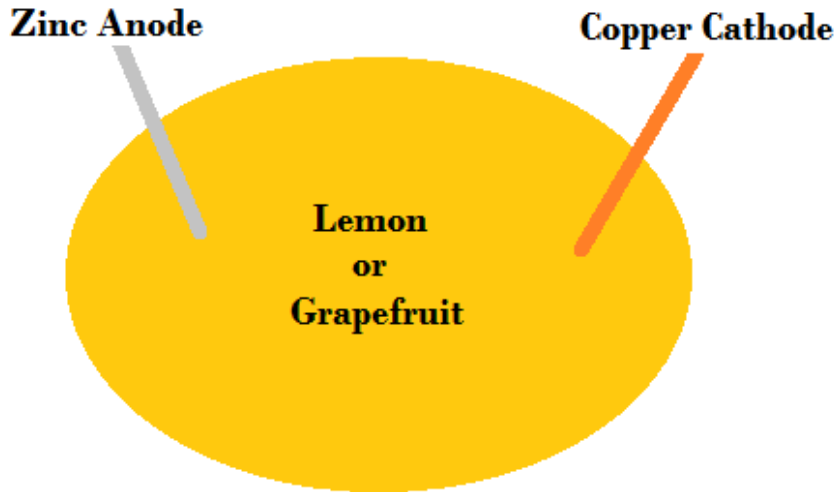**Summary:** This lecture looks at two examples of metal-acid batteries, utilizing the Nernst equation and Pourbaix diagrams to gain an understanding of the system's open circuit voltage (OCV) behavior.
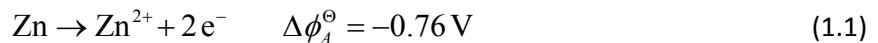
Metal-acid batteries

Example 1: Fruit battery

Conditions:

Zinc metal anode, Copper metal Cathode, Citric acid electrolyte (pH=3 for grapefruit, pH=2 for lemon)

Anodic reaction:

$$Zn \rightarrow Zn^{2+} + 2\,e^{-} \qquad \Delta\phi_A^{\ominus} = -0.76\,V \tag{1.1}$$

Potential cathodic reactions:

$$2H^{+} + 2\,e^{-} \rightarrow H_2 \qquad \Delta\phi_C^{\ominus} = 0\,V \tag{1.2}$$

$$Cu^{2+} + 2\,e^{-} \rightarrow Cu \qquad \Delta\phi_C^{\ominus} = 0.34\,V \tag{1.3}$$

As always, the $\ominus$ denotes standard conditions.

Reaction 1.3 can immediately be eliminated as the concentration of Cu^{2+} would be extremely low in the fruit. The effect that this low concentration would have on the battery's OCV will be explored later. The overall battery reaction is given as 1.4 below.

$$Zn + 2\,H^{+} \rightarrow Zn^{2+} + H_2 \qquad \Delta\phi^{\ominus} = \Delta\phi_C^{\ominus} - \Delta\phi_A^{\ominus} = 0.76\,V \tag{1.4}$$
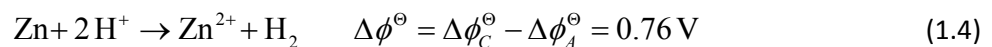
Applying the Nernst equation to this system, yields the following potentials for each half reaction.

Anode:

$$\Delta V = -0.76 + \frac{k_B T}{2e} \ln\left(\frac{a_{Zn^{2+}} a_{e^-}^2}{a_{Zn}} \right) \tag{1.5}$$

Cathode:

$$\Delta V = 0 + \frac{k_B T}{2e} \ln\left(\frac{a_{H^+}^2 a_{e^-}^2}{a_{H_2}} \right) \tag{1.6}$$

For the overall cell, subtract the anode ΔV from the cathode ΔV.

$$V_O = 0.76 + \frac{k_B T}{2e} \ln\left(\frac{a_{H^+}^2 a_{Zn}}{a_{H_2} a_{Zn^{2+}}} \right) \tag{1.7}$$

Knowing that $a_{Zn} = 1$ for a solid metal electrode, 1.6 can be simplified.

$$V_O = 0.76 + \frac{k_B T}{2e} \ln\left(\frac{a_{H^+}^2}{a_{H_2} a_{Zn^{2+}}} \right) \tag{1.8}$$

In the dilute limit, the activities of each species can be estimated by their concentrations or partial pressures normalized by the standard condition concentration or partial pressure (1M or 1atm), respectively; this results in dimensionless concentrations and pressures. So, 1.8 can be rewritten in terms of measurable dimensionless quantities.

$$V_O = 0.76 + \frac{k_B T}{2e} \ln\left(\frac{c_{H^+}^2}{p_{H_2} c_{Zn^{2+}}} \right) \tag{1.9}$$

Define $pH_2 = -\log_{10}(p_{H_2})$ and $pZn = -\log_{10}(c_{Zn^{2+}})$ and evaluate at room temperature (~25°C).

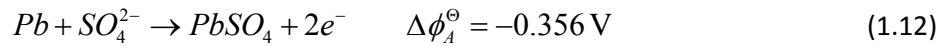$$V_O = 0.76 - 0.06\, pH + 0.03\, pH_2 + 0.03\, pZn \tag{1.10}$$

If we had decided to try to use the copper reaction for the cathode (1.3), the resulting OCV would be given as follows (again using the activity of the solid metal is 1 and defining $pZn = -\log_{10}(c_{Cu^{2+}})$).

$$V_O = 1.1 + \frac{k_B T}{2e} \ln\left(\frac{c_{Cu^{2+}}}{c_{Zn^{2+}}} \right) = 1.1 - 0.03\, pCu + 0.03\, pZn \tag{1.11}$$
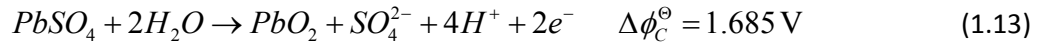
Any small amount of copper ions in solution would be depleted almost immediately, at which point the OCV would diverge to $-\infty$. Thus, it is clear that copper cannot be responsible for the cathodic reaction.
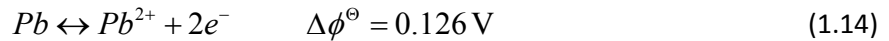
Example 2: Lead-Acid Battery

Anode reaction

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \qquad \Delta\phi_A^\Theta = -0.356\,\text{V} \tag{1.12}$$

Cathode reaction

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \qquad \Delta\phi_C^\Theta = 1.685\,\text{V} \tag{1.13}$$

Lead Electrodeposition and Dissolution

$$Pb \leftrightarrow Pb^{2+} + 2e^- \qquad \Delta\phi^\Theta = 0.126\,\text{V} \tag{1.14}$$

$$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O \qquad \Delta\phi^\Theta = 1.45\,\text{V} \tag{1.15}$$

The $\Delta\phi$ in reactions 1.13 and 1.15 have strong dependencies on electrolyte pH as given by equations 1.16 and 1.17 below.

$$\Delta\phi = 1.685 - 0.12\,\text{p}H \tag{1.16}$$

$$\Delta\phi = 1.45 - 0.12\,\text{p}H \tag{1.17}$$

The overall cell voltage as a function of pH is given by equation 1.18 below.

$$V_O = \Delta\phi_C - \Delta\phi_A = 2.041 - 0.12\,\text{p}H \tag{1.18}$$

A similar battery utilizing the Pb-PbO₂ coupling could function in the absence of the SO_4^{2-} anion, but such a battery would require lead ions to be added from solution directly onto the lead electrode which is an unstable process. In the presence of sulfuric acid (H₂SO₄), there is a twofold benefit for the battery. First, the voltage increases in more acidic environments (low pH). Second, the PbSO₄ forms a protective layer on the two electrodes as shown below, allowing for stable and reversible electrochemistry.
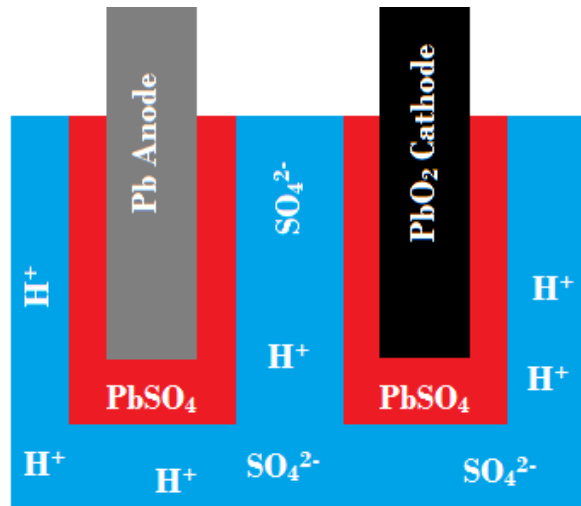
Determining the stable species in the battery at a given voltage is easiest to conceptualize with the aid of a Pourbaix diagram, which plots the $\Delta\phi$ for redox reactions vs pH of the chemical environment. Taking the first reaction (1.12) as an example, at voltages below -0.356V, any lead species will be reduced to lead metal. At voltages higher, some other species will be stable; this depends on whether that higher voltage falls within region I, II, III, or IV.

Pourbaix diagram
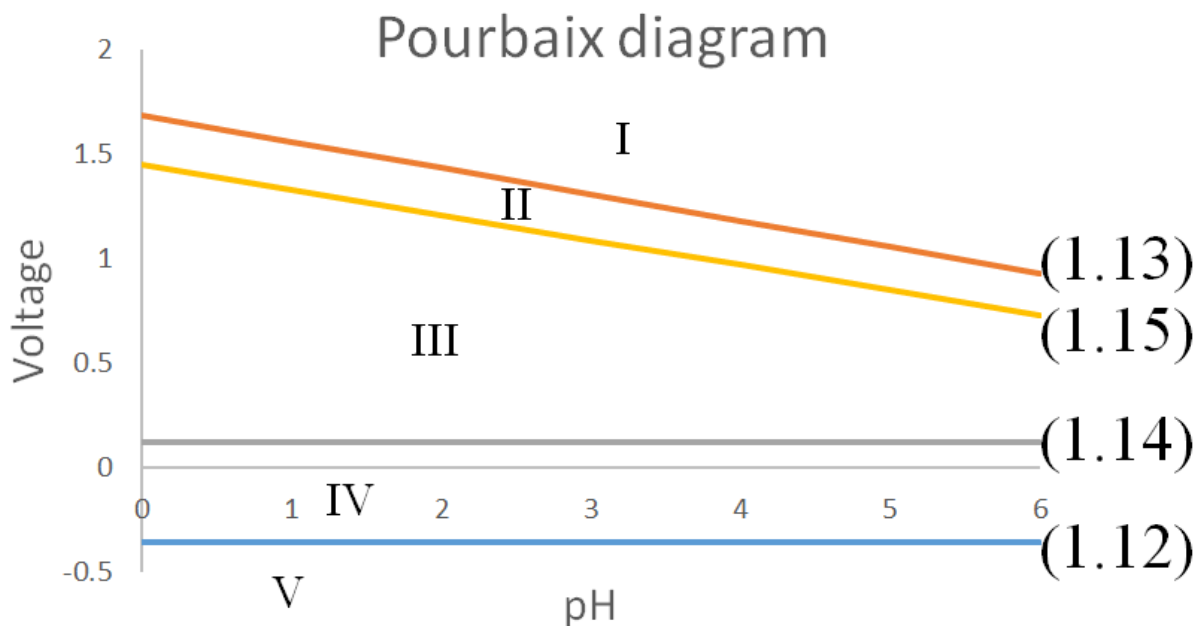
The table below summarizes the favored species in each of the regions (I-IV)

Region	In the presence of SO_4^{2-} in H_2O	In the presence of only H_2O
I	PbO_2	PbO_2
II	$PbSO_4$	PbO_2
III	$PbSO_4$	Pb^{2+}
IV	$PbSO_4$	Pb
V	Pb	Pb

10.626 Electrochemical Energy Systems

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