

Pourbaix Diagram

Notes by MIT Student (and MZB)

1. Battery equilibrium electrochemistry

Suppose an electrochemical reaction happening on the electrode/electrolyte interface:



At equilibrium, the electrode potential is related to activities of the reactants by the Nernst equation:

$$E = E^0 + \frac{kT}{ne} \ln \frac{a_O a_e^n}{a_R} \quad (2)$$

where E^0 is the electrical potential of the electrode measured against a standard hydrogen cell electrode under standard conditions. a_O is the chemical activity of the oxidized state, a_R the chemical activity of the reduced state. At equilibrium, the reaction constant $K_O = \frac{a_O a_e^n}{a_R}$ is thus determined by the electrode potential:

$$K_O = \exp\left(\frac{ne}{kT}(E - E^0)\right)$$

Given the dependence of chemical activities on other thermodynamic parameters, the equilibrium electrode potential will separate the oxidized/reduced phases on a phase diagram. If the electrode potential is raised above the equilibrium potential, oxidization is preferred. If below the equilibrium potential, reduction is preferred.

2. Pourbaix diagram

One certain class of phase diagrams is displayed by the equilibrium electrical potential plotted against the pH, when some of the reactants have chemical activities that vary with pH. For instance if H^+ is part of the electrode reaction, then under dilute approximation, $a_{H^+} \sim c_{H^+}$. The pH of the electrolyte is defined as the negative of the natural log of the H^+ ion concentration in the electrolyte:

$$pH = -\log_{10} c_{H^+} \quad (3)$$

Under room temperature, water as the most common solvent by self-ionization will give $pH = 7$ which is the neutral pH. For an acidic solution $pH < 7$, for basic $pH > 7$.

2.1. The electrochemical window for water stability

Now consider the water electrolysis reactions: Anode reaction:



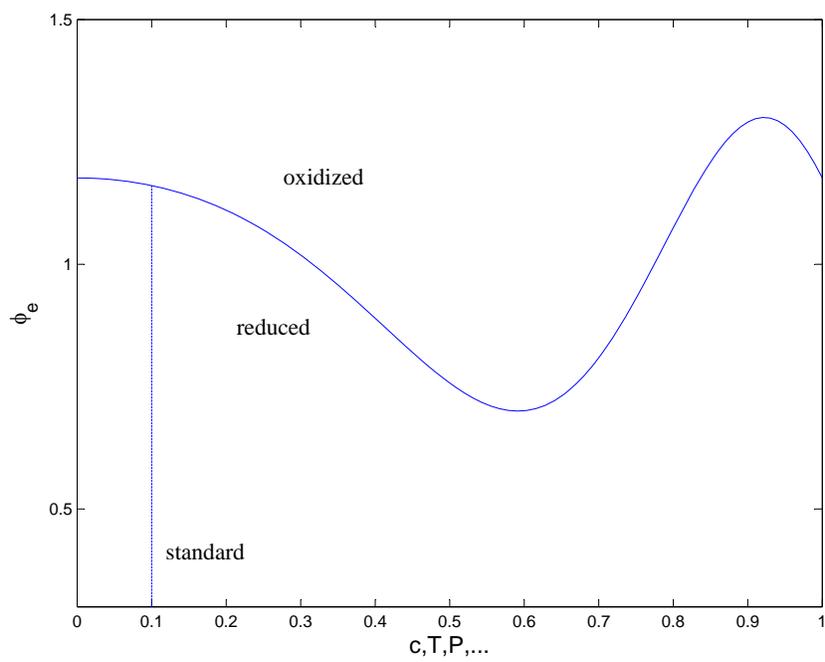
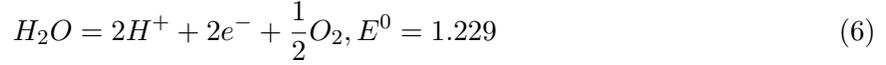


Fig. 1.— Phase diagram of an electrochemical reaction

according to the Nernst equation:

$$E_1 = E^0 + \frac{kT}{2e} \ln \frac{a_{H^+}^2 a_e^2}{a_{H_2}} = -0.06pH(\text{Volts}) \quad (5)$$

Cathode reaction:



according to the Nernst equation:

$$E_2 = E^0 + \frac{kT}{2e} \ln \frac{a_{H^+}^2 a_e^2}{a_{H_2}} = 1.229 - 0.06pH(\text{Volts}) \quad (7)$$

As shown in the Pourbaix diagram of these Fig2, if we impose a potential on the anode higher than E_1 , or the potential on the cathode lower than E_2 , the reactions will favor the production of O_2 and H_2 from H_2O , which is the electrolysis of water itself. Thus the maximum open circuit voltage of a Galvanic cell with water as the solvent in the electrolyte must not exceed the voltage difference in the Pourbaix diagram. This limitation on the open circuit voltage is called the 'electrochemical window' for water stability.

2.2. Remarks on the Pourbaix diagrams

1. Since Pourbaix diagrams describe only equilibrium information, it can tell the reaction directions from thermodynamics but doesn't tell any kinetic information.
2. Pourbaix diagrams are only one certain class of the phase diagrams, which gives a handy description of electrode potential v.s. pH. There are other dimensions of parameters that are not shown on the Pourbaix diagrams. For example, the activity of reactants other than H^+ , temperature, etc. The Pourbaix diagram is a projection of the equilibrium potential surface in a many dimensional parameter space onto the subspace of pH. When other conditions deviate from the standard conditions, the equilibrium potential curve will also move on the Pourbaix diagram.
3. To correctly interpret the Pourbaix diagrams, we should first locate the reactions, i.e., whether the reactions are considered on the anode or cathode. This will as shown in the next section lead to different physics such as electrodeposition or corrosion.

3. Example analysis for a fruit battery

Suppose we now insert a Zn anode and a Cu cathode into a lemon, which contains acid. There will be 4 electrochemical equilibriums in this system:



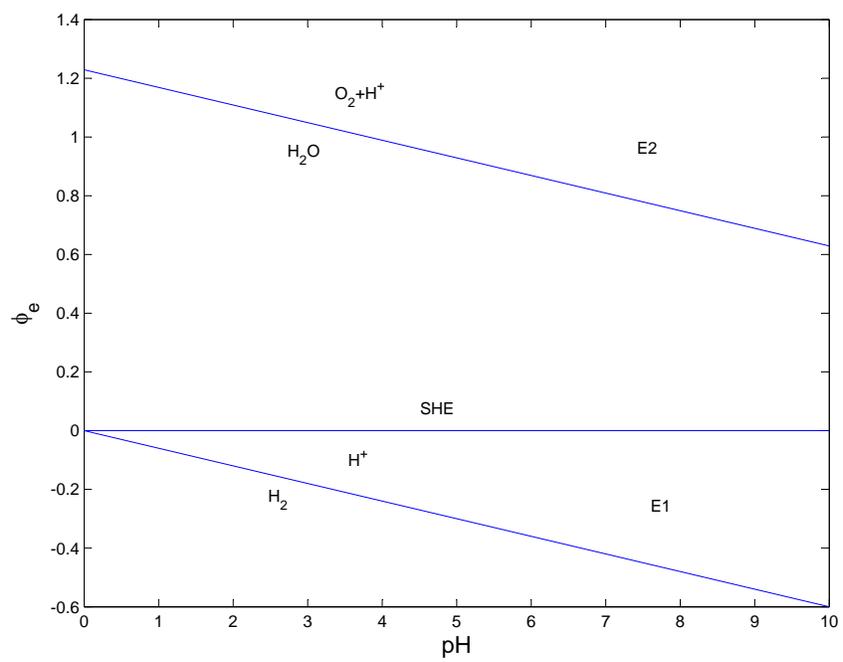
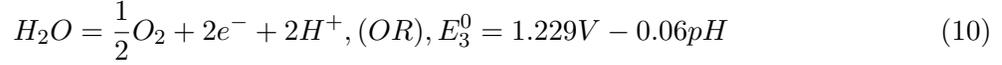


Fig. 2.— The 'electrochemical window' for water stability.



Assume (8) only happen on the anode, and (9) only on the cathode. The Pourbaix diagram is shown in Fig3.

On the cathode, (10) and (11) can both happen, competing with (9). Suppose the cathode potential is around 0.34V and pH is around 0:

1. For (10), it will be going towards reduction, thus thermodynamically will win over (9). However, without catalyst OR is very slow so in reality it doesn't win.
2. For (11), we can read from the Pourbaix diagram that under standard conditions it will be going towards oxidization, which will pair with (9) to make a local net reaction. Normally the local concentration of H_2 on the cathode is very low, so the line for (11) should actually be moved much higher than (9), then it will be going towards reduction, and win over (9).

On the anode, (11) may compete with (8), or pair with (8) to make a local net reaction. Suppose the anode potential is around -0.76V and pH is around 0:

1. Under standard conditions, (11) will be going towards reduction, thus it won't pair with (9) to form a circuit loop. However, it will pair with (8) to make a local net reaction $Zn + 2H^+ = H_2 + Zn^{2+}$ with the anode potential between E_1 and E_4 .
2. If the local H_2 concentration on the anode is very low, then the line for (11) should move up, and it still produces hydrogen gas.
3. If we can somehow maintain a really high enough H_2 concentration or use catalyst to make its activity much higher, and maintain a high pH, such that this line moves down to the dashed one and we are in region 1, then (11) actually goes towards oxidization. It can either pair with the cathode reaction to form a net cell reaction, or pair with (8) to locally reduce Zn, i.e., electrodeposition on the anode.

As one can see from this simple example, when interpreting the Pourbaix diagram, first we should locate the reaction and make clear assumptions about other conditions, then pair the reaction with all the others to see if it's possible to form a net reaction. This net reaction can be a cell reaction when paired with another on the other electrode, or a corrosion/electrodeposition when paired with another on the same electrode.

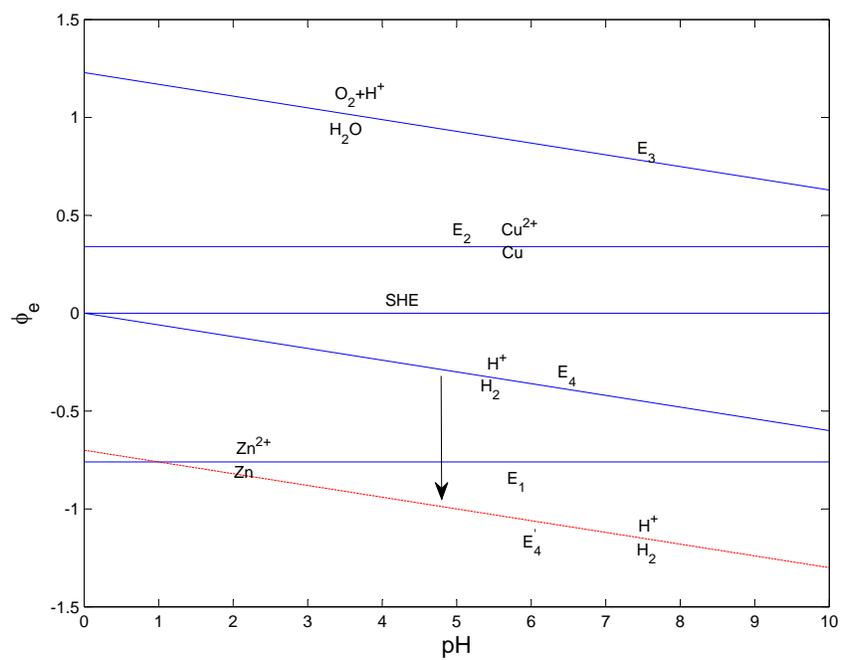


Fig. 3.— The Pourbaix diagram for the electrochemical system of the Zn-Cu-lemon fruit battery.

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