolved in it, as provided by the sodium carbonate. When the battery charger is connected to the solution with a metal anode and cathode, the negatively charged carbonate will migrate to the positively charged anode and sodium will migrate to the cathode. The solution completes the circuit so a current of electrons can flow from the negative wire of the battery charger to the positive wire.

The Anode

The most simple anode to consider is an anode made of stainless steel. In this case, the anode is inert, that is, the stainless steel does not undergo any chemical reactions. Its only function is to provide electrical contact between the positive lead of the charger and the solution. The copper connector of the battery charger must make good contact with the stainless steel but it must not touch the solution. If it does touch, it will dissolve. The copper that dissolves will wind up depositing on the iron object being cleaned and cause it to rapidly rust (see [advanced chemistry](#)

section for details). When 12 volts is applied to the anode some chemistry does occur in the solution touching the anode, which will be explained below.

There are two chemistry terms, *oxidation* and *reduction* that must be explained in order to understand the chemistry that occurs at the anode and cathode. Oxidation is a chemical reaction where something gives up electrons. When a chemical species gives up electrons we say it oxidizes. For example when iron metal oxidizes it loses two electrons to become ferrous iron, Fe^{++} . If iron loses three electrons it oxidizes to become ferric iron, Fe^{+++} . Reduction is when something accepts electrons. For example, if Fe^{++} accepted two electrons it would become iron metal, Fe. We would say, ferrous iron was reduced to iron metal.

Oxygen likes to be reduced. When oxygen is reduced, it accepts electrons, it makes oxide, O^{--} . If we put oxygen together with iron metal, the iron is oxidized (gives electrons to the oxygen) and the oxygen is reduced (accepts the electrons lost from iron). The product is one form of rust, ferric oxide, Fe_2O_3 . It is always true that whenever something is oxidized, something else must be reduced. Electrons must come from somewhere (oxidation), to go somewhere (reduction).

Getting back to the anode..... The anode is hooked to the positive wire of the charger. The positive wire accepts electrons. If the positive wire is accepting electrons something is losing electrons (oxidizing). When 12 volts is applied to the anode, water is oxidized at the anode surface and gives electrons up to the anode. The product is oxygen. The bubbles you see coming from the stainless steel anode are oxygen that resulted from the oxidation of water.

The Cathode

The cathode is connected to the negative wire of the battery charger. The negative wire supplies electrons. Therefore, something must gain electrons at the cathode (reduction). Two things are reduced at the cathode, water and the rusty iron. The reduction of water produces hydrogen. The bubbles coming from the cathode are

hydrogen gas. (A safety note: The fuel for the space shuttle is hydrogen and oxygen. Rust electrolysis should be done in a well ventilated area so that explosive concentrations of hydrogen and oxygen are not reached.)

The evolution of hydrogen plays a beneficial role in the cleaning process. All these tiny bubbles forming at the surface blast things off the surface that aren't stuck tightly. Loose rust, grease and even paint are removed by the action of the hydrogen bubbles. This process is sometimes called cathodic cleaning. I suppose the anode is scrubbed too, but who cares.

The reduction of interest is the reduction of the rust. Rust is typically a mixture of many iron compounds. Which iron compounds are present in rust depend on how much oxygen and water was present when it formed and many other factors. The electrochemical reduction of rust is very complicated.

During electrolysis the rust turns from orange to black. It is natural to wonder what the black stuff is. In most cases, the rust next to the iron is reduced to iron metal. This reduced iron will form a somewhat porous layer of new iron on the object cleaned. After electrolysis the iron object will rust very quickly unless it is protected because this porous layer of new iron has a high surface area and it is particularly susceptible to oxidation (rusting). The rest of the rust may reduce to a variety of compounds depending on the compounds in the original rust and the details of the electrolysis. Typically the black stuff that can be rubbed off after electrolysis is a mixture of iron metal and magnetite, Fe_3O_4 , an oxide of iron. Magnetite is an intermediate product in the reduction of rust to iron metal. It is the black stuff in magnetic recording tapes.

Advanced Chemistry

Rust is a complicated material. Typically, it is a combination of ferrous and ferric oxides, hydroxides, and hydrated oxides and some of these compounds may be present in several crystal forms.

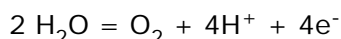
There is much speculation in the chemical and archeological literature about the products that

form when rust is reduced in sodium carbonate. In searching for an answer, people may find a lengthy publication on the DENIX web site (<https://www.denix.osd.mil/denix/Public/ES-Programs/Conservation/Underwater/4-IRON-2.html>). Much of the electrochemistry described is not correct and the conclusions drawn about reduction products are not in agreement with most chemical literature. It was not until 1996 that some chemists from the Swiss Federal Institute and Brookhaven National Lab did definitive work on this subject (see papers by Virtanen in J. Electrochemical Soc. 1996 and 1999). Using a sophisticated X-ray technique they determined what was going on at the cathode when iron oxide is reduced. Normally reductions occur in solution. That is, something has to dissolve before it can be reduced. However, they found that iron oxide will conduct electrons and therefore can be reduced without going into solution. This process is referred to as solid state reduction. The ferric iron atoms in the rust begin to reduce to ferrous oxide, which initially results in a mixture of ferric and ferrous oxides. This combination is called magnetite and is often written as Fe_3O_4 . Eventually, all the ferric oxide becomes ferrous iron. Under less powerful reducing conditions the product would be ferrous carbonate or ferrous hydroxide. However, under the extreme conditions of reduction powered by a 12 V battery charger, they found that ferrous iron can be reduced all the way to iron metal. All this chemistry can occur without any of the iron going into solution. So, based on this work, when we see the rust slowly turning black, we are seeing the formation of Fe_3O_4 which is black and eventually iron metal, which is also black. Finely divided iron is black, not shiny like a solid chunk of iron. All this work was done under laboratory conditions.

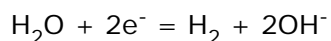
We wanted to find out what happened when a rusty plane iron was reduced in a bucket. We did reductions of heavily rusted iron object in sodium carbonate under conditions normally used from cleaning rusted objects. We used either a 1 or 5 % solution of sodium carbonate and a 12 volt battery charger and continued electrolysis for about 2 hours. The iron piece was dried under an oxygen free atmosphere (nitrogen). The loose black deposit on the iron surface was removed by sticking it to a piece of tape and it was analyzed by X-ray diffraction. We found that the deposit

was magnetite. No iron was detected and no ferric oxides were detected in the black material that readily came off on the tape. Therefore, under our conditions, all the rust was reduced, but the reduction of what had been loose rust did not proceed all the way to iron metal. Perhaps it would have if we had continued electrolysis for a longer time. We had no way of determining whether the rust at the surface of the iron object reduced all the way to iron. We expect that at least some iron was formed at the surface, because after reduction the iron surface rapidly forms red rust (ferric oxide) if it is not quickly dried. Magnetite does not rapidly rust, but finely divided iron will form rust in just a few minutes if it is wet. We conclude, based on our work and that of Virtanen, that rust reduction under the conditions normally used for cleaning, results in the formation of magnetite and possibly some iron metal.

The other chemistry that occurs is the electrolysis of water. At the anode water is oxidized according to this equation



The H^+ formed is quickly neutralized by the carbonate to make carbon dioxide. So, some of the bubbles at the anode may be carbon dioxide as well as oxygen. At the cathode water is reduced



It is important that any copper connector to the anode not touch the solution. If it does, copper will oxidize to cupric ion, Cu^{++} . The connector will be destroyed. Most of the copper ions formed should precipitate as copper carbonate or copper hydroxide, but if any of this dissolved copper reaches the cathode it will be reduced to copper metal on the iron object. Its presence will promote rapid rerusting.

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