Principles of Electronic Nanobiosensors

Unit 3: Sensitivity

Lecture 3.7: Amperometric Sensors: Glucose Sensors I

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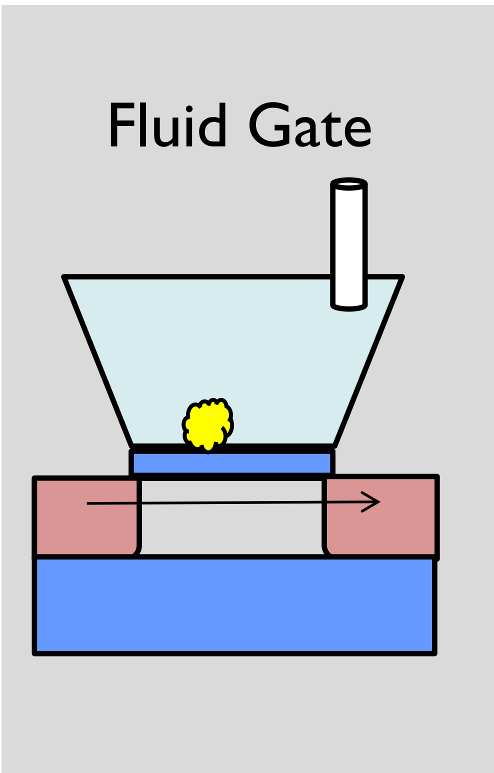
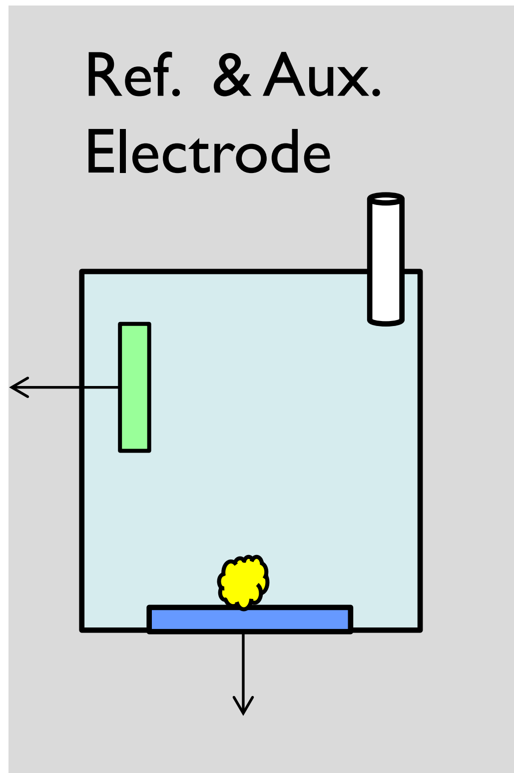
Three types of sensors

Potentiometric



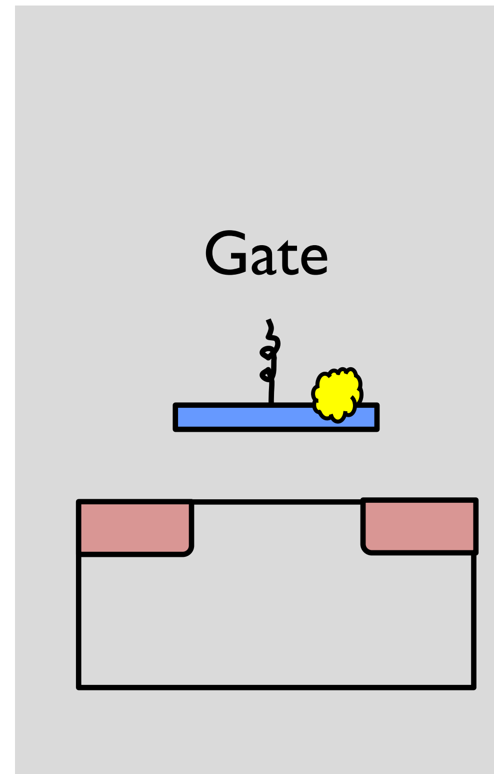
Charge to current

Amperometric



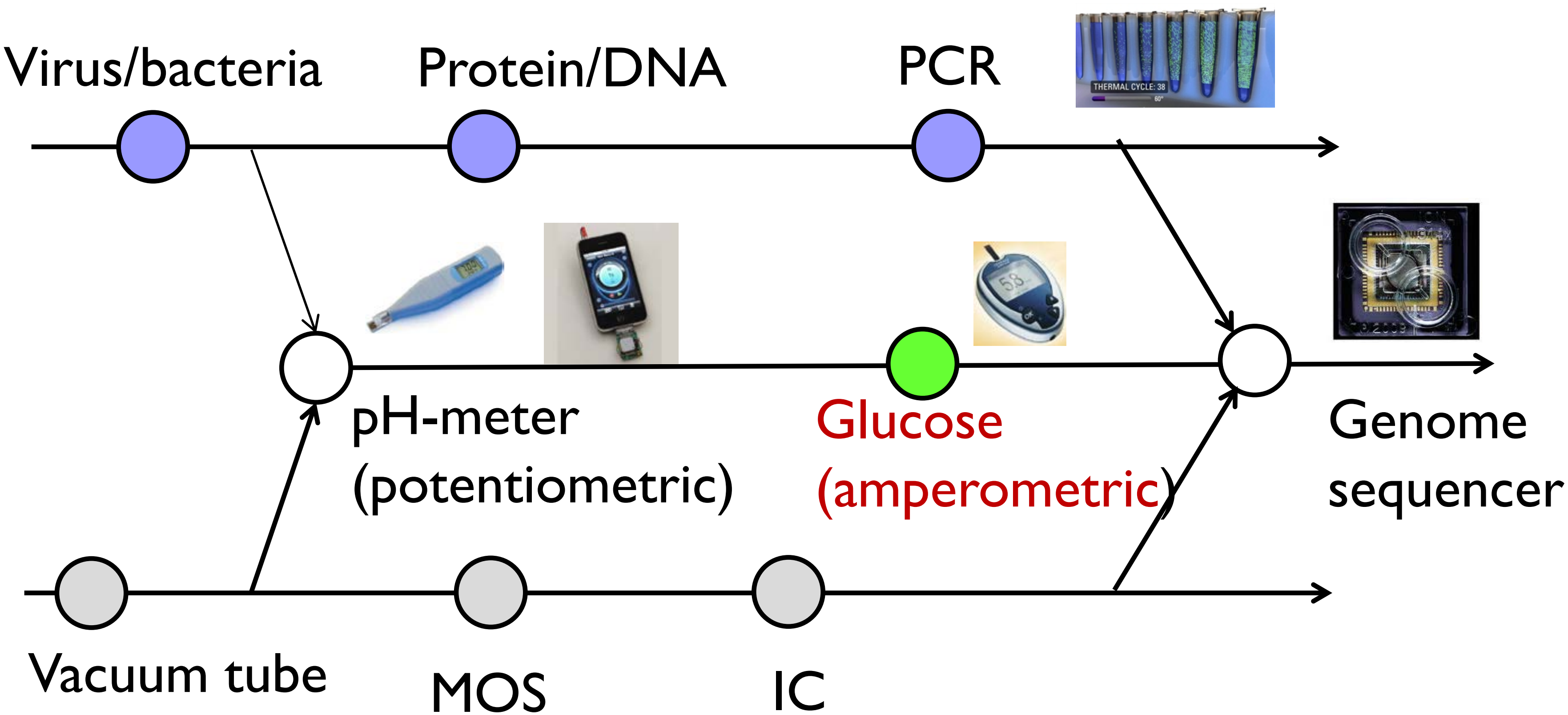
Chemical to current

Cantilever

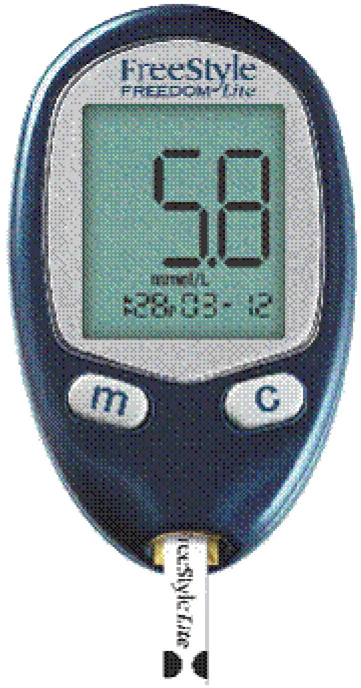


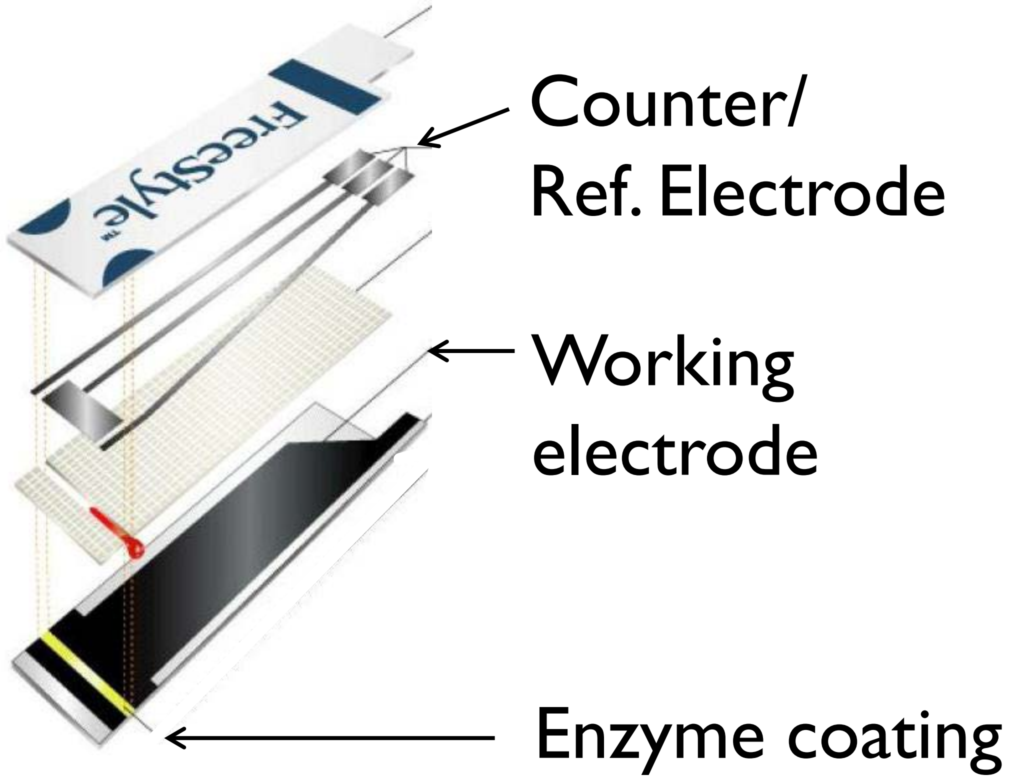
Mass to frequency

A short history of sensors

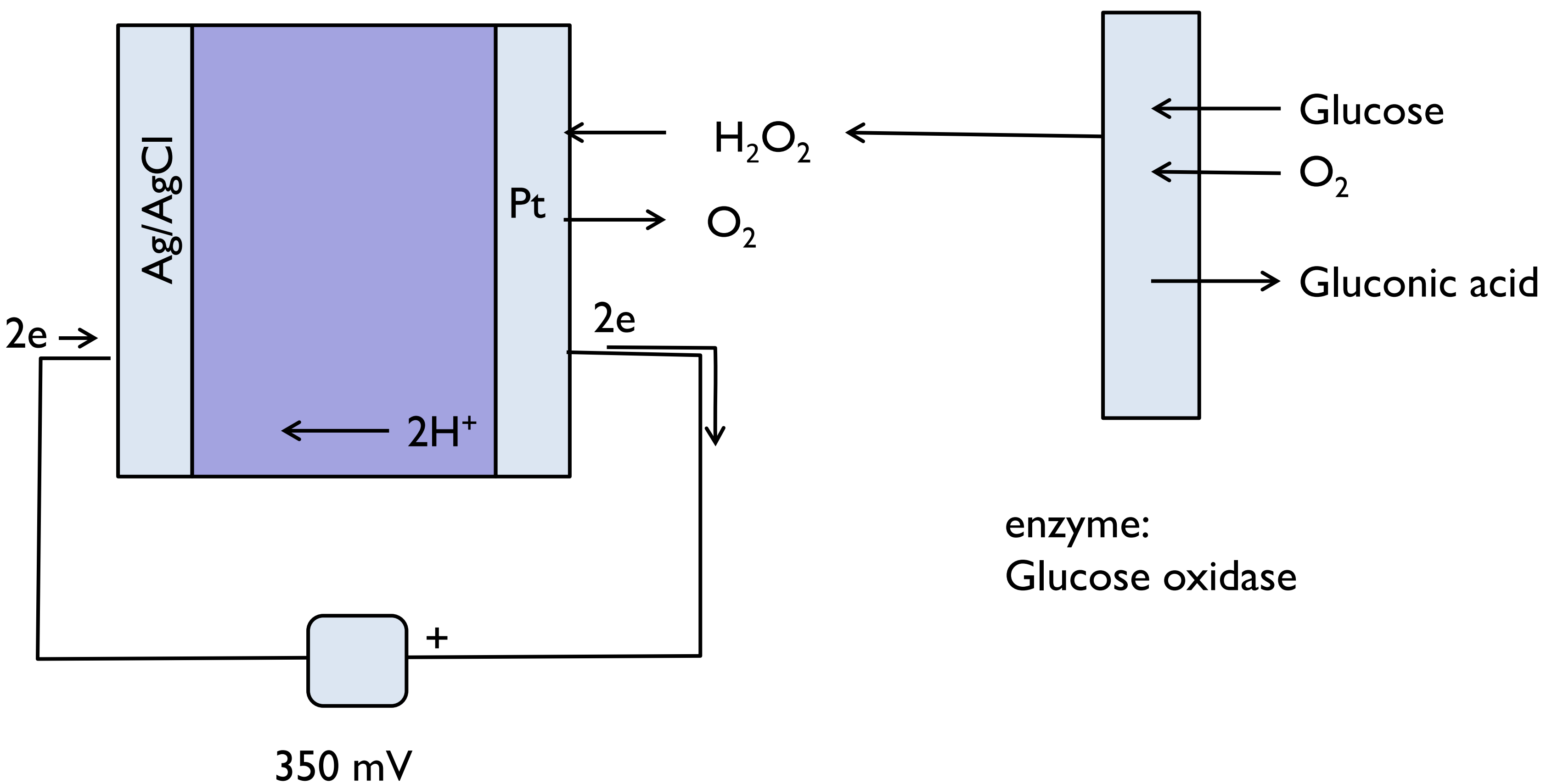


A glucose sensor





Basics of a amperometric sensor



Alam, Principles of Nanobiosensors, 2013

Glucose sensing

$$(1)\ C_6H_{12}O_6 + O_2 \xrightarrow{GO_x} C_6H_{12}O_7 + H_2O_2$$

enzyme:
Glucose oxidase

Gluconic acid

$$(2)\ H_2O_2 \xrightarrow{Pt\,Anode(350\,mV)} O_2 + 2H^+ + 2e^-$$

$$(3)\ AgCl + e^- \xrightarrow{Ag\,Ref.} Ag^0 + Cl^-$$

$$(4)\ 4H^+ + O_2 \xrightarrow{Aux\,Ref.} 2H_2O_2 - 4e^-$$

Alam, Principles of Nanobiosensors, 2013

Why amperometric sensors?

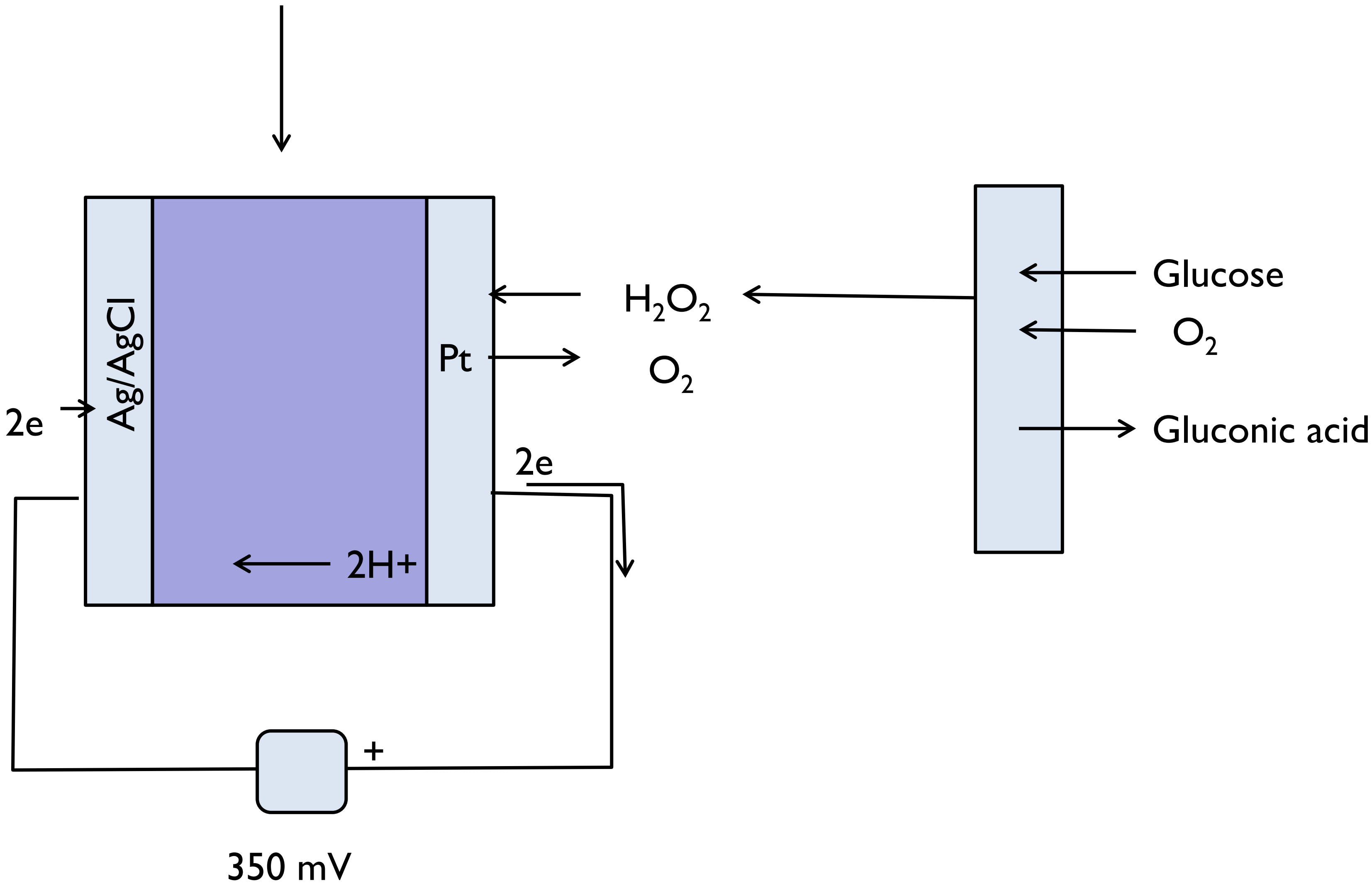
- Obviates the problem of screening
- Electro-chemical reactions provide specificity
- A broad range of modern point-of-care sensors belong to this group (glucose sensor, genome sequencer)

- Still constrained by the limits of settling time
- Multiple-electrode setup difficult to miniaturize
- New diffusion limits related to reaction products
- Parasitic reactions may compromise selectivity

Outline

- Introduction to amperometric biosensing
  - Spontaneous redox reaction vs. electrolysis
  - Importance of reference electrodes
  - Basic H_2O_2 based scheme for Glucose sensing
- Conclusion
- Appendix: Butler-Volmer equation

Let us start with the cell on the left



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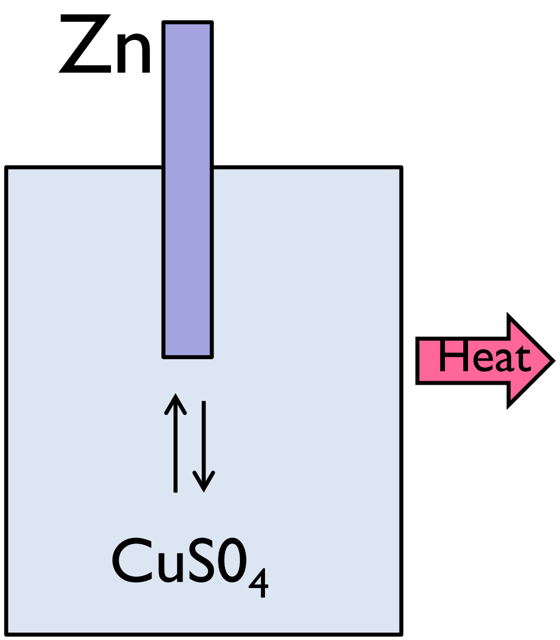
Spontaneous reaction

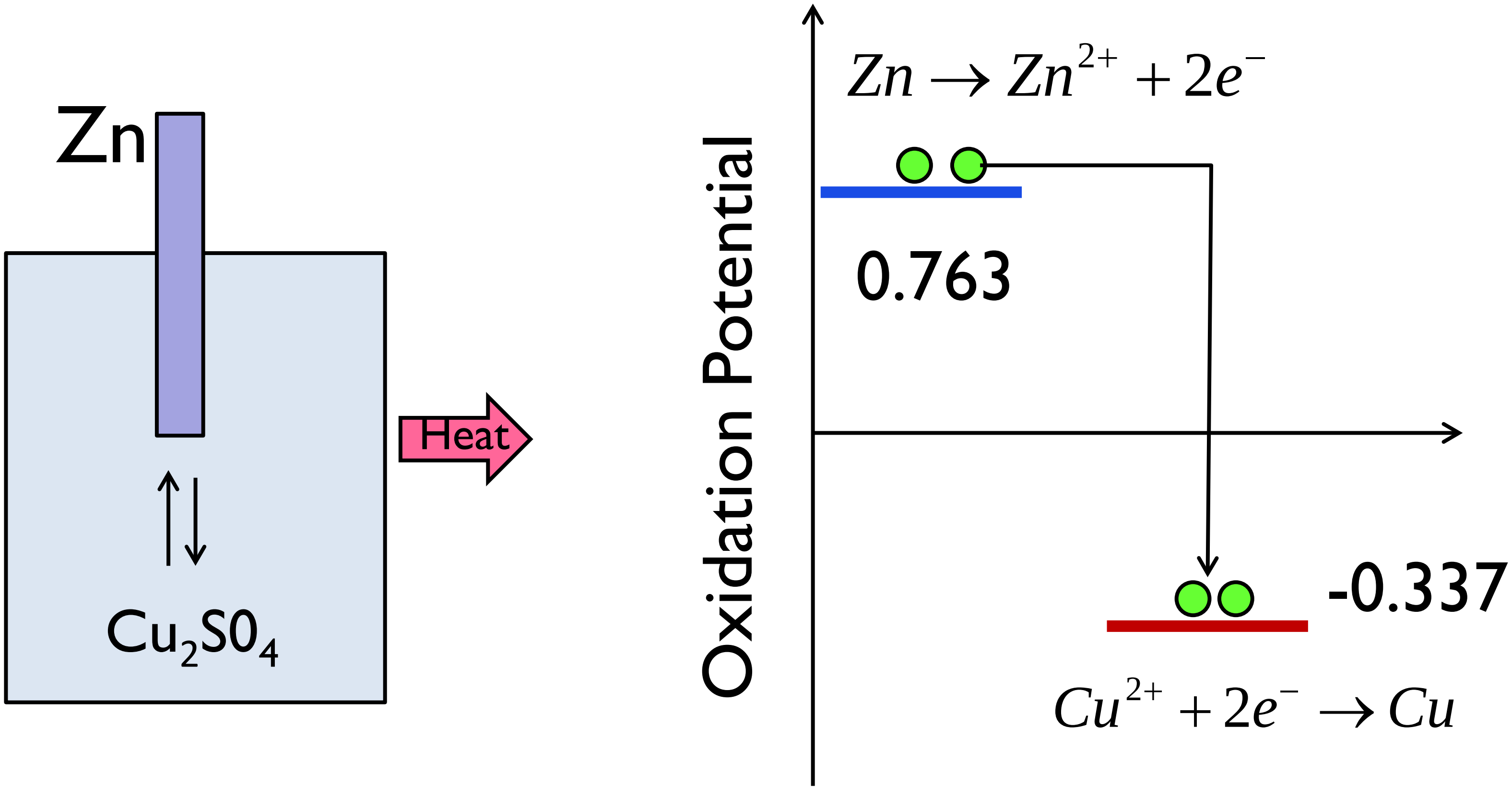
$$Zn \rightarrow Zn^{2+} + 2e^{-}$$ (oxidation at anode)

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$ (reduction in solution)

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$$



Spontaneous reaction and the driving force



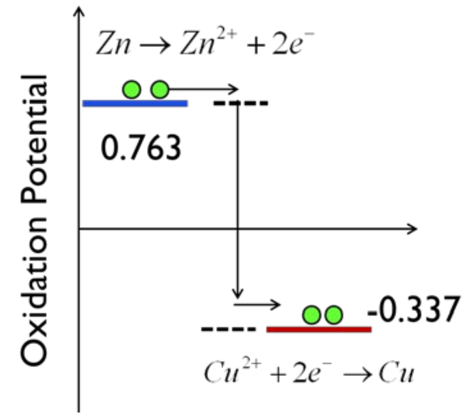
Potential difference drives electron transfer

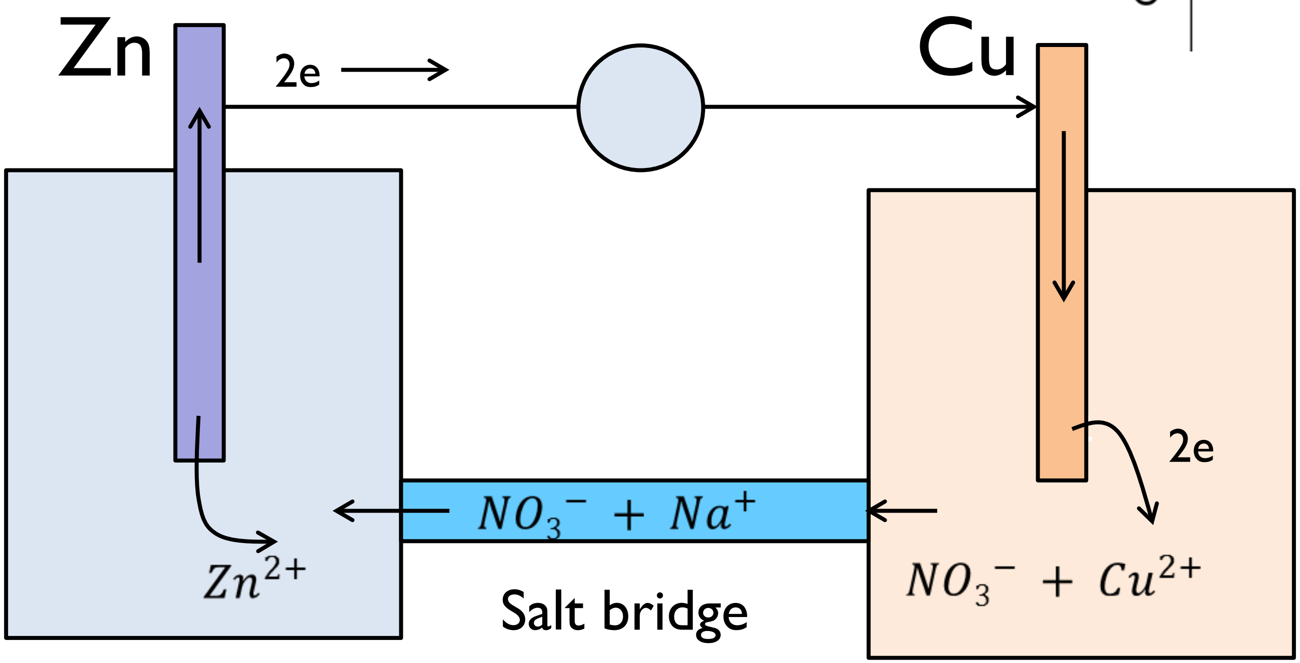
Driving a motor by chemical energy

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$$

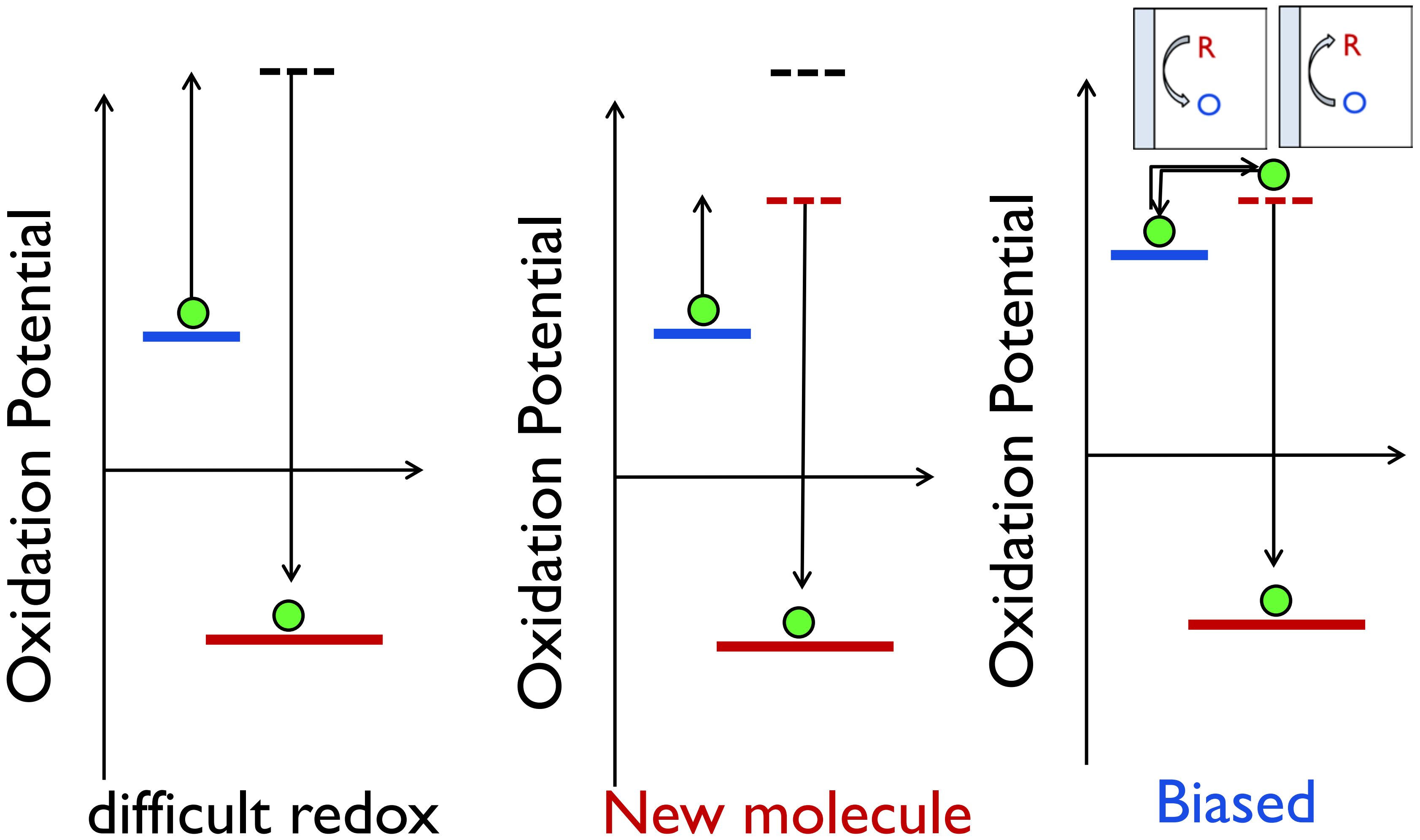
$Zn \rightarrow Zn^{2+} + 2e^{-}$ (oxidation at anode)

$Cu^{2+} + 2e^{-} \rightarrow Cu$ (reduction in cathode)

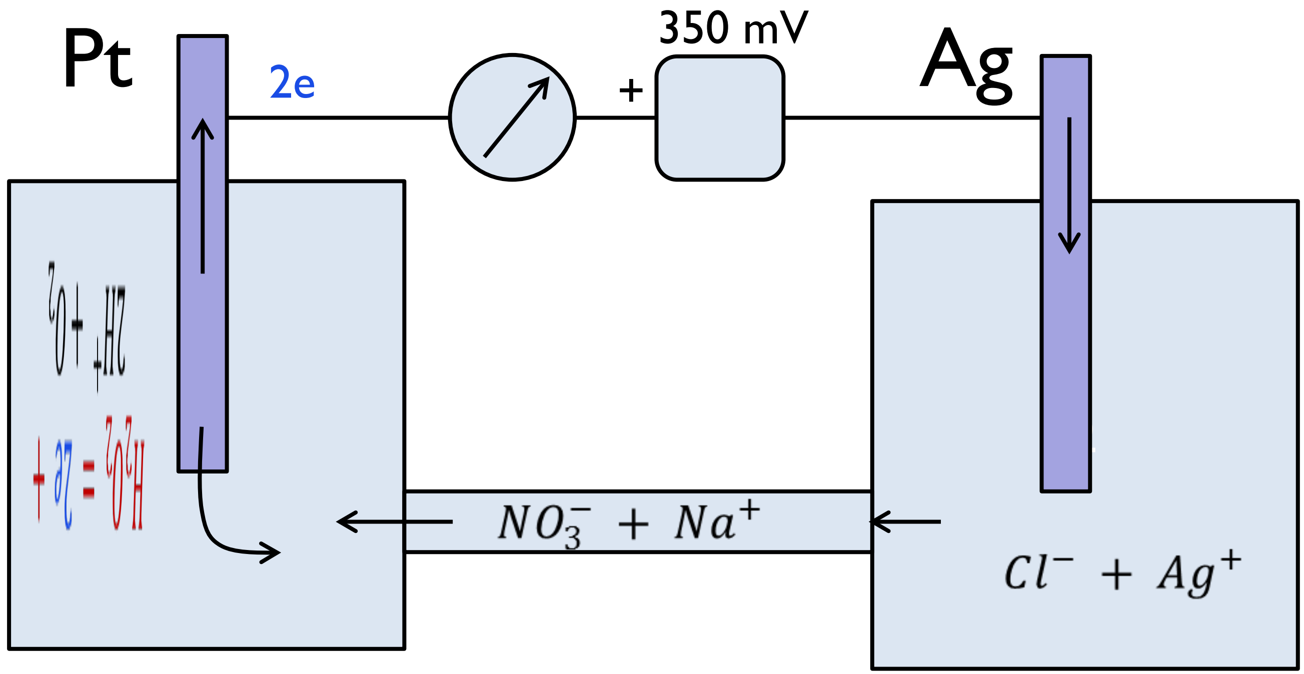


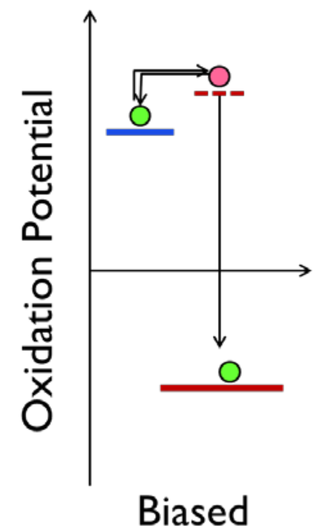


Forced oxidation-reduction



Electrolysis: forced oxidation-reduction





$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$$ (oxidation at anode)

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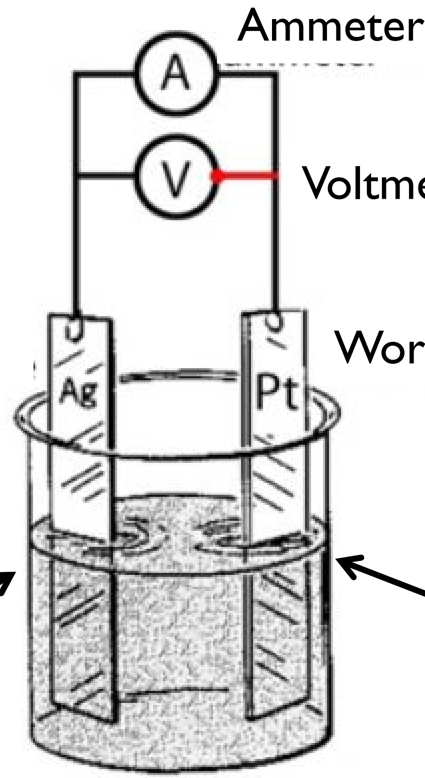
The issue of reference electrode



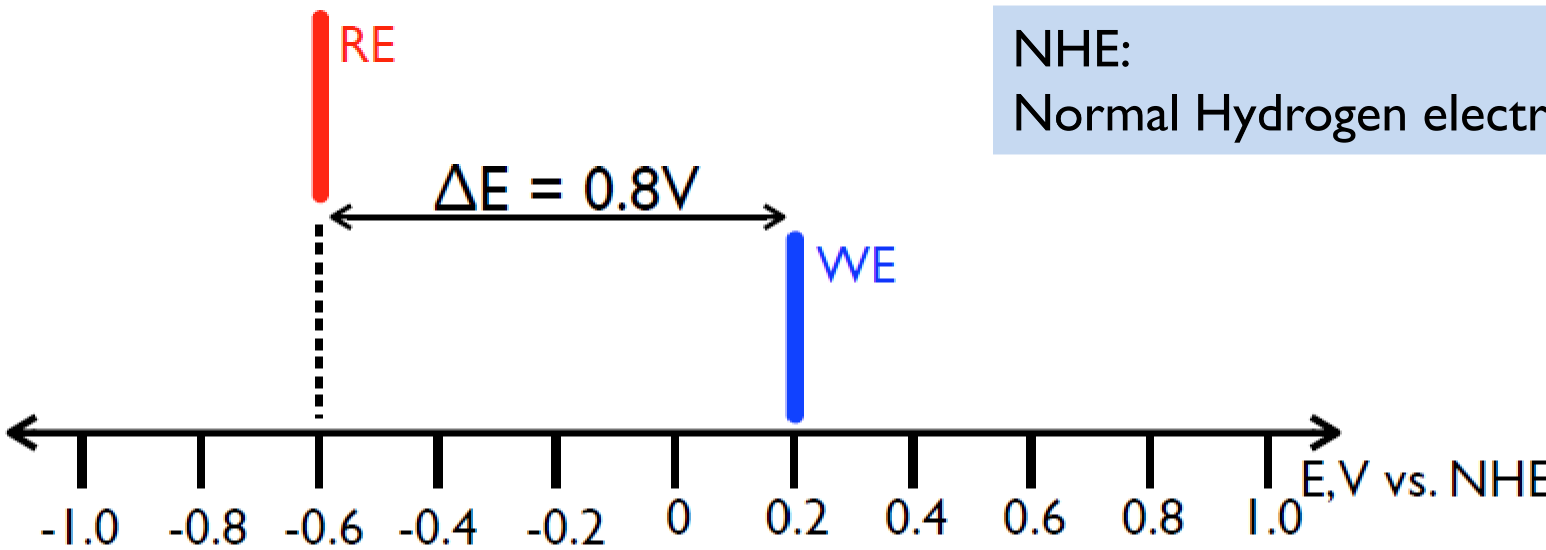
We wish to control the potential of this working electrode…

… but to do that, we need a second electrode in the solution to complete the circuit

Ref – Notes by Andrea Mardegan

Without a Reference Electrode …

$$\Delta E = 0.8V$$

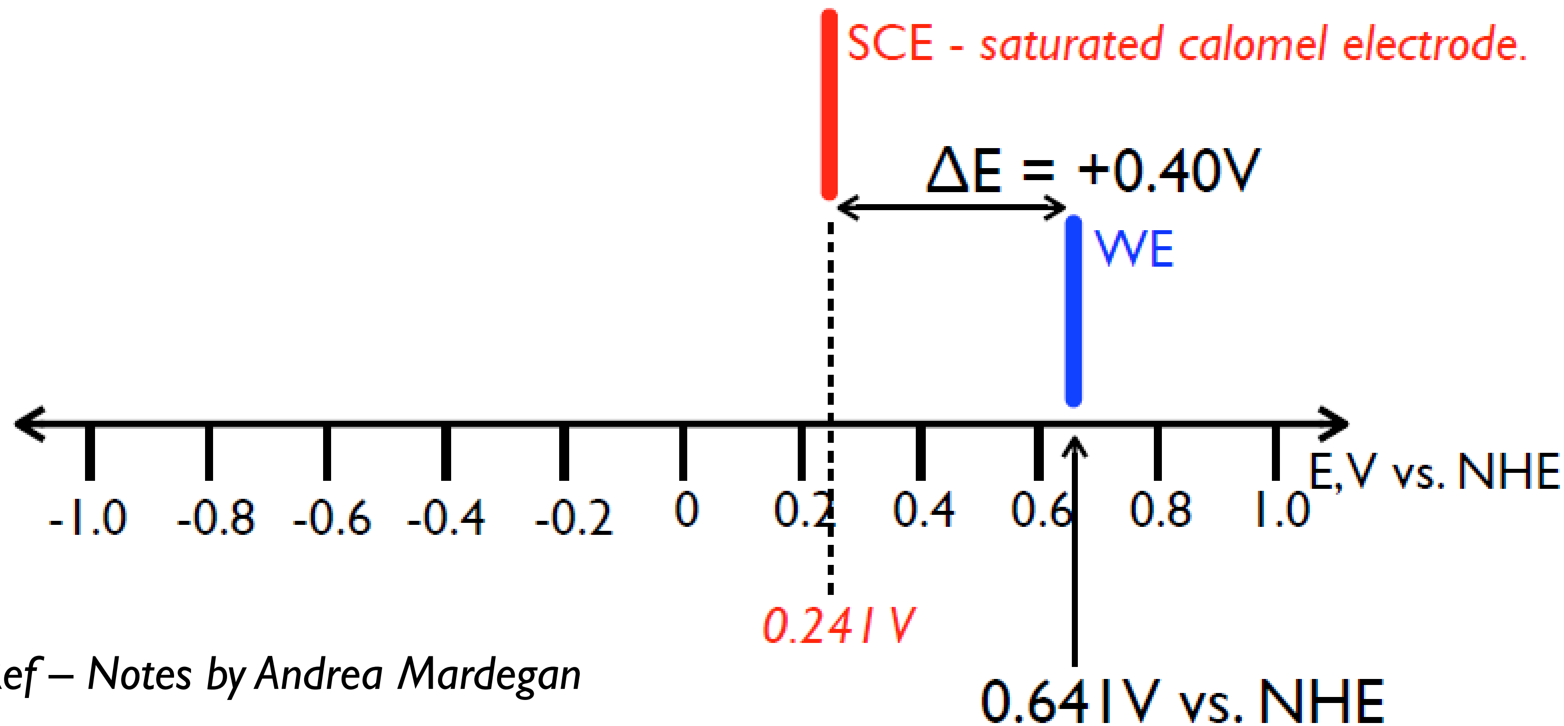


NHE:
Normal Hydrogen electrode

Voltage does not divide symmetrically

The purpose of reference electrode

$$\Delta E = +0.40V$$



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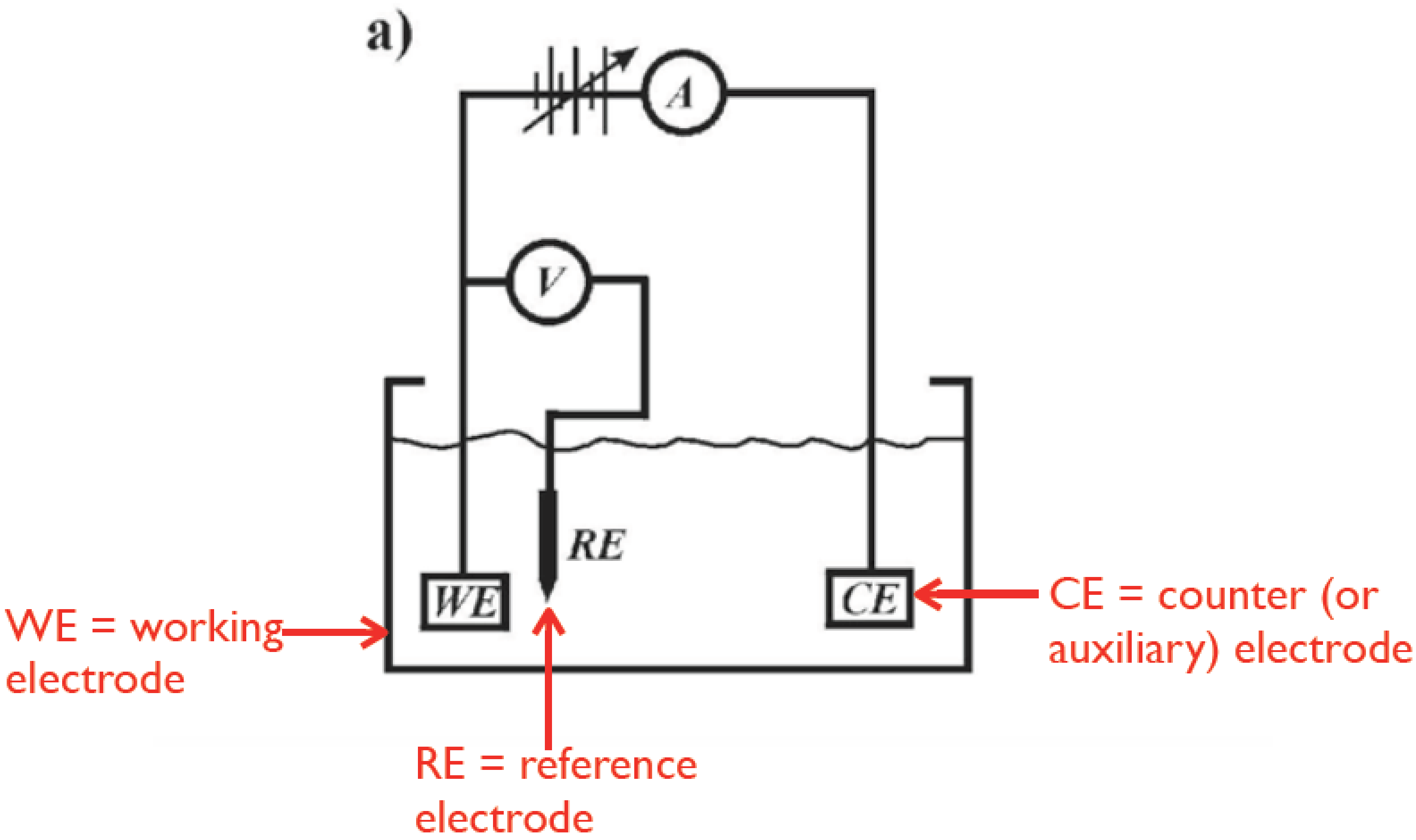
$E_{SCE} = 0.241\ V\ vs.\ NHE$

A three electrode cell



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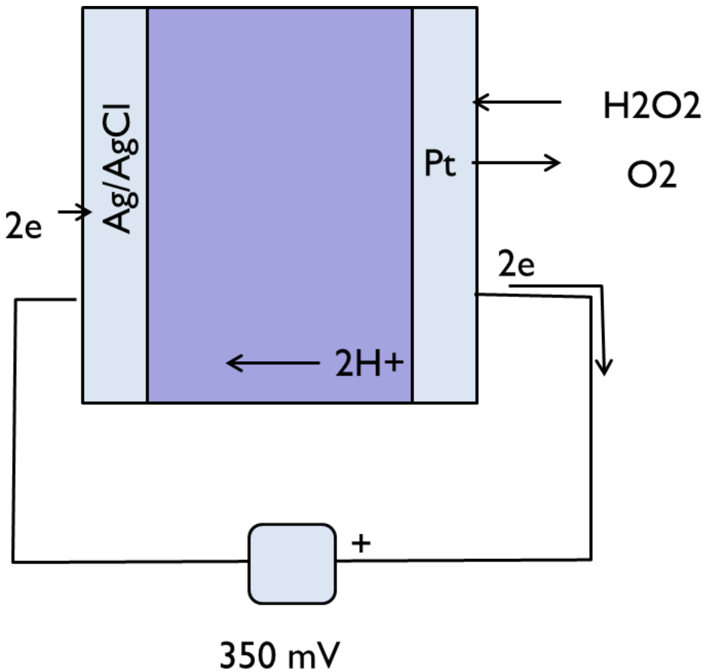
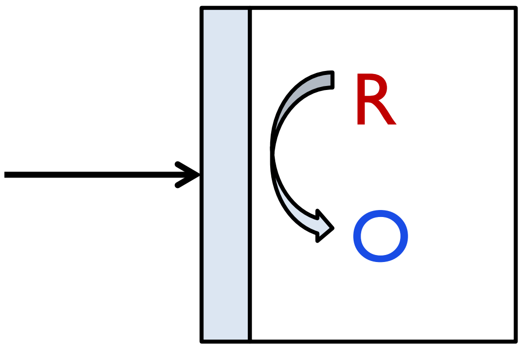
Current proportional to H2O2 concentration

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$





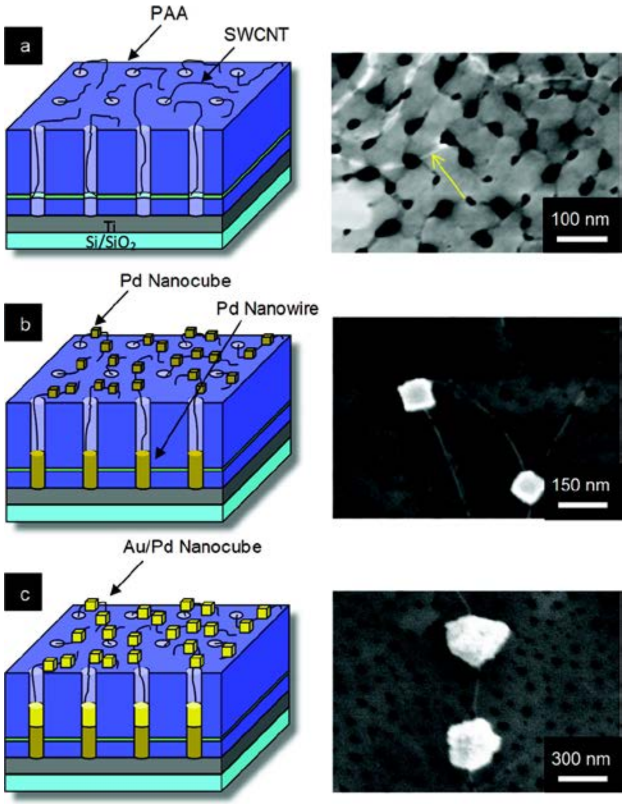
$$R \underset{k_b}{\overset{k_f}{\longrightarrow}} O + ne^-$$

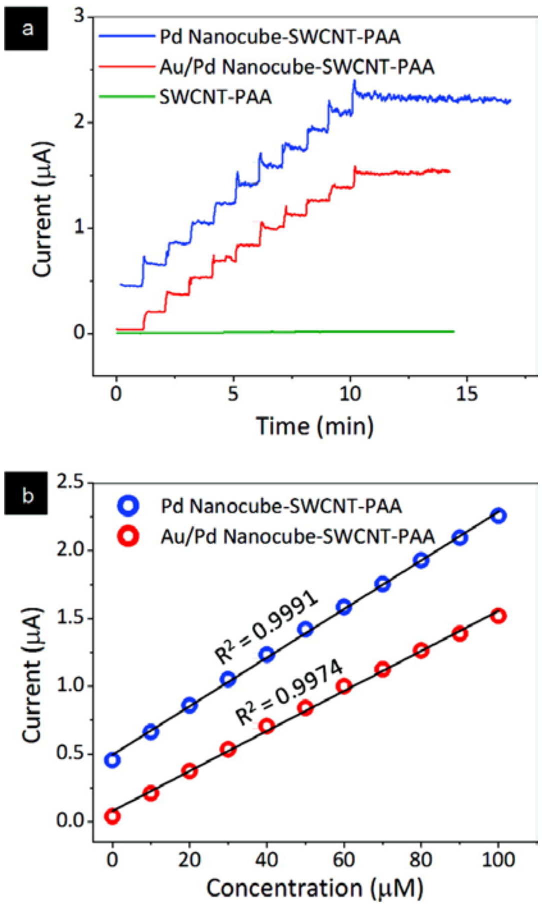
$$I = A_e q\left(k_f \rho_{H_2O_2} - k_b \rho_{O_2}\right)$$

$$I = A_e q\left(k_f \rho_{s,R} - k_b \rho_{s,O}\right)$$

Butler-Volmer equation

Validation of H2O2 response





$$I \propto A_e \qquad I \propto \rho$$

Conclusion

- A amperometric sensor responds linearly to the reactants to be measured and exponentially to the applied voltage.
- Three electrode configuration is ideal, but may not be practical.
- A broad range of biologically relevant products may be measured by amperometric sensors.

Appendix: Derivation of Butler-Volmer Equation

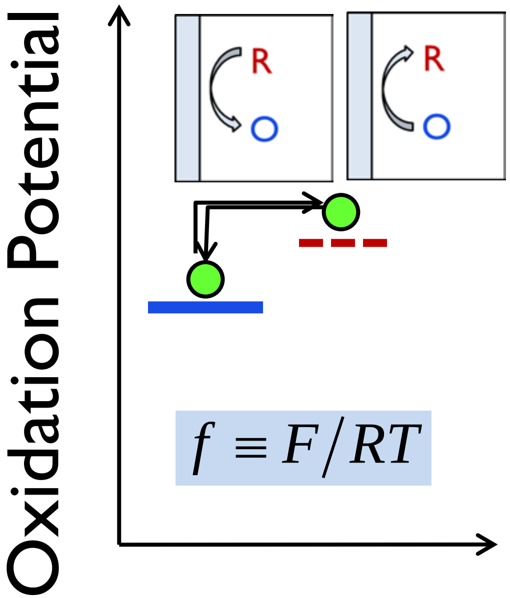
$$R \underset{k_b}{\overset{k_f}{\longrightarrow}} O + ne^-$$

Example:

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

$$k_f = k_{0,f} e^{(1-\alpha)\,\mathrm{nf}(\mathrm{E}-E_0)}$$

$$k_b = k_{0,b} e^{-\alpha n\,\mathrm{f}(\mathrm{E}-E_0)}$$

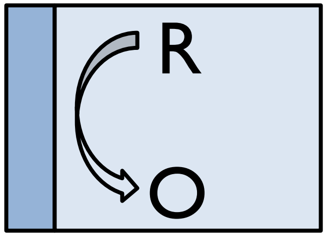


$$\Rightarrow I = qA\left(k_{0,f}\rho_{s,R} e^{(1-\alpha)\,\mathrm{nf}(\mathrm{E}-E_0)} - k_{0,b}\rho_{s,O} e^{-\alpha n\,\mathrm{f}(\mathrm{E}-E_0)}\right)$$

Appendix: Derivation of Butler-Volmer Equation

$$I = qA\left(k_{0,f}\rho_{s,R}e^{(1-\alpha)\mathrm{nf}(\mathrm{E}-E_0)} - k_{0,b}\rho_{s,O}e^{-\alpha n\mathrm{f}(\mathrm{E}-E_0)}\right)$$

Consider, the special case in which the interface is at equilibrium with a solution in which $\rho_{O}^{*} = \rho_{R}^{*}$



In that situation, $E = E_0$

$$k_{0,f}\rho_{O}^{*} = k_{0,b}\rho_{R}^{*}$$

Appendix: Derivation of Butler-Volmer Equation

$$\Rightarrow k_{0,f} = k_{0,b}$$

$$\Rightarrow I = qA\left(k_{0,f}\rho_{s,R}e^{(1-\alpha)\mathrm{nf}(\mathrm{E}-E_0)} - k_{0,b}\rho_{s,O}e^{-\alpha n\,\mathrm{f}(\mathrm{E}-E_0)}\right)$$

In general, if $k_{0,f} \neq k_{0,b}$, we can define a equilibrium potential such that

$$\mathrm{At\,E} = \mathrm{E}_{eq},\ \ I = 0$$

$$\Rightarrow E_{eq} = E_0 + \frac{k_B T}{nq}\ln\left(\frac{k_{0,b}\rho_{s,\mathrm{O}}}{k_{0,f}\rho_{s,\mathrm{R}}}\right)$$

$$f \equiv F/RT$$

Appendix: Derivation of Butler-Volmer Equation

Let $\eta = E - E_{eq}$

$$\Rightarrow I = qA\left(k_{0,f}\rho_{s,R}\right)^{\alpha}\left(k_{0,b}\rho_{s,O}\right)^{1-\alpha}\left(e^{(1-\alpha)\mathrm{nf}\,\eta} - e^{-\alpha n\mathrm{f}\,\eta}\right)$$

$$= i_o\left(e^{(1-\alpha)\mathrm{nf}\,\eta} - e^{-\alpha n\mathrm{f}\,\eta}\right)$$

$$i_o = qAk_o = qA\left(k_{0,f}\rho_{s,R}\right)^{\alpha}\left(k_{0,b}\rho_{s,O}\right)^{1-\alpha}$$

References

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