Oxidation-reduction Reactions: Electroplating, Batteries, Electrolysis and Corrosion

When an iron nail is placed in a $CuSO_4$ solution, its outer Fe layer will be replaced by a layer of copper atoms. The Cu^{++} leaves the solution and becomes Cu metal while Fe metal goes into the solution and becomes Fe^{++}. The half reactions that do this are

$$Fe(s) \Rightarrow Fe^{++}(aq) + 2e^- \quad \text{and} \quad Cu^{++}(aq) + 2e^- \Rightarrow Cu(s) \quad .$$

The SO_4^{--} ions balance the electrical charge of the solution.

The reaction stops when there is no longer any iron in contact with the solution or when the Cu^{++} ions are depleted. In this example, the electrons are transferred directly to the copper ions.

If we place an iron electrode and a copper electrode in a $CuSO_4$ solution, we can force the copper to plate onto the iron by using a voltage source to force electrons onto the iron electrode while removing them from the copper electrode. This is the principle of electroplating of metals and continues after the iron is covered. Reversing the voltage will reverse the process and remove copper plating from a metal.

In the lab, we made battery cells out of a sandwich of a steel (mostly iron) can lid, an orange slice, and a sheet of copper. Upon wiring four of these cells together (connecting copper of one to steel of the next), we were able to power an LED. The copper was positive and the steel was negative. The orange slice was necessary to allow ions to complete the circuit within the sandwich while keeping the Cu^{++} ions from easily reaching the steel lid. The cell works because the two half reactions shown above are energetically favorable and spontaneously occur when the electrons can flow from the iron electrode to the copper electrode.

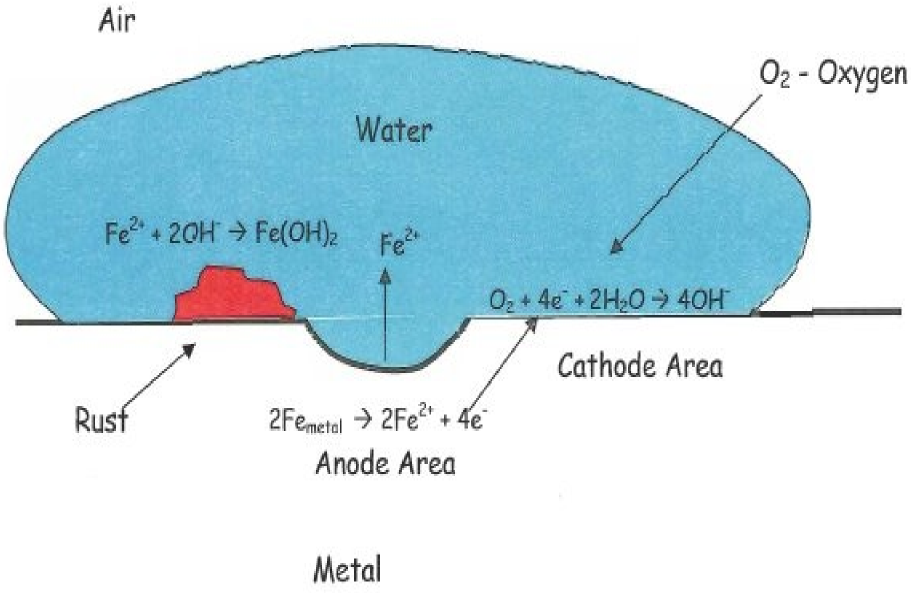
We have already observed electrolysis, the use of electricity to force an unwilling chemical reaction. When we used electricity to make H_2 and O_2 gas from H_2O, and then exploded it, we were using with the reaction $4H_3O^+(aq) + 4e^- \Rightarrow 2H_2(g) + 4H_2O(l)$ at the electrode (called the cathode) connected to the negative side of the battery and $6H_2O(l) \Rightarrow O_2(g) + 4H_3O^+(aq) + 4e^-$ at the electrode (called the anode) connected to the positive side. The overall reaction is then $2H_2O(l) \Leftrightarrow 2H_2(g) + O_2(g)$. Our battery put electrons into the cathode where H_2 gas was freed, and took electrons out of the anode where O_2 gas was freed.

The consumption of H_3O^+ ions at the cathode produces a negative cloud of surplus of OH^- ions around the cathode. Similarly, the production of H_3O^+ at the anode produces a positive cloud of surplus H_3O^+ around the anode. These clouds will impede the flow of electrons into the cathode and out of the anode. Adding the Epsom salt $MgSO_4$ to the water provided Mg^{++} and SO_4^{--} ions that could balance the charges in these clouds without reacting with the electrodes. These pH differences can be made visible using an indicator solution.

Remember we were careful not to use NaCl as our salt because it causes poisonous Cl_2 gas to be produced at the anode instead of O_2.

Fuel cells use high pressures and temperatures to reverse electrolysis, forcing H_2 and O_2 gas to combine and produce electrical energy and H_2O.

The rusting of iron Fe is illustrated by the following diagram obtained from *http://www.corrosionist.com/what_is_Chemistry_of_Corrosion.htm*



Here a small amount iron metal is dissolved in a water drop producing iron ions and freeing up some electrons. These electrons react with water molecules and oxygen molecules dissolved in the water to produce hydroxide ions. The dissolved iron ions then can react with the hydroxide ions to form $Fe(OH)_2$. Once $Fe(OH)_2$ is created, $Fe(OH)_3$ and Fe_2O_3 are also formed.

The net result is that, in the presence of moisture and oxygen, iron has been removed from its strong metallic form and converted to a crumbly oxide. As the rusting proceeds, the anode and cathode areas will gradually cover the entire surface of the structure. Since rust is permeable to air and water, the corrosion slowly continues into the interior of the iron until all the metallic iron has been converted to rust.

Iron construction materials exposed to moisture and air (such as roofing nails, metal fences, and water pipes) are coated with zinc metal that is immune to the rusting type of reaction with water and air. This coating process is called galvanization. Even if the zinc does not coat the iron, it can still provide rust protection because it will preferably act as a "sacrificial" anode and corrode instead of the iron. To act as a "sacrificial" anode, the zinc must be in electrical and ionic contact with the iron and its moisture.

Combustion is considered an oxidation-reduction reaction even though it does not involve an electrical current flow. It does, however, create a polar substance (water) from no polar substances (hydrocarbons). As a result, some rearrangement of charges occurs in combustion.