Fuel Cells and Lead-Acid Batteries

We're going to calculate the open circuit voltage of two types of electrochemical system: polymer electrolyte membrane (PEM) fuel cells and lead-acid batteries. To do this, we're going to make use of two equations from the last lecture. The first is the Nernst equation, which describes the potential difference between the electrode and electrolyte in the half-cell reaction

$$\sum_i s_i \mathrm{M}_i^{z_i} \to n\mathrm{e}^-. \tag{1}$$

The potential difference, which is always defined to be the potential of the electrode minus the potential of the electrolyte, is

$$\Delta\phi = \Delta\phi^\circ - \frac{k_B T}{ne} \ln(\prod_i a_i^{s_i}). \tag{2}$$

$\Delta\phi^\circ$ is the potential difference of this half-cell reaction in a particular reference state. The values of the activity a_i, are then scaled so that the activity of species i in the reference state is 1. Reference states are set to be 1 in convenient units, such as 1 atmosphere of pressure for gases.

The second equation is for open circuit voltage, and comes from combining the Nernst equation at each electrode. The total open circuit voltage of a cell is

$$\begin{aligned} V_O &= \Delta\phi_c - \Delta\phi_a \\ &= \Delta\phi_c^\circ - \Delta\phi_a^\circ - \frac{k_B T}{ne} \ln \frac{\prod_{\text{cathode}} a_j^{s_j}}{\prod_{\text{anode}} a_i^{s_i}}. \end{aligned} \tag{3}$$

This describes the open circuit voltage in terms of the half-cell reactions at the cathode and anode, but we can also describe it in terms of the full cell reaction,

$$\sum_i s_i \mathrm{R}_i \rightarrow \sum_j s_j \mathrm{P}_j. \tag{4}$$

Since the reaction at the anode is going forwards in order to produce electrons, s_i for reactants in the half-cell reaction is the same as s_i in the full cell reaction, while the value of s_i for products is defined to be negative in the half-cell reaction but positive in the full cell reaction. The situation is the opposite for the cathode, because the half-cell reaction proceeds backwards, in order to accept electrons. This means that we can rewrite equation 3 in the form

$$V_O = V^\circ - \frac{k_B T}{ne} \ln \frac{\prod_{\text{products}} a_j^{s_j}}{\prod_{\text{reactants}} a_i^{s_i}}, \tag{5}$$

using the stoichiometric coefficients defined for the full cell reaction. Here we have made the definition

$$V^\circ = \Delta\phi_c^\circ - \Delta\phi_a^\circ, \tag{6}$$

the open circuit voltage of the reaction under reference conditions.

1 Polymer Electrolyte Membrane Fuel Cells

1.1 Hydrogen concentration cell

A hydrogen concentration cell has a porous electrode situated in hydrogen gas for both the anode and the cathode, the difference being the pressure of the hydrogen. The two electrodes are separated by a polymer membrane that permits the flow of hydrogen ions but not hydrogen gas. The reactions are

$$\text{anode: } \mathrm{H_2} \rightarrow 2\mathrm{H^+} + 2\mathrm{e^-} \tag{7}$$

$$\text{cathode: } 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{H_2} \tag{8}$$

$$\text{net: } \mathrm{H_{2(a)}} \rightarrow \mathrm{H_{2(c)}}. \tag{9}$$

$U^\theta = 0$ for each reaction, so $V^\circ = 0$. The open circuit voltage is

$$V_O = \frac{k_B T}{2e} \ln \frac{p_{H_2}^a}{p_{H_2}^c}. \tag{10}$$

Here we have assumed that activity is proportional to pressure: we choose our reference state so that activity is equal to pressure measured in atmospheres. In this particular case we could measure pressure in other units,

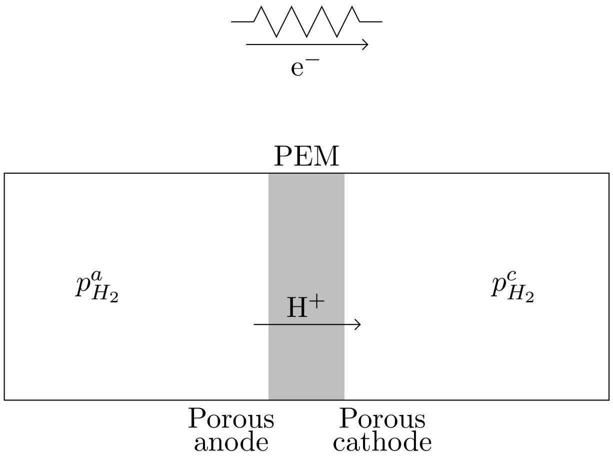

Figure 1: Hydrogen concentration cell

because the units cancel when we take the ratio. To achieve a positive open circuit voltage we need $p^a_{H_2} > p^c_{H_2}$. As $p_{H_2} \to p^c_{H_2}$, open circuit voltage drops to zero. This kind of cell will never give large voltage, because k_BT/e is only 25 mV and logarithms never become particularly large. For example, a cell run between a pressure equal to that at the centre of the sun (around 10^{11} atm, mostly hydrogen) and the earth's atmosphere (where hydrogen is present at around 1 ppm, i.e. a partial pressure of 10^{-6} atm) would only produce approximately 0.5 V.

1.2 Standard PEM fuel cell

A standard PEM fuel cell has hydrogen at the anode and oxygen (converted to water) at the cathode. The reactions are

$$\text{anode: } H_2 \to 2H^+ + 2e^- \qquad U_a^\theta = 0 \tag{11}$$

$$\text{cathode: } \frac{1}{2}O_2 + 2H^+ + 2e^- \to H_2O \qquad U_c^\theta = 1.229 \text{ V} \tag{12}$$

$$\text{net: } H_2 + \frac{1}{2}O_2 \to H_2O \qquad V^\circ = 1.229 \text{ V}. \tag{13}$$

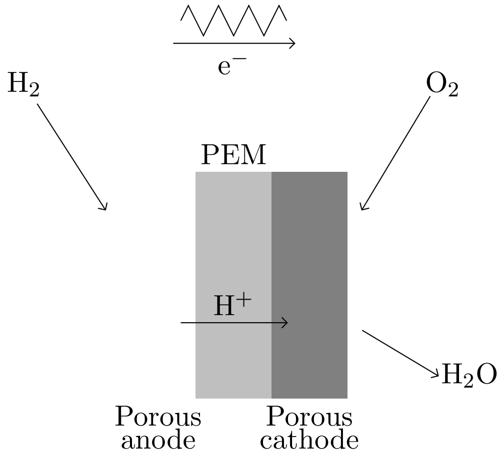

Figure 2: PEM fuel cell

The open circuit voltage is

$$V_O = V^\circ - \frac{k_B T}{2e} \ln \frac{a_{H_2O}}{a_{H_2} a_{O_2}^{1/2}}. \tag{14}$$

Liquid water is a reference state, so as long as water remains in contact with the cathode, a_{H_2O} will be 1. The activity of a gas is its pressure measured in atmospheres, so

$$V_O = V^\circ + \frac{k_B T}{2e} \ln(p_{H_2} p_{O_2}^{1/2}). \tag{15}$$

2 Lead-Acid Batteries

The open circuit voltage of a battery is more complicated than that of a fuel cell. This is because it must depend on the state of charge of the battery, which determines how much of each reactant and product is present, and hence their activities. One example of a battery is the lead-acid battery, used in cars. The anode is lead metal and the cathode is lead oxide, with an electrolyte of sulfuric acid, approximately 6 M (one third H_2SO_4 by mass). This is very acidic (pH around 0), making battery acid potentially very dangerous. This battery has reactions

$$\text{anode: } \mathrm{Pb} + \mathrm{SO_4^{2-}} \rightarrow \mathrm{PbSO_4} + 2\mathrm{e^-} \qquad U_a^\theta = -0.356\ \mathrm{V} \tag{16}$$

$$\text{cathode: } \mathrm{PbO_2} + \mathrm{SO_4^{2-}} + 4\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{PbSO_4} + 2\mathrm{H_2O} \qquad U_c^\theta = 1.685\ \mathrm{V} \tag{17}$$

$$\text{net: } \mathrm{Pb} + 2\mathrm{H_2SO_4} + \mathrm{PbO_2} \rightarrow 2\mathrm{PbSO_4} + 2\mathrm{H_2O} \qquad V^\circ = 2.041\ \mathrm{V}. \tag{18}$$

The open circuit voltage is

$$V_O = V^\circ - \frac{k_BT}{2e} \ln \frac{a_{PbSO_4}^2 a_{H_2O}^2}{a_{Pb} a_{PbO_2} a_{H^+}^4 a_{SO_4^{2-}}^2}. \tag{19}$$

The activity of water and of the solids is 1, so the open circuit voltage will depend on the activities of the hydrogen and sulfate ions. We'll particularly focus on the activity of the hydrogen ion, because it can be involved in several other reactions including corrosion and electrolysis. To explore the effect of hydrogen concentration, we can set the activity of sulfate equal to 1. If its activity is something else, this will simply give some constant offset to the open circuit voltage. In a real battery, sulfate activity will vary, but this effect will be less important than the variation of hydrogen activity, so we'll ignore it. The open circuit voltage is then

$$V_O = V^\circ + \frac{2k_BT}{e} \ln a_{H^+} \tag{20}$$

$$= V^\circ - \frac{2k_BT}{e} \ln 10(-\log_{10} a_{H^+}). \tag{21}$$

$2k_BT/e \ln 10$ is 0.12 V, while $-\log_{10} a_{H^+}$ is the definition of pH. We often use $-\log_{10} c_{H^+}$ as pH, where c_{H^+} is the concentration of hydrogen ions (measured in $\mathrm{mol\,L^{-1}}$). The latter is in fact the definition of p[H]: the two are often used interchangeably because activity is proportional to concentration in a wide range of conditions. Thus pH is correct in the equations that follow, but using p[H] instead would make very little difference. The open circuit voltage of this battery is

$$V_O = (2.041 - 0.12\mathrm{pH})\ \mathrm{V}. \tag{22}$$

To see the range of conditions in which this battery can effectively operate, we consider the Nernst equation for various possible reactions:

Lead / sulfuric acid (half-cell) reactions:

$$\mathrm{PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}} \qquad U_{23} = -0.356 \text{ V} \tag{23}$$

$$\mathrm{PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O} \qquad U_{24} = (1.685 - 0.12\mathrm{pH}) \text{ V} \tag{24}$$

Other lead / water reactions:

$$\mathrm{PbO + 2H^+ + 2e^- \rightarrow Pb + H_2O} \qquad U_{25} = (0.25 - 0.06\mathrm{pH}) \text{ V} \tag{25}$$

$$\mathrm{3PbO + H_2O \rightarrow Pb_3O4 + 2H^+ + 2e^-} \qquad U_{26} = (0.97 - 0.06\mathrm{pH}) \text{ V} \tag{26}$$

$$\mathrm{Pb^{2+} + H_2O \rightarrow PbO + 2H^+} \qquad \mathrm{pH} = 6.35 \tag{27}$$

$$\mathrm{Pb^{2+} + 2e^- \rightarrow Pb} \qquad U_{28} = -0.126 - 0.03\mathrm{p[Pb^{2+}]} \text{ V} \tag{28}$$

$$\mathrm{Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e^-} \qquad U_{29} = 1.45 + 0.03\mathrm{p[Pb^{2+}]} - 0.118\mathrm{pH}) \text{ V} \tag{29}$$

Electrolysis of water:

$$\mathrm{2H^+ + 2e^- \rightarrow H_2} \qquad U_{30} = -0.06\mathrm{pH} \text{ V} \tag{30}$$

$$\frac{1}{2}\mathrm{O_2 + 2H^+ + 2e^- \rightarrow H_2O} \qquad U_{31} = (1.23 - 0.06\mathrm{pH}) \text{ V} \tag{31}$$

The half-cell reactions imply that the voltage decreases with pH, and thus the battery operates most effectively in strong sulfuric acid. However, acidic conditions can promote other potentially undesired reactions, so it is important to compare them thermodynamically. In the list above, we include other corrosion and electrolysis reactions to determine which will be favored under different conditions.

We can represent these reactions on a Pourbaix diagram (see below), showing the stable states for the species involved in the reactions, as a function of potential (relative to the standard hydrogen electrode) and pH. The Pourbaix diagram is thus a thermodynamic phase diagram in voltage-pH space, with transition lines given by the Nernst equation. (Since pH is defined in terms of H^+ activity, the these are straight lines.) The reactions above illustrate several different types of reactions, which appear differently on the Pourbaix diagram. Faradaic reactions involving H^+ appear as tilted lines, generally decreasing with pH. Reactions which do not involve charge transfer, such as (27), have no potential dependence, and thus appear as vertical lines. Reactions not involving H^+ such as (23) and (27) appear as horizontal lines.

From reactions (28)-(29), we see that the Pb^{2+} ion is favored over metallic lead and lead oxide in acidic solutions and low potentials, and thus dissolution of the electrodes is thermodynamically favored under such conditions. However, the presence of SO_4^{2-} in sulfuric acid triggers reactions (23)-(24), which are favored over the dissolution reactions and end up shielding the electrodes with a lead sulfate film. During cycling of the battery, this solid film is partially transferred from one electrode to the other, in a reversible fashion, thus allowing use of the lead-acid cell as a secondary (rechargeable) battery.

When two half-cell reactions occur at the same electrode, resulting in a net charge transfer between the chemical species and no net electron transfer to or from the electrode, the net reaction is referred to as a "corrosion reaction". In such situations, the electrode acts as both the anode and the cathode at the same time. For example, the combination of (23) and (24) leads to the corrosion reaction,

$$\mathrm{Pb}^{2+} + \mathrm{SO}_4^{2-} \rightarrow \mathrm{PbSO}_4 \tag{32}$$

When multiple, competing reactions occur at the same electrode, one must generally consider the kinetics of the reactions to determine the open circuit voltage via the requirement of zero total current. (The case of corrosion in lead-acid batteries is considered in the homework.)

In aqueous solutions one must always consider electrolysis of water causing hydrogen and oxygen evolution, (30)-(31), which defines the "electrolysis window" outside of which gas evolution may consume current and compete with the lead-acid reactions. (Note that the voltage difference for these reactions is the same as in the PEM fuel cell and does not depend on pH.) The electrolysis of water is usually not a problem during discharge of the battery, when voltage is less than V_O, since hydrogen and oxygen are produced only slowly and can escape. During overcharging, when $V \gg V_O$, hydrogen and oxygen can be produced faster than they diffuse away, leading to possible combustion. Note that these phenomena involve kinetics and transport (to be discussed later in the class), and thus cannot be understood only from equilibrium considerations. Instead, the Nernst equation and Pourbaix diagram only serve as a rough guide for which reactions may actually take place in a real system.

For further reading, see G. Prentice, *Electrochemical Engineering Principles.*

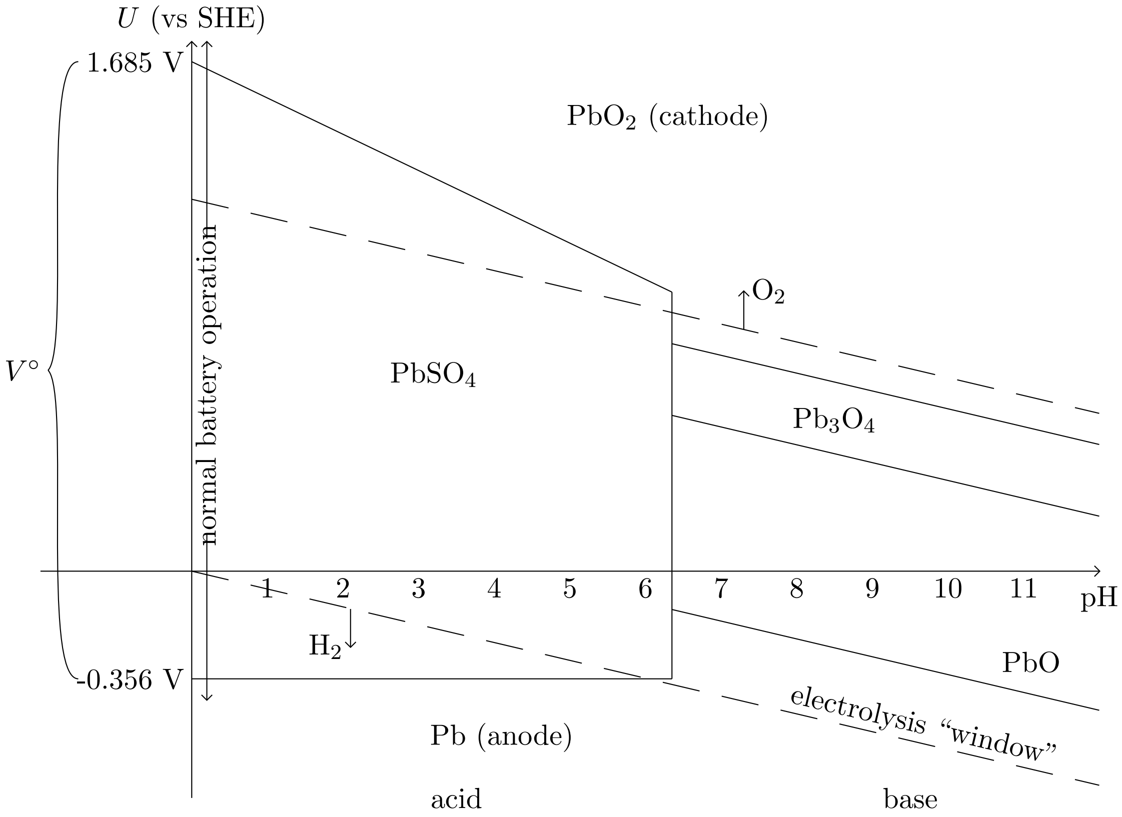

Figure 3: Pourbaix diagram for a lead and sulfuric acid system

Source:http://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2011/lecture-notes/MIT10_626S11_lec09.pdf