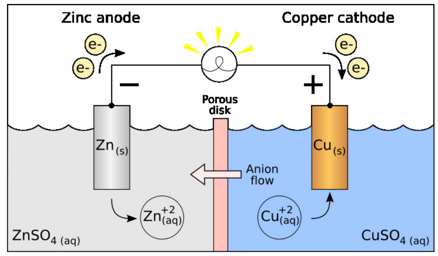
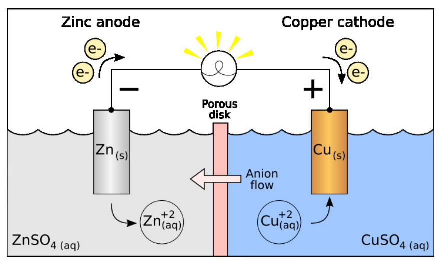
Introducing the Daniell Cell

- In this lesson, we look at the operation of three example cells
- We start with the so-called Daniell cell which is perhaps the simplest to understand
- Each “half cell” consists of a solid metal electrode submerged in an electrolyte solution
- In the negative electrode, the electrolyte is $ZnSO_4$, which dissociates into Zn^{2+} plus SO_4^{-2} when dissolved in water
- In the positive electrode, the electrolyte is $CuSO_4$, which dissociates into Cu^{2+} plus SO_4^{2-} when dissolved in water



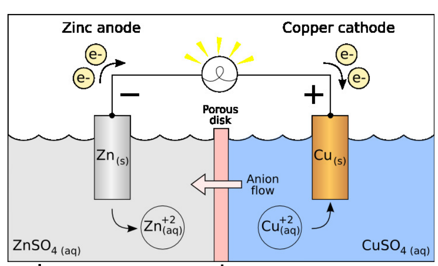
Discharging a Daniell Cell

- On discharge, the zinc electrode dissolves, releasing Zn^{2+} into the electrolyte
- The positive electrode consumes Cu^{2+} (copper is plated onto the copper electrode)
- This produces a temporary deficiency of SO_4^{2-} in the negative-electrode region and a surplus in the positive-electrode region
- Thus, SO_4^{2-} diffuses through the porous disk from the positive-electrode region to the negative-electrode region to compensate
- The opposite process happens on charge



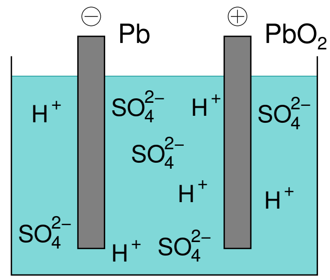
Voltage of a Daniell Cell

- At the negative electrode, we have the redox reaction $Zn^{2+} + 2e^- \leftrightharpoons Zn$, having standard potential $E^0 = -0.76$ V
- At the positive electrode, we have the redox reaction $Cu^{2+} + 2e^- \leftrightharpoons Cu$, having standard potential $E^0 = 0.34$ V
- Overall reaction: $Zn + Cu^{2+} \leftrightharpoons Zn^{2+} + Cu$, having standard potential $E^0 = 0.34\,\text{V} - (-0.76\,\text{V}) = 1.10\,\text{V}$
- Note: “standard potentials” assume specific electrolyte concentrations, temperature
- Therefore, the actual voltage varies somewhat from standard potential in practice



Lead-acid electrochemical cells

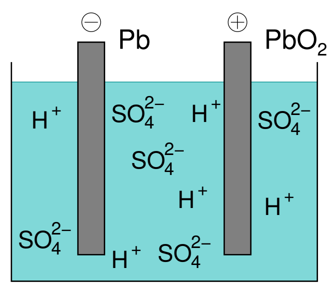
- A lead-acid cell comprises two lead-based plates and an aqueous sulfuric-acid (H_2SO_4) electrolyte
- In the fully discharged state, both electrodes are $PbSO_4$ and the electrolyte is a dilute H_2SO_4
- When discharging, the negative-electrode reaction is $Pb_{(s)} + SO^{2-}_{4(aq)} \leftrightharpoons PbSO_{4(s)} + 2e^-$, and the positive-electrode reaction is $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \leftrightharpoons PbSO_{4(s)} + 2H_2O_{(l)}$
- The total reaction is $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \leftrightharpoons 2PbSO_{4(s)} + 2H_2O_{(l)}$



- Opposite occurs when charging: when fully recharged, the negative electrode is Pb, the positive electrode is PbO_2, electrolyte is a more concentrated solution of H_2SO_4

Lead-acid voltage

- The standard potential of the negative-electrode reaction is $E^0 = -0.356$ V and the standard potential of the reaction at the positive electrode is $E^0 = 1.685$ V
- Therefore, the full cell has standard potential $E^0 = 1.685\,\text{V} - (-0.356\,\text{V}) = 2.041\,\text{V}$
- Voltage varies with concentration of the sulfuric acid (state of charge) and with temperature
- Note that vehicle “12 V” lead-acid batteries comprise six individual lead-acid cells internally wired in series
- Similarly, “6 V” motorcycle lead-acid batteries comprise three individual lead-acid cells internally wired in series

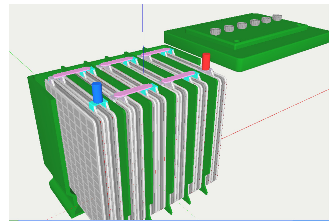


Lead-acid charge/discharge protection

- Need to protect against overcharge:
  - Electrolysis of water evolves H_2 and O_2 gasses
  - Electrolysis of other compounds in electrodes and electrolyte can create poisonous gasses
  - Gasses cause bulging and deformation of sealed batteries
- Need to protect against overdischarge:
  - Lead-sulphate crystals form which often cannot be decomposed, causing capacity loss
- In practice, should: limit depth of discharge; trickle charge when charged but not in use to prevent leakage draining the battery; use pulses to break up lead-dioxide crystals on charge; trickle charge to equalize cells in series

Lead-acid battery construction

- Lead-acid batteries aren't often built with solid lead plates
- Instead, the electrodes are usually constructed from a lead-alloy grid (for strength) covered with a sponge-like lead paste (to increase surface area, for higher power)
- In "flooded" cells, the separator is a simple spacer and the electrolyte is liquid
- In "absorptive glass mat" (AGM) cells, the separator is a glass mat saturated with a minimal amount of electrolyte



- Gassing of AGM cells is not a concern due to minimal electrolyte: cell can be sealed
- Silica can be added to electrolyte to make a gel: also allows for sealed construction and less stratification of H_2SO_4 concentrations (yields longer life but lower power)

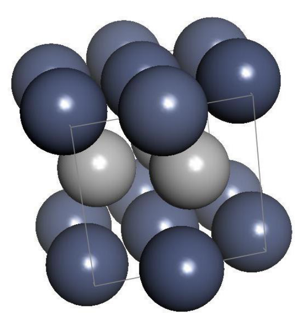
Nickel-metal-hydride (NiMH) cells

- More recently new cell chemistries have been developed using alternative chemical reactions to the traditional redox scheme
- Metal hydride cells depend on ability of some metallic alloys ("hydrides") to absorb large amounts of hydrogen (like a sponge), which can reversibly react in a battery
  - As we will see, lithium-ion cells work in a similar way
- Such metals or alloys are used for the negative electrodes; the positive electrode is nickel hydroxide

- The electrolyte, which is a hydrogen-absorbent aqueous solution such as aqueous potassium hydroxide, takes no part in the reaction but serves to transport the hydrogen between the electrodes.

The NiMH negative electrode

- The "magic" of the NiMH cell is in its negative electrode, which is a rare-earth hydrogen-absorbing metal alloy
  - Either of the "AB_5" form where "A" can be lanthanum, cerium, neodymium, praseodymium and "B" can be nickel, cobalt, manganese, or aluminum
  - Or of the "AB_2" form where "A" can be titanium or vanadium and "B" can be zirconium or nickel, doped with chromium, cobalt, iron, or manganese
- Key point: hydrogen is absorbed into metal alloy without changing its chemical formulation or structure



- Very gentle when compared with standard redox reactions, leading to very long life of NiMH cells

Calculating NiMH voltage

- Negative-electrode reaction $\mathrm{M} + \mathrm{H}^+ + e^- \leftrightharpoons \mathrm{MH}$ where "M" is the metal hydride and where the half-cell standard potential is generally around −0.8 V (depending on the metal)
- Positive-electrode (which is nickel hydroxide ($\mathrm{Ni(OH)_2}$) in NiMH) reaction is $\mathrm{Ni(OH)_2} + \mathrm{OH^-} \leftrightharpoons \mathrm{NiOOH} + \mathrm{H_2O} + e^-$, having a standard potential of $E^0 = 0.5\,\mathrm{V}$
- Thus, the overall reaction is $\mathrm{Ni(OH)_2} + \mathrm{M} \leftrightharpoons \mathrm{NiOOH} + \mathrm{MH}$, having a standard potential $E^0 = 0.5\,\mathrm{V} - (-0.8\,\mathrm{V}) = 1.3\,\mathrm{V}$
- Must guard against overcharge: Oxygen gas is evolved when positive electrode no longer has $\mathrm{Ni(OH)_2}$ left to react with $\mathrm{OH^-}$, but if charged slowly $\mathrm{O_2}$ diffuses, recombines safely with $\mathrm{H^+}$ to form water
- Must also guard against overdischarge: $\mathrm{H_2}$ gas is evolved

Summary

- We have seen examples of Daniell, lead-acid, and NiMH cells
- In each case, we investigated the individual half-cell electrode reactions and were able to predict an overall cell voltage
- Despite many overall similarities, there were significant distinctions
  - The Daniell cell uses two different electrolytes
  - Lead-acid uses sponge lead paste spread on a lead-alloy grid to increase power
  - NiMH uses hydrogen-absorbing metal hydride for one electrode, extending life
- While the BMS algorithms we study are general in nature, we will apply them specifically to lithium-ion, which has distinctions from what we have seen so far
- Therefore, our focus next week will be on understanding lithium-ion cells

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