I. Ion selective electrodes:

- Nerst equation gives you the concentration dependence of cell potential
- for \( \text{N} + \text{M}^+ \rightarrow \text{N}^+ + \text{M} \) cell reaction; where \( Q = [\text{N}^+]/[\text{M}^+] \)
  \[ E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \log_{10} Q = E^\circ - 0.0592/n \log_{10} Q \]
- pH meters:
  a) standard electrode with known potential (anode reaction):
    \[ \text{Ag wire coated with AgCl} \quad \text{Ag(s)} + \text{Cl}^- (aq) \rightarrow \text{AgCl(s)} + e^- \quad E^\circ = -0.22 \text{ V} \]
  b) reference solution of dilute HCl acid:
    surrounding the AgCl (limited solubility; \( K_{sp} \))
  c) glass electrode with membrane as a salt bridge (cathode reaction):
    \[ \text{2H}^+ + 2 e^- \rightarrow \text{H}_2(g) \quad E^\circ = 0.00 \text{ V} \]
    cell potential depends on the \([\text{H}_3\text{O}^+]\) concentration
    \[ \text{Ag(s)} + \text{H}^+_\text{(aq)} + \text{Cl}^-\text{(aq)} \rightarrow \text{AgCl(s)} + \text{H}_2\text{O(g)} \]
    \[ Q = 1 / [\text{H}^+][\text{Cl}^-] \rightarrow [\text{H}^+] \text{ increases} \rightarrow Q \text{ decreases} \rightarrow E \text{ increases} \]
  d) potentiometer:
    opposing cell potential to zero the current flow in the cell circuit
    \[ E^\circ = - U_{\text{external}} \]
    calibration of potential/external voltage to pH 4.0 and pH 9.0
- AgS/Ag electrodes for Ag\(^{+}\), S\(^{2-}\) concentration
- change in glass composition of glass electrode allows for Na\(^{+}\), K\(^{+}\), NH\(_{4}\)\(^{+}\) detectors
- glovebox detectors: moisture and O\(_2\) sensors in ppm range

II. Batteries:

a) lead storage battery – long history due to its longevity and durability (the price to pay is weight)
   anode: \( \text{Pb(s)} \rightarrow \text{Pb}^{2+}_{(aq)} + 2 e^- \quad E^\circ = 0.13 \text{ V} \)
   cathode: \( \text{PbO}_{2(s)} + 3 \text{H}^+ + 2 e^- \rightarrow \text{Pb}^{2+}_{(aq)} + 2 \text{H}_2\text{O} \quad E^\circ = 1.46 \text{ V} \)
   salt bridge: sulfuric acid solution (HSO\(_{4}^{-}\))
   \[ \text{Pb(s)} + \text{PbO}_{2(s)} + 2 \text{H}^+_\text{(aq)} + 2 \text{HSO}_4^-\text{(aq)} = 2 \text{PbSO}_4\text{(s)} + 2 \text{H}_2\text{O(l)} \quad E^\circ = 1.69 \text{ V} \]
   - serial connection of 7 cells gives approximately 12 V
   - recharging: by a current from the alternator (electric generator) driven by the engine
   - electrolyte refill: electrolysis of water, warm engine evaporation of H\(_2\)O – only refill with H\(_2\)O

b) early dry cell batteries (Leclanche end of the 19\(^{th}\) century)
   anode: \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2 e^- \quad E^\circ = 0.76 \text{ V} \) (inner battery case)
   cathode: \( 2 \text{NH}_4^+ + 2 e^- \rightarrow 2 \text{NH}_3 + \text{H}_2 \quad E^\circ = 0.00 \text{ V} \) (from solid NH\(_4\)Cl)
   gases: \( \text{H}_2 + 2 \text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \text{H}_2\text{O} \)
   \( 2 \text{NH}_3 + \text{Zn}^{2+} + 2 \text{Cl}^- \rightarrow \text{Zn(NH}_3)_2\text{Cl}_2 \)
   drawback: \( \text{Zn}/\text{NH}_4^+ \) is not isolated, i.e. short circuit \( \rightarrow \) direct reaction to give \( \text{Zn(NH}_3)_2\text{Cl}_2 \)
   Fortunately it is slow (kinetically controlled), but leads to limited shelf-life
   - Zn/NH\(_4\)\(^{+}\) acidic battery – relatively fast Zn corrosion

  c) alkaline dry cell batteries
   anode: \( \text{Zn} + 2 \text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2 e^- \)
   cathode: \( 2 \text{MnO}_2 + \text{H}_2\text{O} + 2 e^- \rightarrow \text{Mn}_2\text{O}_3 + 2 \text{OH}^- \)
d) NiCd dry cell batteries in alkaline medium

\[
\begin{align*}
\text{anode:} & \quad \text{Cd} + 2 \text{OH}^- \rightarrow \text{Cd(OH)}_2 + 2 \text{e}^- \\
\text{cathode:} & \quad \text{NiO}_2 + 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{Ni(OH)}_2 + 2 \text{OH}^- 
\end{align*}
\]

e) fuel cells

- combustion of methane
  \[
  \text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)
  \]
  at 1 atm, 25 °C; \( \Delta G^o = -817.9 \text{ kJ} \); \( \Delta H^o = -890 \text{ kJ} \); \( \Delta S^o = -242 \text{ J/K} \)
  
  total heat content > available work due to loss of entropy

  heat → drive turbine → electricity \( \sim 200-300 \text{ kJ/mol} \)
  electrochemical cell → electricity \( \sim 800 \text{ kJ/mol} \) (but never 817.9 kJ/mol)

\[
\epsilon^o = - \frac{\Delta G^o}{nF} = 1.04 \text{ V}
\]

- anode: \( \text{CH}_4 \rightarrow '\text{C}^{4+} + 8 \text{e}^- + 4 \text{H}^+ \)
- cathode: \( 2 \text{O}_2 + 8 \text{e}^- + 4 \text{H}^+ \rightarrow '\text{O}^{2-} + 2 \text{H}_2\text{O} \)

- hydrogen technology (\( \text{H}_2 \) tank vs. in-situ generation)
  \[
  2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l)
  \]
  most ideal environmentally \( \Delta G^o = -474 \text{ kJ/mol} \) \( \epsilon^o = 1.23 \text{ V} \)

\[
\begin{align*}
\text{anode:} & \quad 2 \text{H}_2 + 4 \text{OH}^- \rightarrow 4 \text{e}^- + 4 \text{H}_2\text{O} & \epsilon^o = 0.00 \text{ V} \\
\text{cathode:} & \quad \text{O}_2 + 4 \text{e}^- + 2 \text{H}_2\text{O} \rightarrow 4 \text{OH}^- & \epsilon^o = 1.23 \text{ V}
\end{align*}
\]

III. Corrosion:

a) How spontaneous the “rusting” process? (at which condition \( \text{O}_2 \) is the strongest oxidizing agent?)

- neutral solution: \( \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \) \( \epsilon^o = 0.40 \text{ V} \)
- slightly acidic solution: \( \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2 \) \( \epsilon^o = 0.68 \text{ V} \) (\( \text{CO}_3^2- \), \( \text{HCO}_3^- \), \( \text{CO}_2 \text{dissolved} \))
- strong acidic solution: \( \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \) \( \epsilon^o = 1.23 \text{ V} \)
- metal surfaces:
  \[
  \begin{align*}
  \text{Fe} & \rightarrow \text{Fe}^{3+} + 3 \text{e}^- & \epsilon^o = 0.04 \text{ V} & \text{rusting} \\
  \text{Ag} & \rightarrow \text{Ag}^{+} + \text{e}^- & \epsilon^o = -0.80 \text{ V} & \text{only in strong acidic solution} \\
  \text{Au} & \rightarrow \text{Au}^{3+} + 3 \text{e}^- & \epsilon^o = -1.50 \text{ V} & \text{no way!}
  \end{align*}
  \]

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^- & \epsilon^o = 1.66 \text{ V} & \text{rust – no problema! or is it?}
\]

b) Protection by oxide layer

- Al metal has high cell potential → formation of \( \text{Al(OH)}_3 \) stops corrosion
- \( \text{Fe}_2\text{O}_3 \) cracks/peels of exposing fresh Fe surfaces

c) Prevention:

- passive: paints, durable passive oxide (Cr, Sn), galvanization by Zn (ZnO/ZnCO\textsubscript{3} layer), alloying (Cr, Ti)
- active: cathodic protection – connection to metal with more negative \( \epsilon^o \) (better reducing agent, generates excess electrons, Mg in underground pipes, Ti beams in ship hulls)