Oxidation-Reduction Reactions

$$Fe^{3+} + Ce^{3+} \rightarrow Fe^{2+} + Ce^{4+}$$

$Ce^{3+} \rightarrow Ce^{4+} + e$

Oxidation

$Fe^{3+} + e \rightarrow Fe^{2+}$

Reduction

Oxidation-Reduction Reactions

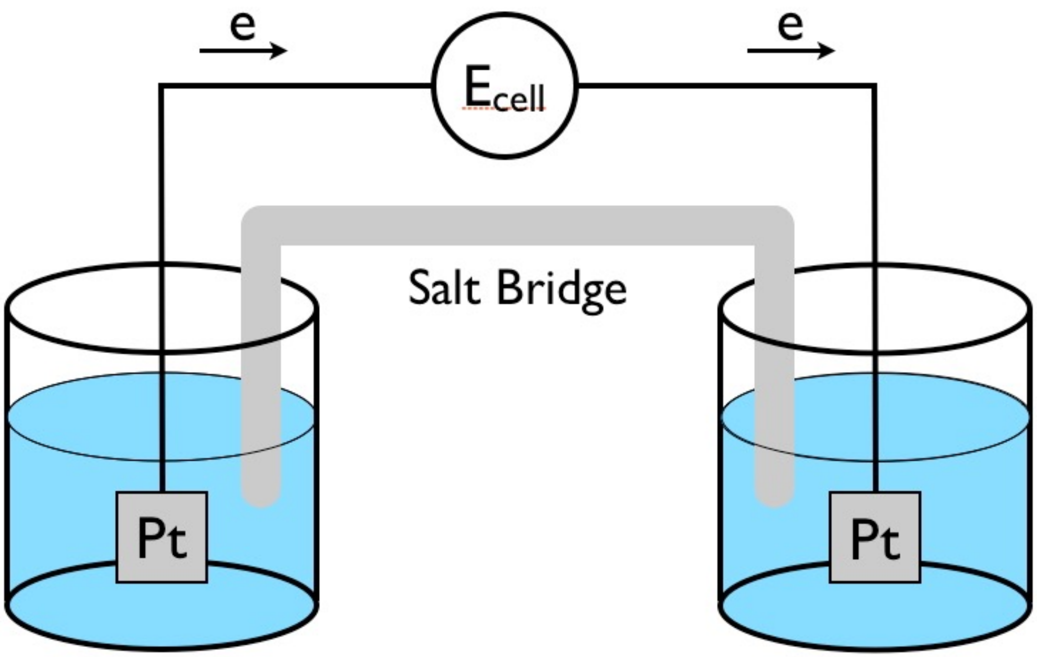
$$Fe^{3+} + Ce^{3+} \rightarrow Fe^{2+} + Ce^{4+}$$

$Ce^{3+} \rightarrow Ce^{4+} + e$

Oxidation

$Fe^{3+} + e \rightarrow Fe^{2+}$

Reduction



$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

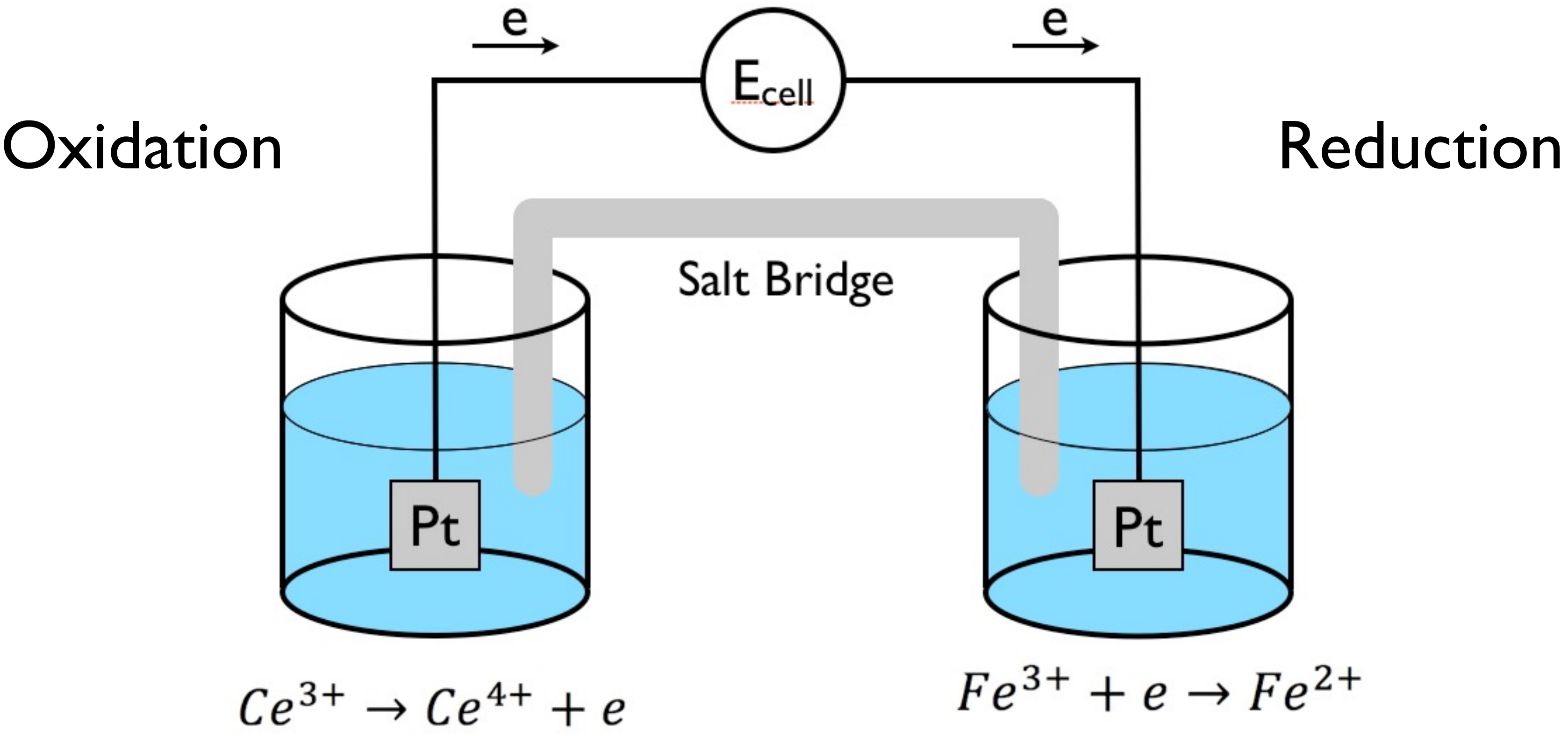
Oxidation-Reduction Reactions

$$\Delta G = -nFE_{cell}$$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} lnQ$$

$$\Delta G = \Delta G^0 + RTlnQ$$

where $\Delta G^0 = -nFE^0_{cell}$

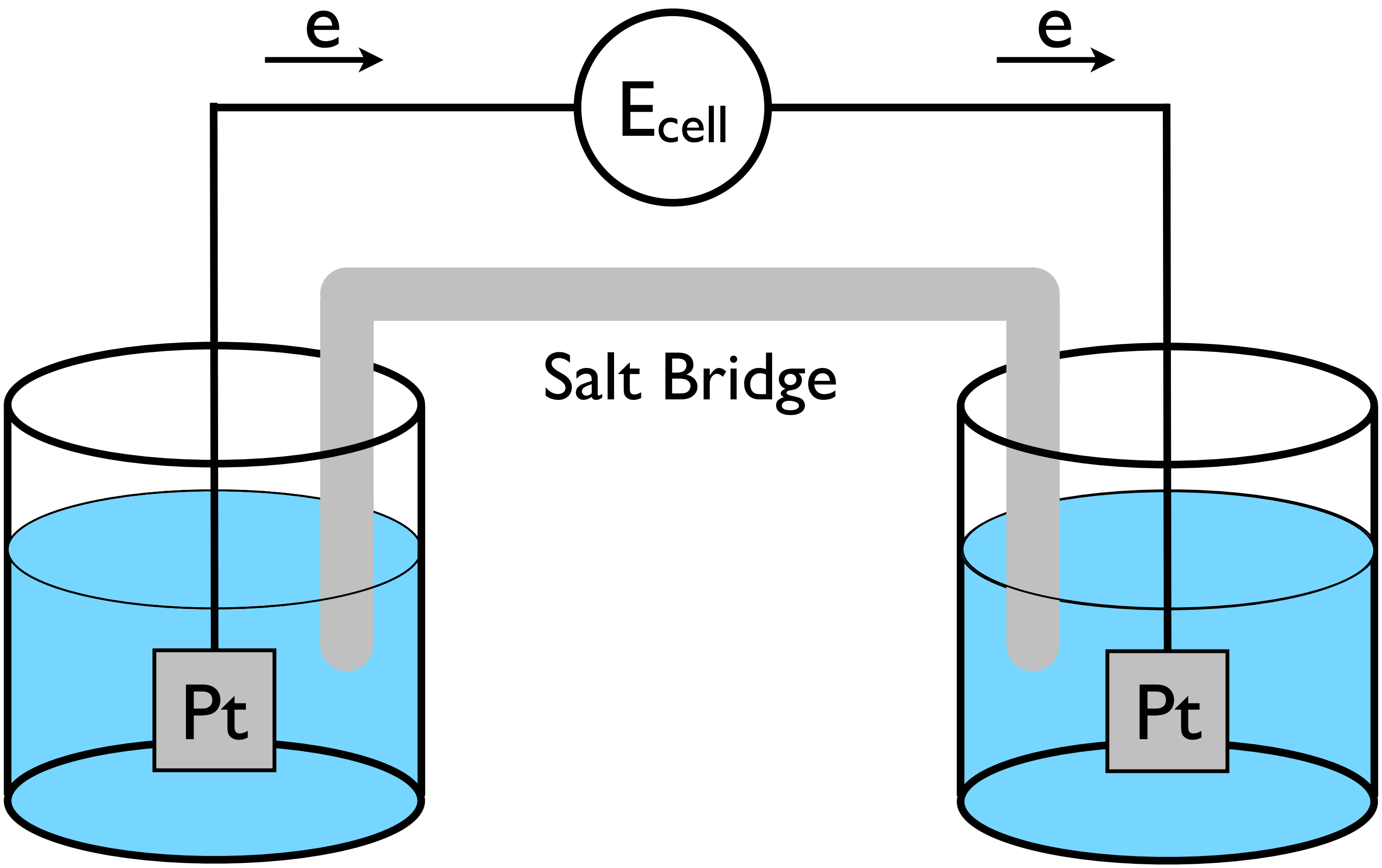


$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

Half Cell Potentials

$$E_{cell} = E_{red} - E_{ox}$$



$$Ce^{3+} \rightarrow Ce^{4+} + e$$

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

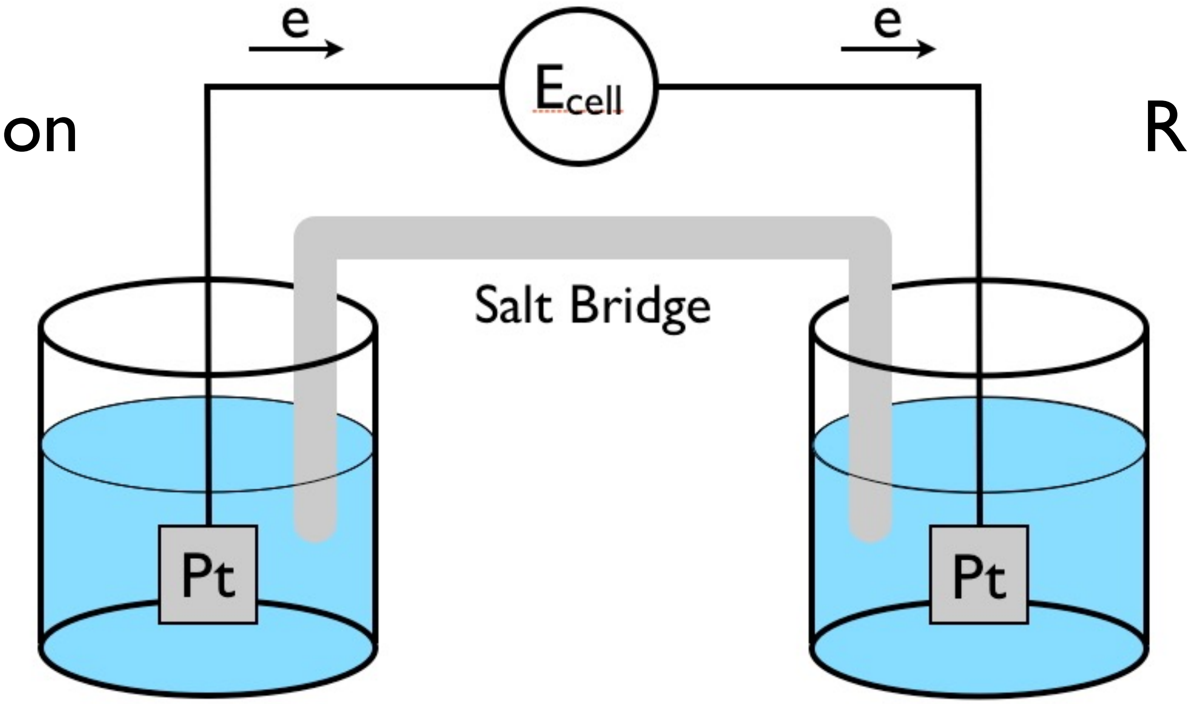
Half Cell Potentials

$Ce^{4+} + e \rightarrow Ce^{3+}$

$Fe^{3+} + e \rightarrow Fe^{2+}$

$$E_{Ce} = E^0_{Ce} - \frac{RT}{F} ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E_{Fe} = E^0_{Fe} - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$



Oxidation

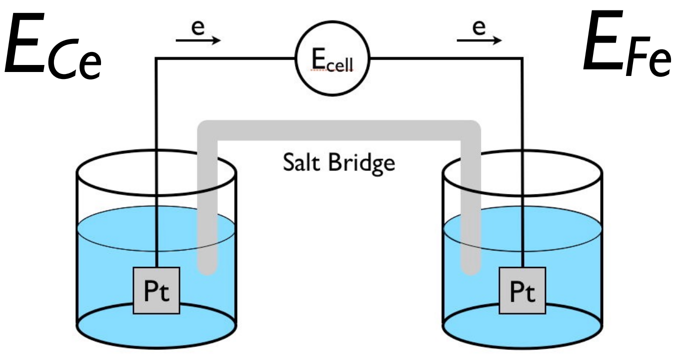
Reduction

$Ce^{3+} \rightarrow Ce^{4+} + e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

Half Cell Potentials

$$E_{cell} = E_{Fe} - E_{Ce}$$



Half Cell Potentials are always written as reductions:

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

$$E_{Fe} = E^0_{Fe} - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{Ce} = E^0_{Ce} - \frac{RT}{F} ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E_{cell} = E_{red} - E_{ox}$$

$$E_{cell} = E_{red} - E_{ox}$$

Since we always use half cell differences, we can add an arbitrary constant to all half cells. By convention, we assume that the E^o for the normal hydrogen electrode (NHE) is equal to zero:

Half Cell Reaction for Hydrogen (NHE):

$$H^+ + e \rightarrow \frac{1}{2} H_{2(g)}$$

$$E_H = E_H^0 - \frac{RT}{F} ln \frac{{P_{H_2}}^{1/2}}{[H^+]} \qquad E_H^0 = 0$$

Potentiometry

Metal Indicator Electrodes

$$Ag^{+} + e \rightarrow Ag_{(s)}$$

$$E_{Ag} = E^{0}_{Ag} - \frac{RT}{F} ln \frac{1}{[Ag^{+}]}$$

Silver Electrode:
Used to measure
[Ag+] in solutions

$$E^{0}_{Ag} = +0.799V$$

Reference Electrodes

$$AgCl_{(s)} + e \rightarrow Ag_{(s)} + Cl^{-}$$

$$E_{AgCl} = E^{0}_{AgCl} - \frac{RT}{F} ln \frac{[Cl^{-}]}{1}$$

Silver Chloride
Reference Electrode:
Only depends on [Cl-]

$$E_{AgCl} = +0.228V$$

$[Cl^-] = 1.0$ M

Potentiometry

Silver Electrode: Used to measure [Ag+] in solutions

$$\mathbf{E}_{cell} = E_{Ag} - E_{AgCl}$$

$$E_{Ag} = 0.799 - \frac{.0592}{1} log\left(\frac{1}{[Ag+]}\right) \qquad E_{AgCl} = +0.228V$$

$$\mathbf{E}_{cell} = 0.571 - \frac{.0592}{1} log\left(\frac{1}{[Ag+]}\right)$$

$$[Ag^{+}] = 1.0 \times 10^{-3} M \qquad \mathbf{E}_{cell} = +0.393V$$

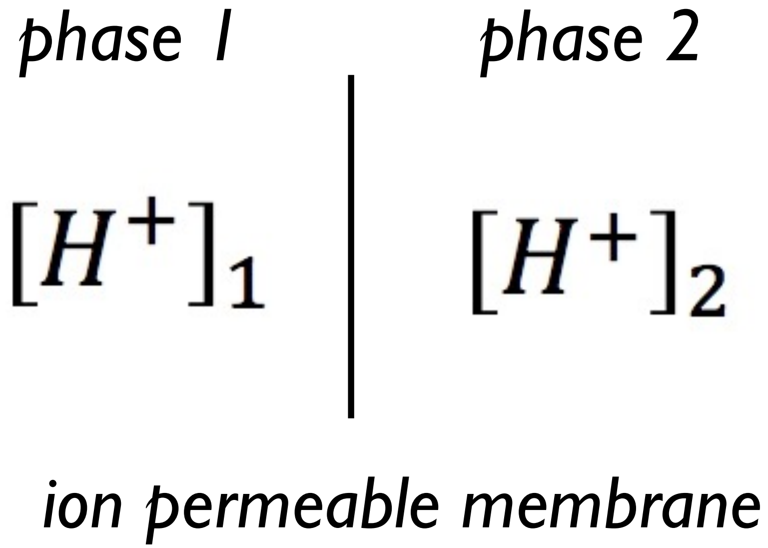
Other Types of Electrodes

Membrane and Ion Selective Electrodes (ISEs)

$$E_{cell} = E_{red} - E_{ox} + E_j$$

E_j is a junction potential that is sensitive to only one ion:

$$E_j = -\frac{RT}{F} ln \frac{[H^+]_1}{[H^+]_2}$$



phase 1

phase 2

$[H^+]_1$

$[H^+]_2$

ion permeable membrane

E_{red} and E_{red} are typically both references electrodes (e.g., AgCl)

Other Types of Electrodes

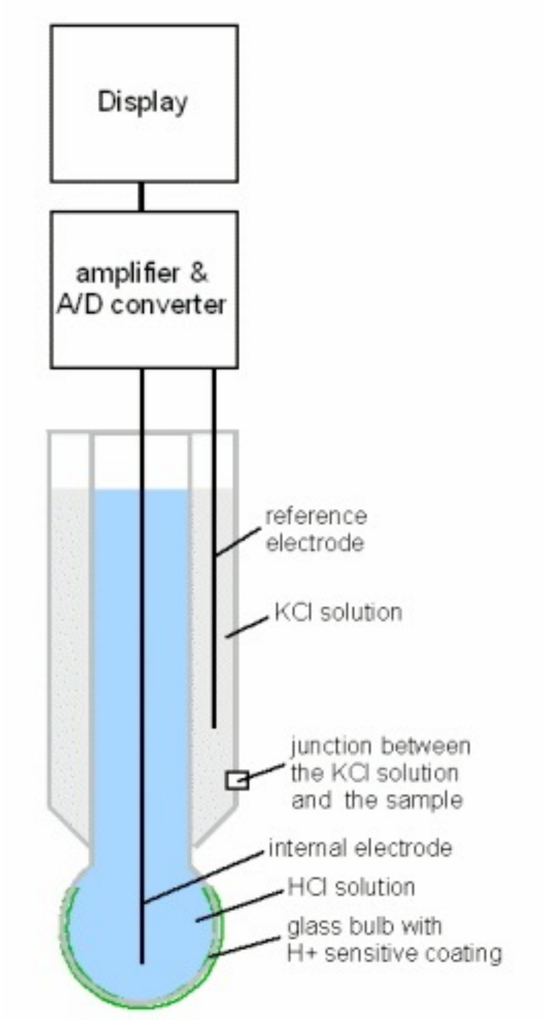
Membrane and Ion Selective Electrodes (ISEs)

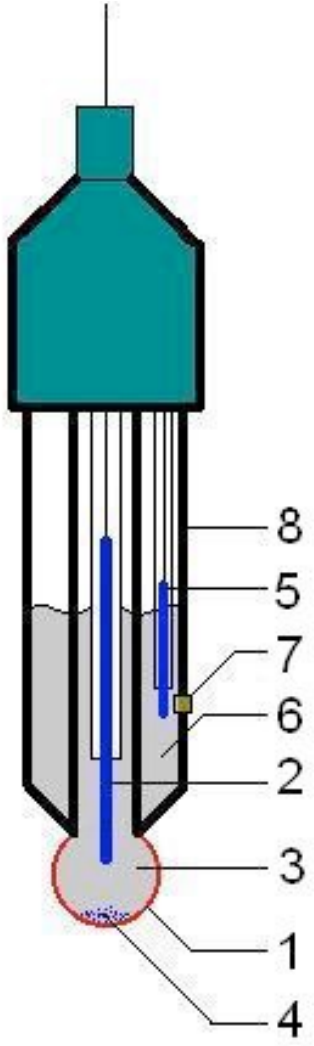
pH Electrode

Ca^{2+} Electrode

NO_3^- Electrode

Corning glass
membrane





Other Types of Electrodes

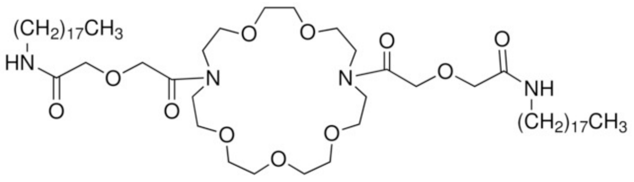
Membrane and Ion Selective Electrodes (ISEs)

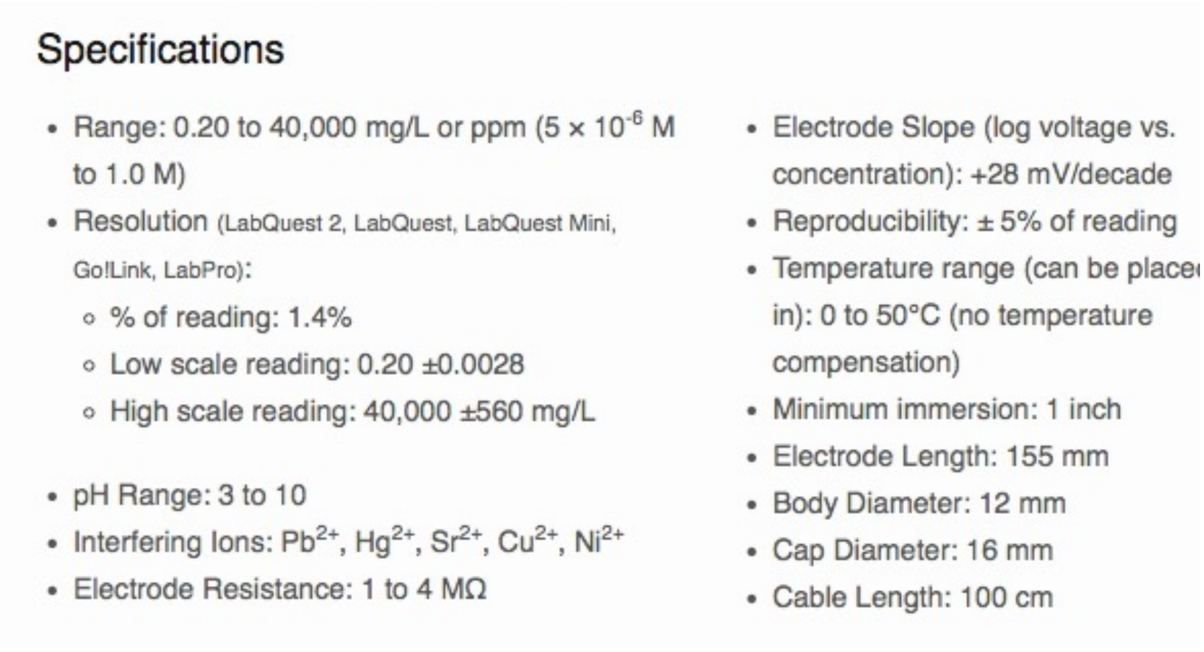
pH Electrode

Ca^{2+} Electrode

NO_3^- Electrode

Polymer (PVC)membrane electrode containing a calcium ionophore





Specifications

- Range: 0.20 to 40,000 mg/L or ppm (5 × 10^{-6} M to 1.0 M)
- Resolution (LabQuest 2, LabQuest, LabQuest Mini, Go!Link, LabPro):
  - % of reading: 1.4%
  - Low scale reading: 0.20 ±0.0028
  - High scale reading: 40,000 ±560 mg/L
- pH Range: 3 to 10
- Interfering Ions: Pb^{2+}, Hg^{2+}, Sr^{2+}, Cu^{2+}, Ni^{2+}
- Electrode Resistance: 1 to 4 MΩ
- Electrode Slope (log voltage vs. concentration): +28 mV/decade
- Reproducibility: ± 5% of reading
- Temperature range (can be place in): 0 to 50°C (no temperature compensation)
- Minimum immersion: 1 inch
- Electrode Length: 155 mm
- Body Diameter: 12 mm
- Cap Diameter: 16 mm
- Cable Length: 100 cm

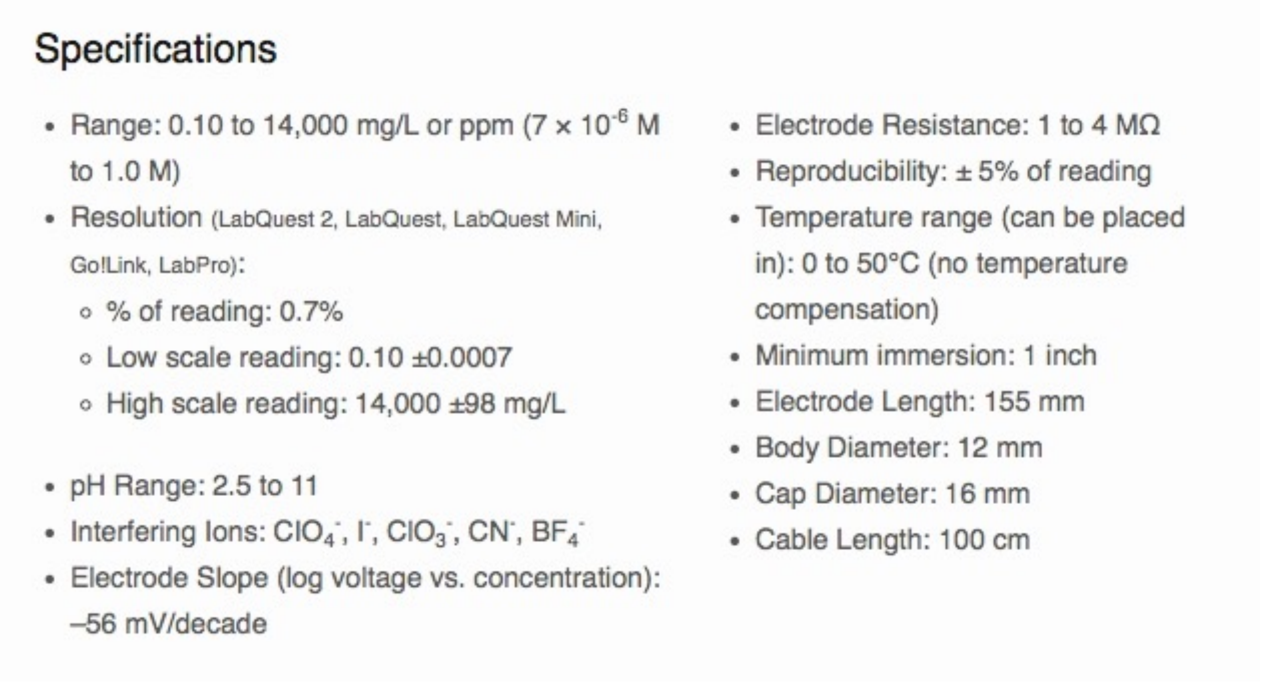
Other Types of Electrodes

Membrane and Ion Selective Electrodes (ISEs)

pH Electrode

Ca^{2+} Electrode

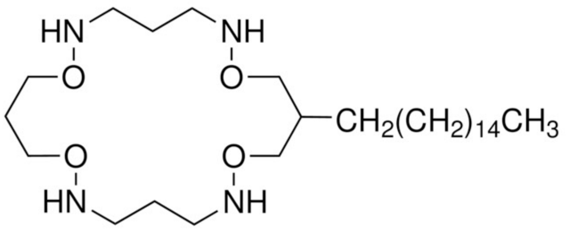
NO_3^- Electrode



Specifications

- Range: 0.10 to 14,000 mg/L or ppm (7×10^{-6} M to 1.0 M)
- Resolution (LabQuest 2, LabQuest, LabQuest Mini, Go!Link, LabPro):
  - % of reading: 0.7%
  - Low scale reading: 0.10 ±0.0007
  - High scale reading: 14,000 ±98 mg/L
- pH Range: 2.5 to 11
- Interfering Ions: ClO_4^-, I^-, ClO_3^-, CN^-, BF_4^-
- Electrode Slope (log voltage vs. concentration): –56 mV/decade
- Electrode Resistance: 1 to 4 MΩ
- Reproducibility: ± 5% of reading
- Temperature range (can be placed in): 0 to 50°C (no temperature compensation)
- Minimum immersion: 1 inch
- Electrode Length: 155 mm
- Body Diameter: 12 mm
- Cap Diameter: 16 mm
- Cable Length: 100 cm

Polymer (PVC)membrane electrode containing a nitrate ionophore



Galvanic vs Electrolytic Cells

A reaction is spontaneous if $\Delta G < 0$

$$\mathbf{E}_{cell} = \frac{-\Delta G}{nF} > 0$$

"Galvanic Cell"

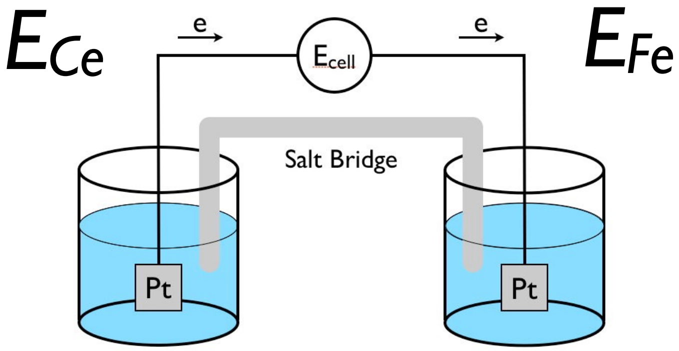
A reaction is NOT spontaneous if $\Delta G > 0$

$$\mathbf{E}_{cell} = \frac{-\Delta G}{nF} < 0$$

"Electrolytic Cell"

Half Cell Potentials

$$E_{cell} = E_{Fe} - E_{Ce}$$



Half Cell Potentials are always written as reductions:

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

$$E_{Fe} = E^0_{Fe} - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{Ce} = E^0_{Ce} - \frac{RT}{F} ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

E°(Fe) = +0.77 V

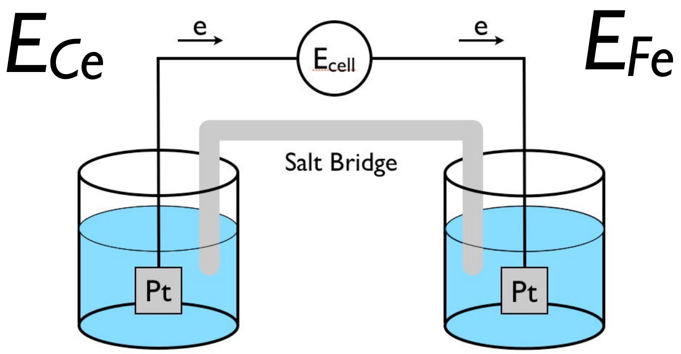
E°(Ce) = +1.61 V

E°(Cell) = E°(Fe) - E°(Ce) = - 0.91 V

Spontaneous?

Half Cell Potentials

$$E_{cell} = E_{Fe} - E_{Ce}$$



Half Cell Potentials are always written as reductions:

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

$$E_{Fe} = E^0_{Fe} - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{Ce} = E^0_{Ce} - \frac{RT}{F} ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

E°(Fe) = +0.77 V

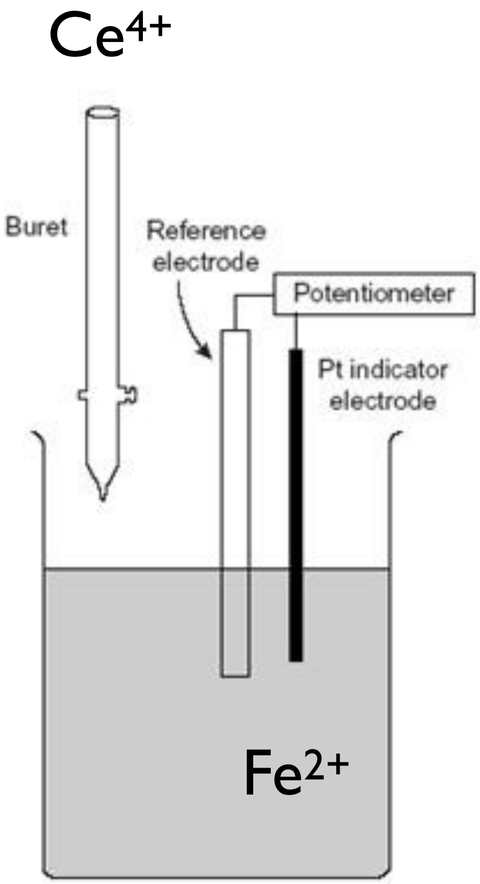
E°(Ce) = +1.61 V

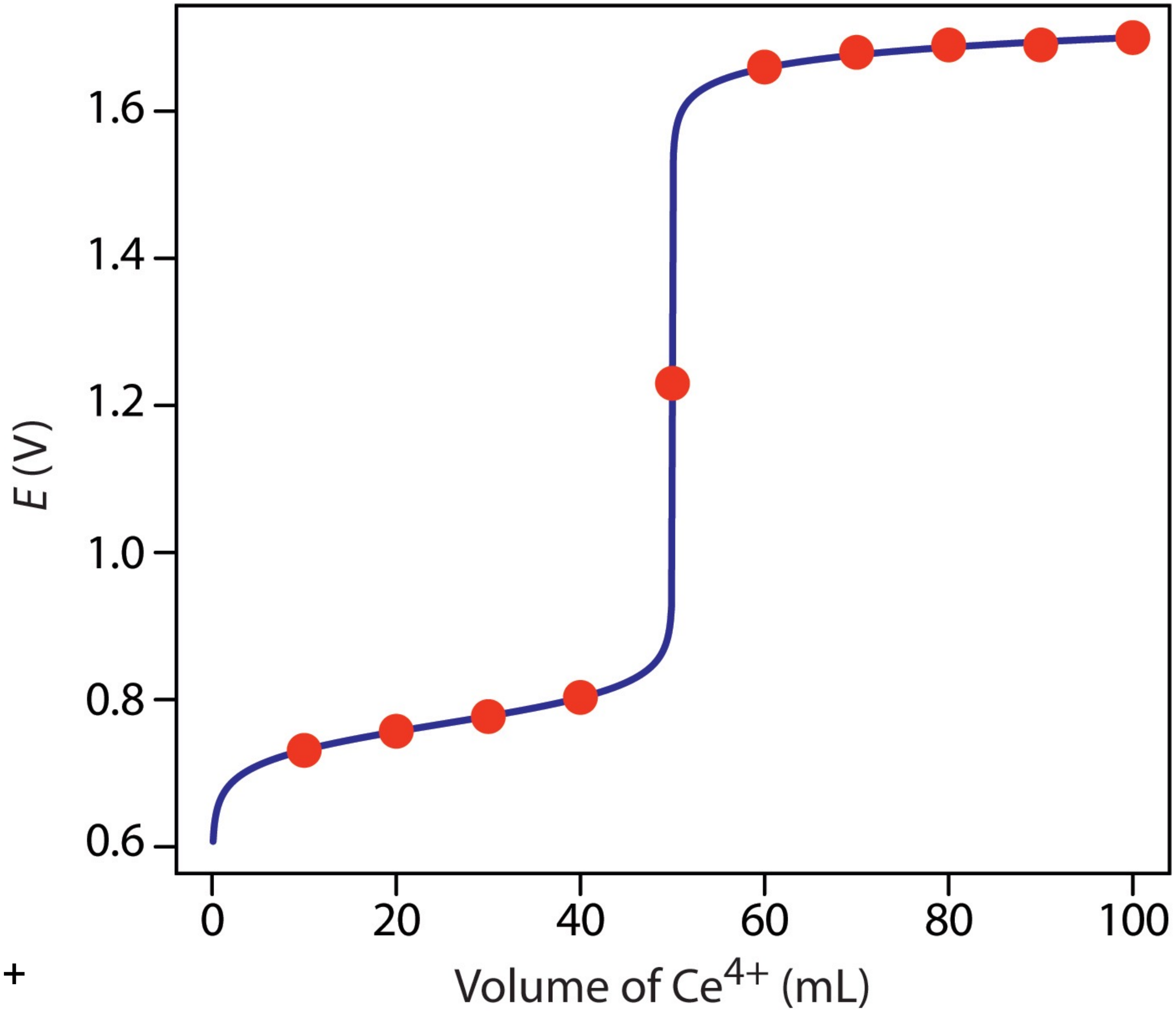
E°(Cell) = E°(Fe) - E°(Ce) = - 0.91 V

Not Spontaneous - Electrolytic Cell!

The reverse reaction is spontaneous - Galvanic Cell.

Redox Titrations





$Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}$

This reaction is spontaneous!

$$\mathbf{E}_{cell} = +.910V$$

UC Davis chemwiki.

Example: Electrolysis of Water

$$2H_2O \leftrightharpoons 2H_{2(g)} + O_{2(g)}$$

At the positively charged anode, an oxidation reaction occurs, generating oxygen gas (these equations are for acidic pH):

Spontaneous?

Oxidation at anode: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e$

At the negatively charged cathode, a reduction reaction occurs, generating hydrogen gas:

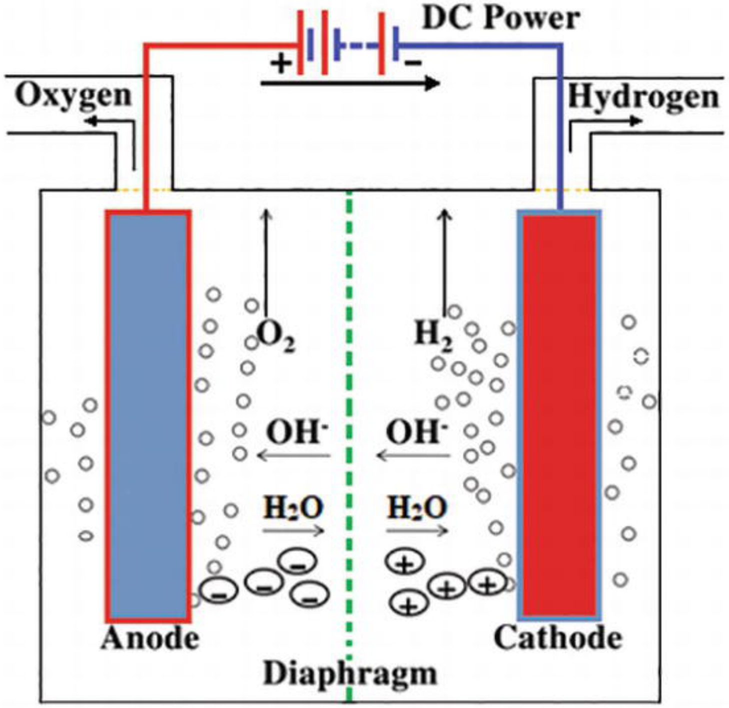
Reduction at cathode: $2\ H^+(aq) + 2e^- \rightarrow H_2(g)$

Half Cell Potentials:

$O_2(g) + 4\ H^+(aq) + 4e^- \rightarrow 2\ H_2O(l)$ $E° = +1.229\ V$

$2\ H^+(aq) + 2e^- \rightarrow H_2(g)$ $E° = -0.8277\ V$

$E°(cell) = E°(red) - E°(ox) = -0.8277 - 1.229 = -2.056\ V$



Example: Electrolysis of Water

$$2H_2O \leftrightharpoons 2H_{2(g)} + O_{2(g)}$$

At the positively charged anode, an oxidation reaction occurs, generating oxygen gas (these equations are for acidic pH):

$$\mathbf{E}_{cell} < 0$$

Not Spontaneous: Electrolytic Cell!

Oxidation at anode: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e$

At the negatively charged cathode, a reduction reaction occurs, generating hydrogen gas:

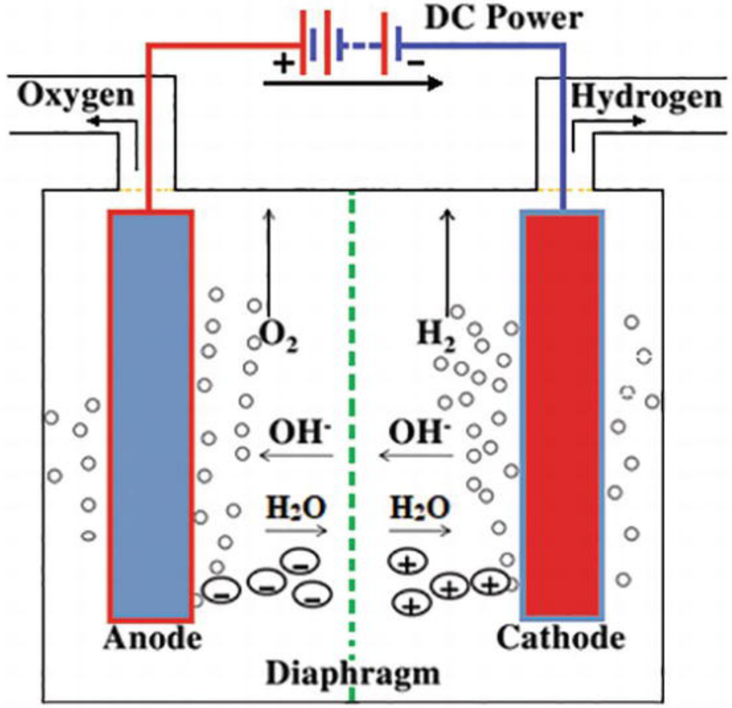
Reduction at cathode: $2\ H^+(aq) + 2e^- \rightarrow H_2(g)$

Half Cell Potentials:

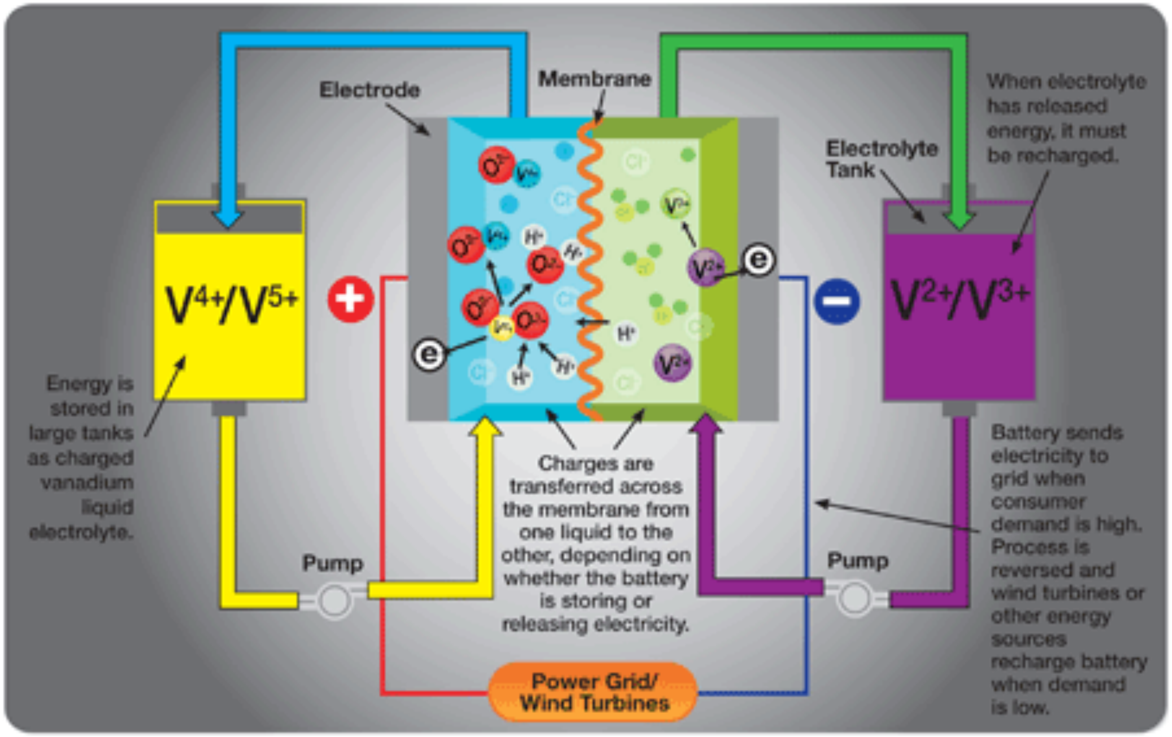
$O_2(g) + 4\ H^+(aq) + 4e^- \rightarrow 2\ H_2O(l)$ E° = +1.229 V

$2\ H^+(aq) + 2e^- \rightarrow H_2(g)$ E° = -0.8277 V

E°(cell) = E°(red) - E°(ox) = -0.8277 – 1.229 = -2.056 V



Vanadium Redox Flow Battery



Seattle Business Magazine

Four stable oxidation states:

$V^{2+}, V^{3+}, VO^{2+}, VO_2^{+}$

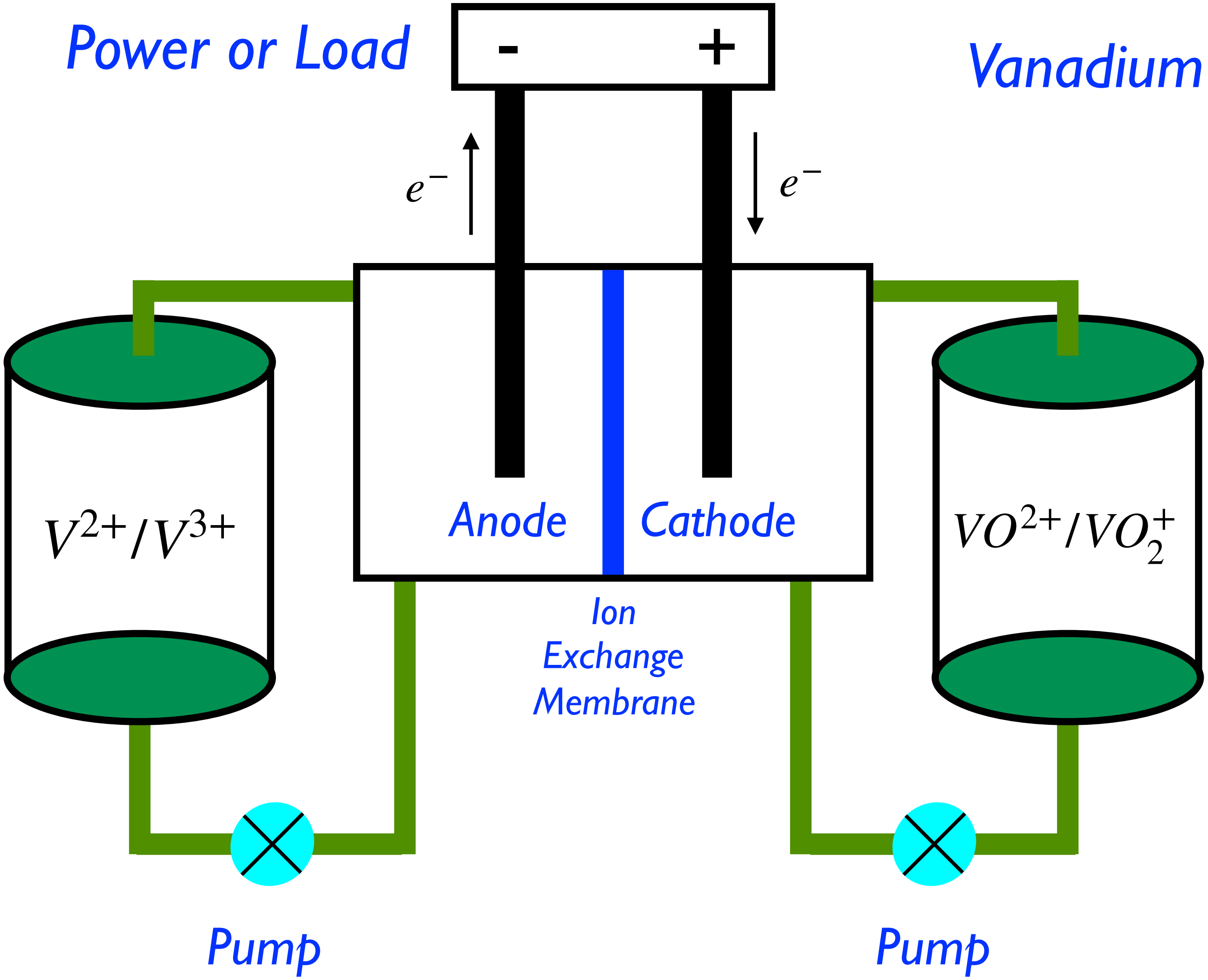
Galvanic Discharging Reaction

Anode (Oxidation): $V^{2+} \rightarrow V^{3+} + e^-$ (E° = -0.26 V vs. SHE)

Cathode (Reduction): $VO_2^+ + 2\,H^+ + e^- \rightarrow VO^{2+} + H_2O$ (E° = 0.99 V)

E°(Cell) = E°(Red) - E°(Ox) = 0.99 + 0.26 = +1.25V

Vanadium Redox Flow Battery



$$V^{2+} \rightleftharpoons V^{3+} + e^-$$

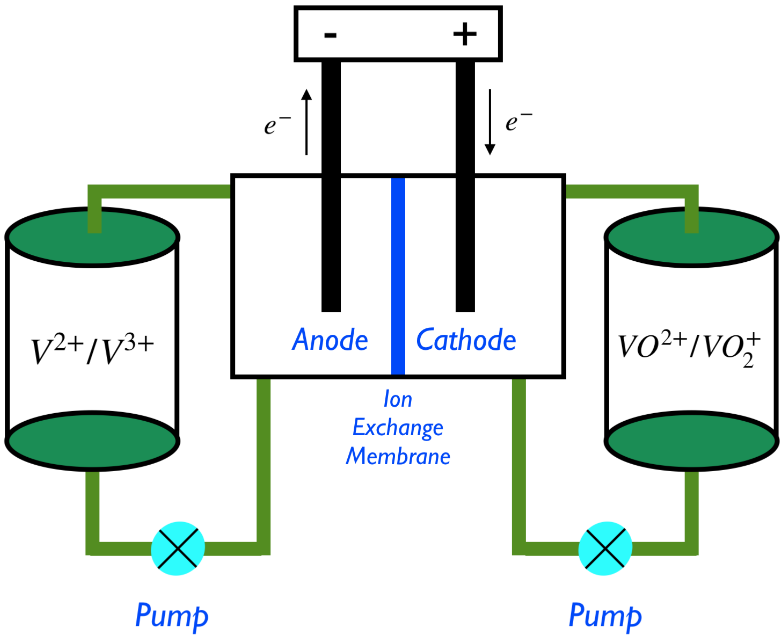
Oxidation

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$

Reduction

Chem M3LC

Vanadium Redox Flow Battery



Cathode Half Cell Potential: E^0_{red} = 1.00V

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$

Anode Half Cell Potential: E^0_{ox} = -.26V

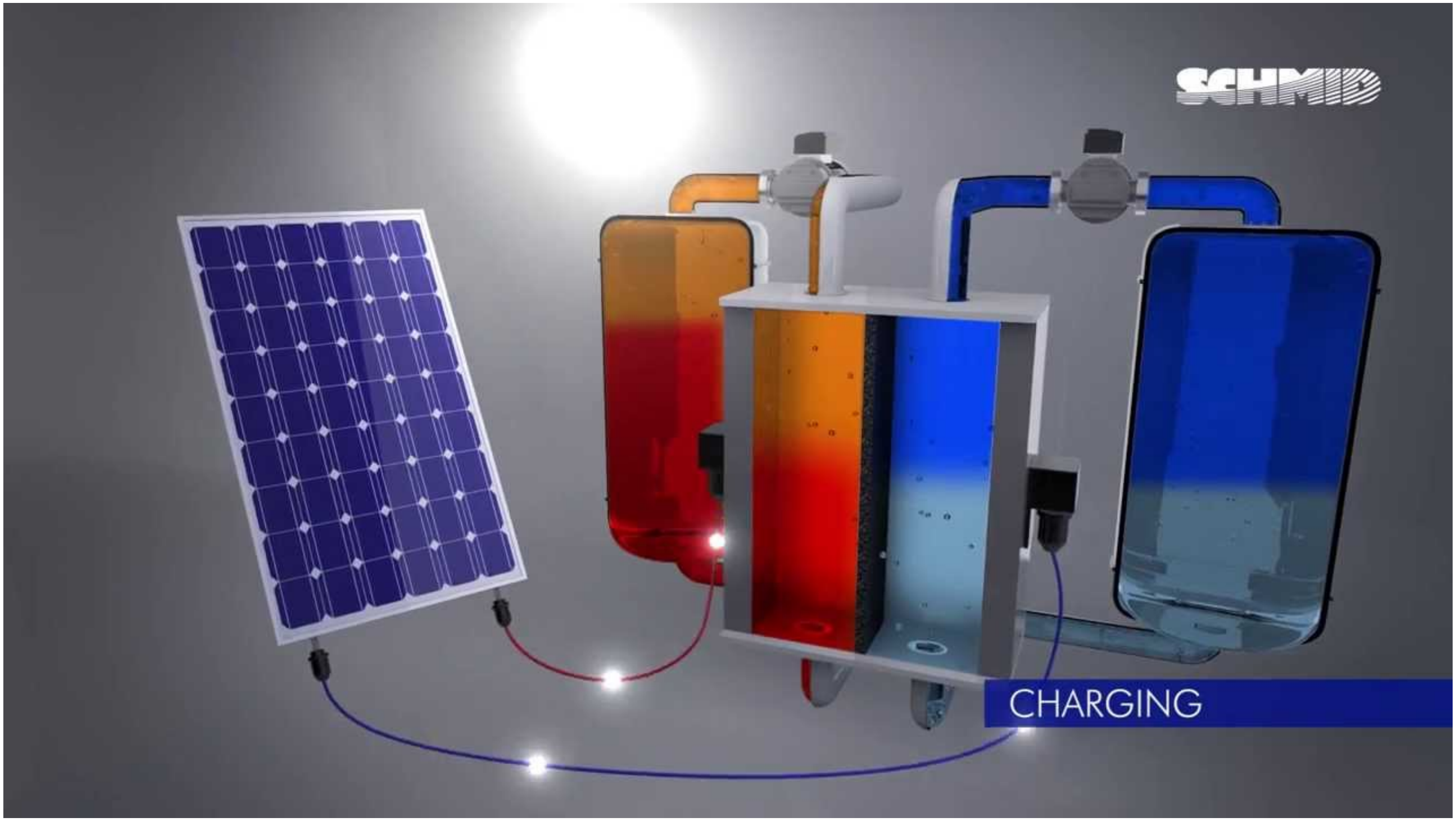
$$V^{3+} + e^- \rightleftharpoons V^{2+}$$

$$E_{cell} = E_{red} - E_{ox}$$

$$E^0_{cell} = 1.00V - (-0.26V) - = +1.26V$$

Spontaneous Discharge Reaction

Vanadium Redox Flow Battery



Solar Panel Charging

Chem M3LC

Vanadium Redox Flow Battery

Canadian Installation

Vanadium Redox Flow Battery

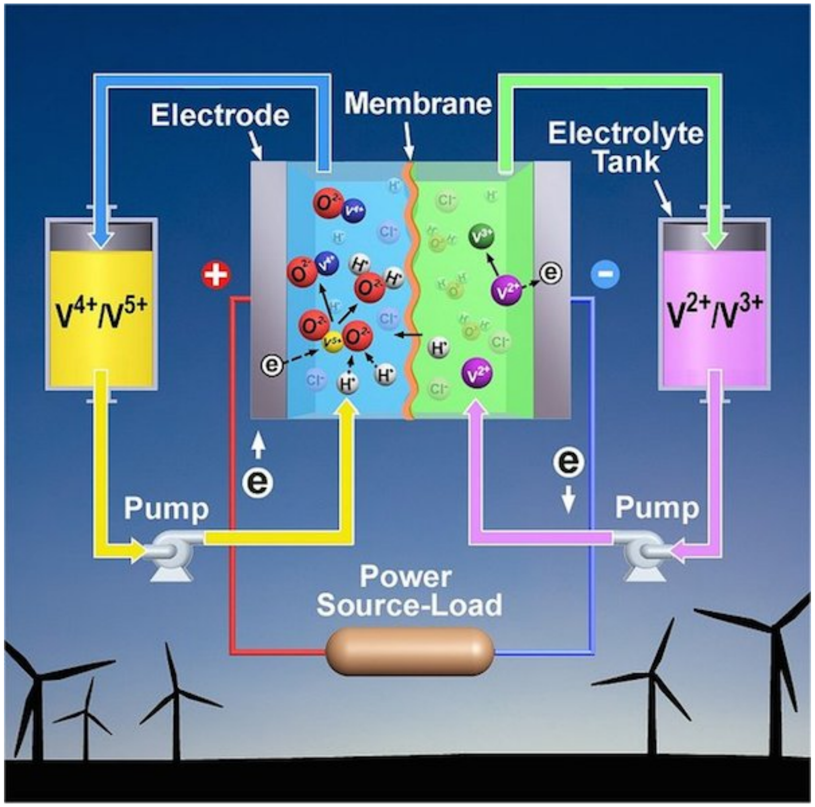
Vanadium Oxidation States

V^{2+} V^{3+} VO^{2+} VO_2^{+}

World's Largest Battery? 200MW/800MWhr

Chem M3LC

Vanadium Redox Flow Battery



References

[1] X. Li et al., "Ion Exchange Membrane for Vanadium Redox Flow Battery (VRB) Applications," Energy Environ. Sci. 4, 1147 (2011).
[2] M. Skyllas-Kazacos et al., "Progress in Flow Battery Research and Development," J. Electrochem. Soc. 158, R55 (2011).
[3] C. Ponce de Leon et al., "Redox Flow Cell for Energy Conversion," J. Power Sources 160, 716 (2006).
[4] L. Li et al., "A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage," Adv. Energy Mat. 1, 394 (2011).

Excerpted from Xing Xie: http://large.stanford.edu/courses/2011/ph240/xie2/

Picture from https://cleantechnica.com/2015/06/21/flow-battery-vs-tesla-battery-smackdown-looming/

Half Cell Reactions and the Redox Potential

The cell potential can be calculated from the difference between two Half Cell Potentials:

$Fe^{3+} + e \rightarrow Fe^{2+}$

$Ce^{4+} + e \rightarrow Ce^{3+}$

$$E_{Fe} = E_{Fe}^0 - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{Ce} = E_{Ce}^0 - \frac{RT}{F} ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E_{cell} = E_{Fe} - E_{Ce}$$

Half Cells are written as reductions. The E^{0}s are tabulated based on the normal hydrogen electrode (NHE) scale, which defines E_H^0 as zero:

$H^+ + e \rightarrow \frac{1}{2} H_{2(g)}$

$$E_H = E_H^0 + \frac{RT}{F} ln \frac{{P_{H_2}}^{1/2}}{[H^+]}$$

$$E_H^0 = 0$$

E_{Fe} is called the Half Cell Potential, or the **Redox Potential** for the Fe^{2+}/ Fe^{3+} couple.

The Redox Potential can be measured in any aqueous system, and sets the concentration ratios of ALL of the redox species in the solution.

Electrochemical Alpha Fractions

The total concentration of Fe in a solution is given by C_{Fe}^{TOT}:

$$C_{Fe}^{TOT} = [Fe^{2+}] + [Fe^{3+}]$$

This concentration is divided into the oxidized and reduced forms. The fraction of the total Fe in each form is called the alpha fraction:

$$\alpha_{Fe^{2+}} = \frac{[Fe^{2+}]}{C_{Fe}^{TOT}} \qquad \alpha_{Fe^{3+}} = \frac{[Fe^{3+}]}{C_{Fe}^{TOT}} \qquad \alpha_{Fe^{2+}} + \alpha_{Fe^{3+}} = 1$$

Using the Fe half cell reaction, we can derive equations for the two alpha fractions that depend on the value of E_{Fe}:

$$\alpha_{Fe^{2+}} = \left[1 + exp\left(\frac{F}{RT}(E_{Fe} - E_{Fe}^{0})\right)\right]^{-1}$$

$$\alpha_{Fe^{3+}} = \left[1 + exp\left(-\frac{F}{RT}(E_{Fe} - E_{Fe}^{0})\right)\right]^{-1}$$

Electrochemical Alpha Fractions

$$\alpha_{Fe^{2+}} = \left[1 + exp\left(\frac{F}{RT}(E_{Fe} - E^0_{Fe})\right)\right]^{-1}$$

$$\alpha_{Fe^{3+}} = \left[1 + exp\left(-\frac{F}{RT}(E_{Fe} - E^0_{Fe})\right)\right]^{-1}$$