

## Explanation for the reactions in a saltwater battery with zinc and copper electrodes

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I am a physicist, not a chemist. I'm trying to get a basic understanding of the reactions taking place in a battery using a saltwater electrolyte with copper and zinc terminals. I'm writing a general science level article about it. I have found that the reactions taking place at the terminals are:

 $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$   $(\Delta G = -0.76 \text{ V})$ Zinc terminal:

 $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$  $(\Delta G = -0.34 \text{ V})$ Copper Terminal:

I think I understand the first reaction in terms zinc leaving the terminal and going into solution kind of as if it were dissolved ZnCl<sub>2</sub> (does that make sense?). But I need help understanding the second reaction. I've inserved a copper terminal into the solution. But not copper ions. Am I to understand it like this: when I put the copper terminal in the solution, copper ions immediately drift off, perhaps for the same reason the zinc ions do, but then deposit back onto the terminal in the presence of the electrons released when the zinc goes into solution?

I'd like an explanation somewhere between that it just happens and full on redox theory, if that is possible.

physical-chemistry

electrochemistry

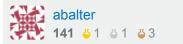
redox

electrons

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## 2 Answers



This answer deals with the situation, when but electrodes are in the same salt water solution.

Assuming your salt solution contains sodium chloride



$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq),$$

then your reaction at the zinc terminal will certainly be

$$Zn(s) + 2Cl^{-} \longrightarrow ZnCl_{2}(aq) + 2e^{-}$$
.

On the copper terminal water will be electrolysed

$$H_2O + 2e^- \xrightarrow{Cu} \frac{1}{2}H_2 \uparrow + ^-OH$$
,

or using autoprotolysis

$$\begin{split} 2\,H_2O & \rightleftharpoons H_3{}^+O + {}^-OH \\ H_3{}^+O + e^- & \stackrel{Cu}{\longrightarrow} \frac{1}{2}\,H_2 \uparrow \ + H_2O. \end{split}$$

This will happen since sodium has a much lower electron affinity than water/hydronium

$$Na^{+} + e^{-} \longrightarrow Na$$
  $E^{\circ} = -2.71 \text{ V}$   
 $2 \text{ H}_2\text{O} + 2 e^{-} \longrightarrow \text{H}_2 + 2^{-}\text{OH}$   $E^{\circ} = -0.83 \text{ V}$   
 $2 \text{ H}^{+} + 2 e^{-} \longrightarrow \text{H}_2$   $E^{\circ} = 0 \text{ V}.$ 

Depending on what salt solution you are using, different cations might be reduced. You can find a collection of values at wikipedia.

In a battery (Galvanic cell) there are usually coupled half cells, and in this case this would probably be  $Zn|Zn^{2+}||Cu^{2+}||Cu$ .

This means, that the Zinc terminal is in a zinc containing solution and the copper terminal is in a copper containing solution. In this case your assumption is correct

Zinc terminal:  $\operatorname{Zn}(s) + \operatorname{ZnCl}_2(aq) \rightleftharpoons 2\operatorname{Zn}^{2+}(aq) + 2\operatorname{Cl}^- + 2\operatorname{e}^-$ 

Copper Terminal:  $CuCl_2(aq) + Cu(s) + 2e^- \rightleftharpoons 2Cu(s) + 2Cl^-$ 

There has to be a salt bridge to neutralise charge differences (ion flow). Note that in that case zinc ions will go into solution, while copper ions will be removed from the solution. If the concentration of copper drops close to zero, then no current can be measured. The galvanic cell can be charged by "reversing" the process, apply opposite current. Then zinc ions will be removed from solution and copper will go into solution. In reality, this is a equilibrium process.

edited Jan 22 '16 at 3:47

answered Jun 12 '14 at 5:15



thanks! That really clears up a lot. In my article I simply said that one electrode sheds electrons and that the other picks them up and that the electrolyte fascilitates this process. The formula you give show that I got this right. Without the Cl-, the zinc wouldn't be oxidized and the Cu++ not reduced, at least not as much. You did go over my head with the equations with the Cu over the arrow and the 1/2 H2 and the up arrow. Remember, I'm not a chemist;) — abalter Jun 12 '14 at 22:41

The Copper over the arrow simply means, that this is catalysed by copper/ takes place at the copper terminal. The arrow pointing upwards simply means, that this compound evaporates/ is a gas and leaves the system. (An arrow pointing downwards would mean that a solid precipitates.) – Martin -  $\nabla - \mathcal{F} \searrow \checkmark$  Jun 13 '14 at 4:03

Very helpful answer. Thanks! Could you clarify why autoprotolysis only happens at the copper terminal and doesn't happen at the zinc terminal (for sodium chloride solution)? Why does hydronium ion not steal an electron from the zinc as well? – akhmed May 10 '18 at 9:05

1 @akhmed Autoprotolysis will happen everywhere, but hydrogen will only evolve at the copper terminal since there the electron flow is right. Also interesting in regards to water and conductivity is the Grotthus mechanism. In total the concentration of hydronium is too low for it to react with zinc directly. – Martin - マーチン ♦ May 10 '18 at 9:17

Awesome. Thanks a lot! I was also pointed to <u>this paper</u>. As I understood it, the hydronium's electron stealing process goes like this: [step 1] a proton must detach from hydronium and form M-H bond first (so M-H bond must be strong enough), then [step 2] two M-H meet each other on the metal surface and  $H_2$  gas forms (so M-H bond must not be too strong either or hydrogen gas will never form). It appears Zn-H is weak so step 1 doesn't occur often. – akhmed May 10 '18 at 22:57



2



The key point you are missing is that the thermodynamic values you report are for standard conditions, meaning that there would also be 1 M  $\rm Zn^{2+}$  and 1 M  $\rm Cu^{2+}$  in the solutions. The Nernst equation can be used to determine the non-standard condition potential (in your case, sticking a copper wire into a solution with effectively no copper ions. In practice, this would be very hard to do, as adventitious ions (and other reactions not considered) will contribute to the cell potential when the intended ion concentrations are so low.



This concept can be used to determine the concentration of copper ions in solution, and may be of interest in explaining the phenomenon to a general audience. Two Cu/Cu<sup>2+</sup> half-cells with the *same* concentration of copper ions will result in a cell potential of zero; however, if one of the cell concentrations is known (for argument's sake, say 1 M) then the "unknown" ion concentration could be found using the Nernst equation.

edited Nov 12 '15 at 0:26



answered Jun 12 '14 at 3:31



A quick answer to get you started - I'll be happy to elaborate if necessary. – bobthechemist Jun 12 '14 at 3:31

I really appreciate you taking a look! Unfortunately, you went over my head and well over that of my audience. It sounds like my understanding is basically correct that once in solution, both  $Zn^{2+}$  and  $Cu^{2+}$  ions end up in solution, but that the copper has a higher affinity to rejoin its terminal than the zinc ions do. I still don't understand how this gets free electrons onto the copper terminal. Nor do I fully understand the role of the electrolyte. Everyone says that the ions carry the electrons from the cathode to the anode, but how? — abalter Jun 12 '14 at 4:01  $\nearrow$ 

Go back to the <u>salt bridge question</u> and note the figure I made. Each beaker is a half-cell which, in order to function properly as an energy source must contain the oxidized and reduced forms of an electron-transfer reaction. What you refer to as terminals (and Chemists refer to as electrodes) are the reduced forms and the ions are the oxidized forms. The reason electrons flow through the wire is because the thermodynamically favored reaction is for Zn to be oxidized and Cu(2+) to be reduced. – bobthechemist Jun 12 '14 at 12:13

(part 2) If you were to place a piece of Zn metal into a beaker filled with Cu(2+), you would "see" Cu metal plate onto the Zn and the blue color of the copper solution would fade. The electrolyte is there solely to decrease the resistance of the solution. Do you mind elaborating on your audience and purpose of the presentation, which will help me improve this answer. – bobthechemist Jun 12 '14 at 12:16

Thanks @bobthechemist. That clears up a lot. I had never before thought of the fact that there would be both zinc and copper would go into the solution as ions, but that the copper has the higher propensity to go back on the electrode. I like how you explained that both the oxidized and reduced species exist, but there is a thermodynamic difference in which is favored for each species. That really clears up a lot. — abalter Jun 12 '14 at 22:37



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