ENGME 545
Electrochemistry

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Electrochemistry can be found in energy storage (batteries, fuel cells), sensors (extremely sensitive ones), manufacturing (often metals, large scale and small high-fidelity), water treatment (capacitive deionization), high precision chemical industry (pharmaceutical industry).

Important components in e-chem is electrons, ions (these are slower than electrons), energy density (how much), power density (how fast), solvents (where ions move around, batteries often have liquids in them), mass transfer and reaction kinetics.

In electro-chemistry we can control flow of electrons or the chemistry. Electric potential of an electrode is changed (this can be metal, carbon, etc.). In the electrode, there are free electrons; adding negative potential raises energy of electrons. By themselves, potential does not do much. However, a solution with a species of discrete energy levels (molecular orbitals, energy states) is needed. There is a highest occupied molecular orbital, which is an energy state that is filled with electrons; this concept is also true in semi conductors, where there is a full band and a valence (empty) band. The energy state that is unoccupied is the lowest unoccupied molecular orbital. When high enough energy is applied to the electrode, there is a thermodynamic driving force to get to the lower energetic state of the species; this is called reduction. Since the electron comes with a charge, there is a charge imbalance. Our species becomes negatively charged. If our species of already positively charged (cation), it could now become neutral. In the positive electrode, we lower the energy level, we can now remove an electron from our species: oxidation. If we started off with negative species, we'd get neutral, or if it was already positive, we could make it more positive.

Reduction in cathodes, oxidation in anodes. In battery, electrons would be getting out of the negative terminal (?).

In water electrolysis, we often need some acidity to have ions. Reduction of protons happen to the hydrogen at the cathode to get elemental hydrogen; these have to exist as molecules so H+ and H+ binds to get H2. The reduction of protons yields a molecule of H2.

Fermi energy is lowered at the anode; the species giving away the electrons is actually water. Oxygen is produced; this is oxidation. Splitting water into hydrogen and oxygen does not happen spontaneously; energy is needed. Energy is converted into the fact that the gas has more energy. The net equation is 2 H2O to 2 H2 and O2: $2\,H_2O \longrightarrow 2\,H_2 + O_2$.

By reversing this, we can convert hydrogen and oxygen gas into water, in exchange for gaining energy. This reaction happens spontaneously, so a load can be applied. Voltage drop and the current flow defines the energy.

The reaction isn't performed in the same place, otherwise we would get an explosion. The chemical reaction is split into half-reactions. Electrochemistry splits this up.

Redox is the combinantion of the two half reaction: reduction and oxidation. These are coupled to each other. Forcing the reaction by applying a voltage is called an electrolytic cell; thermodynamically, this is energetically uphill. The energy can be released through a galvanic cell (which spontaneously converts chemical energy into electrical energy), or an explosion; this is energetically downhill. ΔG , Gibbs free energy, is greater than 0 in electrolytic cell, and the energy potential is negative. In galnavic cell, $\Delta G < 0$ (if spontaneous), and the electric potential is $E > 0$.

Interfaces are denoted by a slash. Left to write, we'd write this as: Electrode-1 (oxidation) / Ions, species in same phase / Electrode-2 (reduction).

For water electrolyzer, this would be written as: $Ir_2O_2/H^+, {SO_4}^{2-}, H_2O/Pt$. Sulfuric acid is the typical acid used in battery cells. In a fuel cell, this is flipped: $Pt/H_2\,(g)/H^+, {SO_4}^{2-}, H_2O/O_2\,(g)/Ir_2O_2$.

We have to ensure that reagents are separated in galvanic cells. If the chemical fuel cell were mixed together, there is a chance they'd just react together. Physically separated in galvanic cells. Efficiency of a galvanic cell is higher than having things react to run a heat engine (limited by Carnot cycle). Electrochemistry isn't 100% efficient, but better than Carnot typically.

Salt bridge allows ions to move. In galvanic cells, we try to keep the ions separate. If we had zinc-copper cell, the ions would just plate on the electrodes. Double slash indicates the bridge. So, as an example: $Zn/Zn^{2+}, {SO_4}^{2-}//K^+, Cl^-//Cu^{2+}, {SO_4}^{2+}/Cu$.

A couple of strategies to identify what can happen to ions is the periodic table. We generally discuss oxidation states of the elements by themselves, as an ion, or as a compound. A pure element does not have charge: its oxidation state is zero. For an elemental ion, its charge is the oxidation state. Chlorine gas has an oxidation state of 0, but Cl^- has a state of -1. Lithium metal is zero when an element, but Li^+ has a state of +1. Groups 1, 2, and 7 are particularly easy, e.g. NaCl. However, there are exceptions. Lead oxide PbO_2, car battery, has Pb^{4+} since O^{2-} is very often 2 negative. For PbO, they each are 2. Traditional lithium ion battery uses $LiCoO_2$ in the cathode; since Li is almost always +1, O is almost always -2, then Co^{3+}.

In electrochemistry, common polyatomic ions are perchlorate, sulfate, hydroxide.

In lithium-ion battery, the cathode is copper with graphite, where graphite

can hold lithium. The anode is typically aluminum with Li_xCoO_2 coating. The middle has $LiPF_6$. The discharge (galvanic) cycle has: $Cu/Li_yC_6\,/Li^+, {PF_6}^-/Li_xCoO_2$ where $0 < y < 1$, and $0.5 < x < 1$ determine depleted or fully charged. The oxidation reaction is ${Li^+C_6}^{-1/6} \longrightarrow yLi^+ + e^- + Li_{1-y}C_6$. The reduction happens on the cobalt oxide side: $2\,Li^+_{0.5}{Co^{+3.5}{O_2}^{-2}} + Li^+ + e^- \longrightarrow 2\,Li^+{Co^{+3}{O_2}^{-2}}$. Oxidation state of the cobalt in the reduction process is lower.

Example 1 practice (slide 16): $Pt\,(s)/H_2\,(g)/H^+, Cl^-, H_2O/AgCl\,(s)/Ag\,(s)$. Here, note that solubility of silver chloride is low, so some would just be floating around not reacting. The oxidation step is $H_2 \longrightarrow 2\,H^+ + 2\,e^-$. For the reduction (two of this happens): $Ag^+Cl^- \longrightarrow Ag^0 + Cl^-$. The net reaction is $H_2 + 2\,AgCl \longrightarrow 2\,Ag + 2\,HCl\,(aq)$

Thermodynamically, all the electrodes have an energy level. We can only really compare energy levels, so 'reference' electrodes are used: these are standard electrodes, and we simply do the reference of this. The reference electrode is the Standard Hydrogen Electrode (SHE): $Pt/H_2/H^+(\ a = 1,$ aqueous$) \rightarrow E = 0\,V$. This is theoretical, since it assumes that hydrogen ion can have an activity of 1. The normal hydrogen electrode (NHE) is platinum in 1 molar acid with hydrogen, which is at a pH of 0. The reversible hydrogen electrode (RHE) is using non-acidic conditions: platinum in an aqueous medium where the potential of the electrode is based on the pH: $E = -0.059 \times pH$ [V] in contrast to SHE. Other standard electrodes include mercury (not common anymore), silver and silver chloride. These have a well-defined potential in comparison to the SHE.

If HCl (aq), we'd get oxygen first, then chlorine if too much voltage; we'd have to control the voltage very carefully in this case. For the gas, it's not a very problem, we use a solid membrane, we use a gel with electrode, a tryple phase boundary, gas flows by the surface, surface containing (?), only when gas acid electrode comes, only then the reaction happens. This determines how fast we can run it, how much current we get. We'd typically put load in the AgCl case. One of the two ions move instead of chlorine just going out.

If acidic water, then wouldn't (if we used HCl acid) we get chlorine gas? If it is gas being fed into a fuel cell, is there enough surface area for gas to react? would example 1 practice be performed with hydrogen chloride (gaseous)? In example 1, is there a lot of heat generated since there is no load? What happens to the silver that forms?

1 Thermodynamics of Electrochemistry

Key takeaway last time was that a chemical reaction is separated in to two electrodes as half-reactions: in anode, electron is removed in oxidation; in cathode, electrode is added in reduction. The difference between the two events determines the cell voltage.

The component that can move the electrons in/out is the electrode. The substance itself is the redox active species.

One direction should be spontaneous, which is the galvanic cell; the driven is electrolytic cell and energy has to be spent. In reversible cells, we obtain a

battery.

The two electrodes have to be in an electrolyte. The electrolyte is not electronically conductive; that would indicate a short circuit. Only ionic conduction happens to maintain charge balance and close the circuit. In electrolytes, both positive and negative charges move.

The standard reduction potential shows, if one of the electrode is the SHE or NHE, the voltage of the reduction at the other electrode. Being further away from the hydrogen demands a lot of energy to reduce (for charged metals) or hard to oxidize (for un-reacted halides and some reacted cations).

For $\mathrm{Au/Sn^{2+}, I^-, H_2O, H^+/H_2/Pt}$, the NHE is on the reducing side. As voltage is raised from 0.05V to 0.15V, we get $\mathrm{Sn^{2+} \longrightarrow Sn^{4+} + 2\,e^-}$. Then, at 0.54 V, we would get $\mathrm{2\,I^- \longrightarrow I_2 + 2\,e^-}$. Then at 1.23V, $\mathrm{2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-}$. If, instead of slowly raising the voltage, we suddenly applied 0.6V, both tin and iodine should be reduced. Same is true for 0.54V. Thermodynamically, this also happens at 0.539V.

For $\mathrm{Pt/H_2/Fe^{3+}, Sn^{4+}, I^-, H_2O, H^+ / Pt}$. As voltage becomes more negative from 0.9V to 0.77V, iron gets reduced. Then, at 0.15V, tin gets reduced. Then, at 0 we would get hydrogen splitting. At -0.25V, we get solid nickel deposition, however, this is not a good idea: hydrogen is being produced and is explosive.

For a case where we have platinum electrode, and a silver bromide coated silver electrode in bromic acid solution, we can either have $\mathrm{Ag\ /\ AgBr\ /\ H^+, Br^-, H_2O\ /\ Pt}$, or $\mathrm{Pt\ /\ H^+, Br^-, H_2O\ /\ AgBr\ /\ Ag}$. Note that this is not a standard cell since there is no hydrogen gas already present. From the standard reduction potential table, we can obtain the electric potentials. Note that one of them is 1.229V for $\mathrm{O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O}$, however, we do not have oxygen gas; consequently, we can only have oxidation, not reduction. Similarly, $\mathrm{Br_2 + 2\,e^- \longrightarrow 2\,Br^-}$ at 1.0874V is not possible, since bromine is absent; only the oxidation is possible. However, $\mathrm{AgBr + e^- \rightleftharpoons Ag + Br^-}$, since both are present; the reduction is 0.0711V. Finally, the hydrogen gas evolution is possible. Consequently, if we apply a reductive voltage on platinum, the cathode has a reduction of hydrogen gas evolution (at the platinum), and at the anode we have oxidation of bromine ions into silver bromide: $\mathrm{2\,H^+ + 2\,Br^- + Ag \longrightarrow AgBr + H_2}$. This would happen at -.0741V. If we appl an oxidizing potential to the platinum, we have: $\mathrm{AgBr + e^- \longrightarrow Ag + Br^-}$ and $\mathrm{2\,Br^- \longrightarrow Br_2 + 2\,e^-}$, at 1.087V.

An electrochemical cell is determined by the direction that it will be run. Applying positive current w.r.t. Ag/AgBr creates 'anodic' current; applying positive yields cathodic current. Old books have oxidizing currents on the left, and the x axis represents energy of the electrons.However, new ones have flipped axis, with negative potentials on the left.

Electrodes with large electic potentials where nothing happens is called an ideal polarized electrode. The electrode is w.r.t. to the electrolyte. Non-polarizable electrode is the opposite; the energy of the electrodes do not change, and can undergo oxidation/reduction very quicly; for example, the Ag/AgBr and Ag/AgCl. These are typically used as reference electrodes, since they remain stable in their electric potential.

Non-participating electrodes are those that do not have a net redox reaction, and is just for providing electrons; it could be catalytic. For example, platinum in the hydrogen reactions. In contrast, participating electrodes are those that can strip and deposit, such as copper: this acts as the electrode ad the electroyltic species. Metal being oxidized is called corrosion, or stripping (common terminology in batteries), or dissolution. Depositing the metal is called deposition, and also plating.

Alloying electrodes, intercalation, and conversion, are common for present. For example, graphite gets intercalated with lithium in lithium-ion batteries. Alloy of silicon and lithium is an example $\mathrm{Si} + x\,\mathrm{Li} + \mathrm{xe}^- \longrightarrow \mathrm{SiLi}_x$

Gibb's free energy is given as

$$G = H - TS \tag{1}$$

where H is the enthalpy and S is the entropy. We typically look at this in the differential form

$$\mathrm{d}G = \mathrm{d}H - T\,\mathrm{d}S - S\,\mathrm{d}T \tag{2}$$

Typically, we work in isothermal conditions, where $\mathrm{d}T = 0$ and $\mathrm{d}q + \mathrm{d}w + \mathrm{d}(pV) = \mathrm{d}H$. In a reversible system, $\mathrm{d}q_{rev} = T\,\mathrm{d}S$. we also typically operate under constant pressure. Consequently,

$$\mathrm{d}G = \mathrm{d}w_{rev} + \mathrm{d}(pV) \tag{3}$$

states that the reversible work is described by the change in Gibb's free energy (excluding pV).

Electrical work is the amount of charged for a given potential drop (the voltage), $|\Delta G| = \vec{q}\cdot\Delta\phi = n\cdot F\cdot E$, where F is the Faraday constant. The Faraday constant is the charge of a mole of electrons, $F = e \cdot N_A = 96485\ \frac{\mathrm{C}}{\mathrm{mol}}$. The n is the number of electrons in the process that are being transferred (the moles). E is the cell potential. Historically, cell positive used to be just positive. Positive ΔG is non-spontaneous. As a result, the new equation uses electromotive force E_{rxn}. If $\Delta G < 0$ is spontaneous, with $E_{rxn} > 0$. For $\Delta G > 0$ requires energy, and $E_{rxn} < 0$. Consequently, the equation is

$$\Delta G = -n \cdot F E_{rxn} \tag{4}$$

which relates thermo to electrochemistry.

The chemical potential is given by μ. If the potential of the product is less, $\mu_B < \mu_A$, then $\Delta G = \mu_B - \mu_A$ is spontaneous. At equilibrium, $\Delta G = 0$; at this point, $\mu_A = \mu_B$.

The chemical potential of a species depends on the reference added with the activity $a_A = X_A$ [A] :

$$\mu = \mu^0 + RT \ln a \tag{5}$$

where $[A]$ denotes the concentration of the species A. At low concentrations, the concentration and activity are nearly the same (?).

We can consequently write

$$\Delta G = \mu_B^0 + RT \ln a_B - (\mu_A^0 + RT \ln a_A)$$

and the standard Gibbs free energy is

$$\Delta G^0 = \mu_B^0 - \mu_A^0. \tag{6}$$

This allows us to write

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{a_B}{a_A} \right). \tag{7}$$

At equilibrium,

$$\Delta G^0 = -RT \ln \left(\underbrace{\frac{a_B^{eq}}{a_A^{eq}}}_{k_{eq}} \right)$$

where $k_eq \approx \frac{[B]_eq}{[A]_eq}$ is the equilibrium constant. Keep in mind that this is a ratio, not any specific concentration.

Often, stoichiometric coefficients are used, represented by v_x in this class for material x. For $\mathrm{v_A\,A + v_B\,B \rightleftharpoons v_C\,C + v_D\,D}$ has the equilibrium constant at

$$k_{eq} = \frac{[C]^{v_c}[D]^{v_D}}{[A]^{v_A}[B]^{v_B}}$$

and for example, $\mathrm{2\,Fe^{3+} + Sn^{2+} \rightleftharpoons 2\,Fe^{2+} + Sn^{4+}}$ has a equilibrium constant that would be a specific ratio of concentrations.

The equilibrium constant can be related to the electromotive force (emf) as

$$E_{rxn}^0 = \frac{RT}{nF} \ln (k_{eq}) \tag{8}$$

and the emf can be related to the standard Gibb's free energy difference

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{a_B^{v_B}}{a_A^{v_A}} \right) = -n \cdot F E_{rxn} \tag{9}$$

and this yields the Nernst equation

$$E_{rxn} = E_{rxn}^0 - \frac{RT}{nF} \ln \left(\frac{a_B^{v_B}}{a_A^{v_A}} \right) \tag{10}$$

which is the primary equation for electro-chemistry.

Now, we can determine if a particular electrochemical cell is spontaneous or non-spontaneous.

In the reduction of zinc ion to zinc metal against a standard hydrogen electrode, we have SHE be the oxidizing side. We then have $\mathrm{Pt/H_{2/}H^+, Cl^-, Zn^{2+}/Zn}$.

In the reduction reaction, we have $Zn^{2+} + 2\,e^- \longrightarrow Zn$, and in oxidation we have $H_2 \longrightarrow 2\,H^+ + 2\,e^-$. The net reaction is $Zn^{2+} + H_2 \longrightarrow Zn + 2\,H^+$. We now look up the standard reduction potentials. For the reduction, $E^0 = -0.76V$, and for the oxidation side it is 0 since we are already using SHE. Now, using equation 10, we have

$$E^0_{rxn} = \underbrace{\frac{RT}{nF} \ln\left(\frac{a_{Zn}}{a_{Zn^{2+}}}\right)}_{E^0_{red}} - \underbrace{\frac{RT}{nF} \ln\left(\frac{a_{H_2}}{a^2_{H^+}}\right)}_{E^0_{ox}}$$

Note that we must not change signs. Note that this is less than 0, so it creates a $\Delta G > 0$, and hence, an electric potential has to be applied for this to work.

Typically, a stable electrode is used at the side that has hydrogen production.

The E^0 for hydrogen half reaction can be taken to be 0 because we stated that the activity of it is 1.

By using the formal potential formula, where E can be directly measured using a voltmeter, we can directly measure the concentrations. This is what happens in pH sensors.

The Nernst equation only works if both items are present in the half reaction; if one of the terms go to 0, the log goes to infinity. This is only useful for 2 binary terms are present, such as silver and silver bromide.

2 Interfacial Potentials

The first problem set has been posted, due next week.

Last class, k_{eq}, ΔG^0 , and E^0_{rxn} cell potential were related using the equations

$$\Delta G^0 = RT \ln(k_{eq}) \tag{11}$$

$$\Delta G^0 = -nF E^0_{\text{rxn}} \tag{12}$$

$$E^0_{\text{rxn}} = \frac{RT}{nF} \ln(k_{\text{eq}}) \tag{13}$$

where n is the number of electrons being transferred from one species to another. This is why we write down electrons in the half reactions, even though the redox reaction does not showcase this; when doing this, ensure that number of electrons is same in both half reactions for the above to work. Additionally, we assume that the above is for activity of 1. If the activity was different, we'd use the Nernst equation per half-reaction in comparison to SHE:

$$E_{\text{red/ox}} = E^0_{\text{red/ox}} - \frac{RT}{nF} \ln\left(\frac{a_R^{v_R}}{a_O^{v_0}}\right) \tag{14}$$

and the activity is approximately the concentration of the products and reactants if dissolved and low concentration.

Example $\mathrm{PbO_2 + Pb + 4\,H^+ + 2\,SO_4{}^{2-} \longrightarrow 2\,PbSO_4 + 2\,H_2O}$ Here, we look at the oxidation states that are reduced. First, we see that there is elemental lead: this has oxidation state of 0 in reaction. The oxidation state of the proton is +1. Now, on the right side, the proton is still +1, since oxygen is still -2. On the left, oxygen also has -2, so the $\mathrm{PbO_2}$ has +4 for that Pb. The sulfate is ionic, and its whole charge is -2, and stays the same on the right. Therefore, on the right side, the lead must be +2. We see that one of the lead gets reduced., and the other gets oxidized.

The reduction reaction is:

$$\begin{aligned}
&\text{Reduction :} \quad \mathrm{PbO_2 + 4\,H^+ + SO_4{}^{2-} + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O} \quad E^0 = 1.798\,\mathrm{V} \\
&\text{Oxidation :} \quad \mathrm{Pb + SO_4{}^{2-} \longrightarrow PbSO_4 + 2\,e^-} \quad E^0 = -0.351\,\mathrm{V}
\end{aligned}$$

Instead of doing this step by step, we could also look at the half reaction table and see how the half reactions make up the full reaction. Looking at the table, we see that the $E^0_{\mathrm{rxn}} = E^0_{\mathrm{red}} - E^0_{\mathrm{ox}} = 2.05\,\mathrm{V}$. Since the potential is positive, this is a galvanic cell. This is the lead-acid battery: $\mathrm{Pb\,/\,PbSO_4\,/\,H^+}$,$\mathrm{SO_4{}^{2-}}$,$\mathrm{H_2O\,/\,PbSO_4\,/\,PbO_2}$. Even though this is 2V, the lead-acid car battery is 12V because there is 6 cells. While batteries charge and discharge, the concentrations change, and changes the activity. In lead-acid battery, the activity of the metal does not change, and the acid is abundant, hence the battery voltage is typically stable. This is not the case in lithium-ion batteries, hence we see larger voltage changes.

The materials used in cells is limited by constraints such as safety; on paper, we can make any cell but in reality there are other considerations.

Electrochemistry has been used to measure properties of various materials since it is easy to measure voltage. We can, for example, measure cell potential as a function of temperature:

$$E^0(T) \implies \Delta G^0(T)$$

which enables us to then measure entropy:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p = nF\left(\frac{\partial E_{\mathrm{rxn}}}{\partial T}\right)p \tag{15}$$

and also measure the enthalpy:

$$\Delta H = nF\left(\frac{\partial E_{\mathrm{rxn}}}{\partial T}\right)_p - E_{\mathrm{rxn}} \tag{16}$$

This enables converting thermochemistry into electrochemistry. This may not always be possible, for example, if the reactions cannot be separated into half reactions due to their states (e.g. gas).

We know that $\Delta H = Q - W$, we can estimate produced heat for these systems.

Suppose we have $\mathrm{Zn}\,/\,\mathrm{Zn}^{2+}\,,\mathrm{Cl}^{-}\,/\,\mathrm{AgCl}\,/\,\mathrm{AgCl}$. The

$$\begin{aligned} \text{Oxidation}: \quad & \mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^{-} && E^0 = -0.76\,\mathrm{V} \\ \text{Reduction} \quad & 2\,\mathrm{AgCl} + 2\,\mathrm{e}^{-} \longrightarrow 2\,\mathrm{Ag} + 2\,\mathrm{Cl}^{-} && E^0 = 0.223\,\mathrm{V} \end{aligned}$$

which has a net emf of 0.983V. The change in Gibbs free energy in standard conditions is $\Delta G^0 = -2FE^0 = -190\,\frac{\mathrm{kJ}}{\mathrm{molZn}}$, and $\Delta H^0 = -233\,\frac{\mathrm{kJ}}{\mathrm{molZn}}$, which finally yields $T\Delta S = -43\,\frac{\mathrm{kJ}}{\mathrm{molZn}}$.

We hook this system up to a resistor, and put a calorimeter around the cell and the resistor. Note that heat formation is almost always 100% efficient. The sum of the two calorimeter reading must be the enthalpy ΔH^0. We can change the resistance. If we run the cell reversibly, as $R \to \infty$, then the resistor calorimeter would measure $-\Delta G^0$: this is the maximum work that our cell can provide; the cell calorimeter would measure the entropy—the energy that must disappear—as $-T\Delta S$.

Now, if we short-circuit with $R \to 0$, then all the energy is dissipitated in the cell as heat: this would yield $-\Delta H^0$. The slower we discharge the cell, the more useful energy we extract from the cell.

This is one of the reasons why using a battery faster yields a lower voltage.

A system is thermodynamically reversible if it follows the Nernst equation exactly even while the cell is running. This happens if we run the cell infinitely fast and the concentrations change accordingly.

Chemical reversibility is slightly different. It considers the feasibility first. If we have $\mathrm{Pt}\,/\,\mathrm{H_2}\,/\,\mathrm{H}^{+}\,,\mathrm{Cl}^{-}\,/\,\mathrm{AgCl}\,/\,\mathrm{Ag}$, the cell can be reversed. If we have $\mathrm{Zn}\,/\,\mathrm{H}^{+}\,,{\mathrm{SO_4}}^{2-}\,,\mathrm{H_2O}\,/\,\mathrm{Pt}$, the zinc gets oxidized, and the proton gets reduced; this cannot be reversed because there is no hydrogen as it dissipitates readily. In the reverse side, we'd simply just split water.

The chemical potential of a species i in its phase α is denoted as μ_i^α. This is given as

$$\mu_i^\alpha = \left(\frac{\partial G}{\partial n_i}_{P,T,n_{j\neq i}}\right) = \mu_i^{0\alpha} + RT\ln(a_i^\alpha) \tag{17}$$

How does the Gibbs free energy change if the concentration is changed slowly given everything constant (pressure, temperature, and other species that are not i). Note that α is *not* an exponent!

Whenever there is charge involved, we should use the electrochemical potential rather than the regular chemical potential:

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i \cdot F \cdot \phi^\alpha \tag{18}$$

where z_i is the charge of the species (including the charge/sign), ϕ^α is the electrostatic potential of the phase (can be controlled by manipulating the electrodes for example).

If the electrochemical species had no charge, then the chemical and electrochemical potential are *identical*. For pure solids (the species as the whole unit), it is uncharged, and the activity is also considered to be 1. For electrons, they must have a charge, but their activity is 1, so: $\bar{\mu}_e^\alpha = \mu_e^{0\alpha} - F\phi^\alpha$.

If we have $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}$, then $\mu_A + \mu_B = \mu_C$. If we have a solid that dissolves, then $\mathrm{AB} \rightleftharpoons \mathrm{A}^+ + \mathrm{B}^-$ in the phase $\alpha = s$. Note: the book uses s to denote *solution*, not solid!. Here, $\bar{\mu}^{AB}_{AB} = \bar{\mu}^s_{A^+} + \bar{\mu}^s_{B^-}$, which, by our discussion of solids, it should be same as $\mu^{0\,AB}_{AB} = \mu^{0\,s}_{A^+} + RT\ln(a^s_{A^+}) + F\cdot\phi^s + \mu^{0\,s}_{B^-} + RT\ln(a^s_{B^+}) - F\phi^s$; here, the $F\phi^s$ cancels. This enables us to calculate the Gibbs free energy change as it dissolves:

$$\Delta G^0_{\mathrm{sol}} = \mu^{0\,AB}_{AB} - \mu^{0\,s}_{A^+} - \mu^{0\,s}_{B^-} = RT\ln(a^s_{A^+}\cdot a^s_{B^-}) = RT\ln(k_{\mathrm{sp}}) \tag{19}$$

where k_{sp} is the solubility product. This means that we can drive the solubility of the whole compound in a solution by simply raising the concentration of just one of its ions. For example, if we place both $\mathrm{NaCl} + \mathrm{CaCl_2}$ in water, we can add more chloride to reduce solubility. Each of these compounds have their own solubility product. Note that charge neutrality has to be maintained: $[\mathrm{Na}^+] + [\mathrm{Ca}^{2+}] \times_2 = [\mathrm{Cl}^-]$. This is important because we can often mistakenly end up with precipitate.

Example $\mathrm{Cu}\,/\,\mathrm{Zn}\,/\,\mathrm{Zn}^{2+}\,,\mathrm{Cl}^-\,/\,\mathrm{AgCl}\,/\,\mathrm{Ag}\,/\,\mathrm{Cu}_r$. Here, the copper is just there to provide electron mobility. We can look at the electrons being transferred: $\mathrm{Zn} + 2\,\mathrm{AgCl} + 2\,\mathrm{e}^-\,(\mathrm{Cu}_r) \rightleftharpoons \mathrm{Zn}^{2+} + 2\,\mathrm{Ag} + 2\,\mathrm{Cl}^- + 2\,\mathrm{e}^-\,(\mathrm{Cu})$. We write down the electrochemical potentials:

$$\bar{\mu}^{\mathrm{Zn}}_{\mathrm{Zn}} + 2\cdot\bar{\mu}^{AgCl}_{\mathrm{AgCl}} + 2\bar{\mu}^{\mathrm{Cu_r}}_e = \bar{\mu}^s_{\mathrm{Zn}^{2+}} + 2\bar{\mu}^{\mathrm{Ag}}_{\mathrm{Ag}} + 2\bar{\mu}^s_{\mathrm{Cl}^-} + 2\bar{\mu}^{\mathrm{Cu}}_e$$

Here, we use the three special cases earlier about solids and electrons, which allows the simplification

$$2\bar{\mu}^{\mathrm{Cu_r}}_e - 2\bar{\mu}^{\mathrm{Cu}}_e = -2F(\phi^{\mathrm{Cu_r}} - \phi^{\mathrm{Cu}}) = -2F\cdot E$$

and this can be converted to... (see slides at this point, near the end)

The potentials of the ions in a solution must cancel out. The standard species potential can then be taken to yield

$$-2FE = -2FE^0 + RT\ln(a^s_{\mathrm{Zn}^{2+}}\cdot(a^s_{\mathrm{Cl}^-})^2)$$

which brings back the Nernst equation

$$E = E^0 - \frac{RT}{2F}\ln(a^s_{\mathrm{Zn}^{2+}}\cdot(a^s_{\mathrm{Cl}^-})^2).$$

Notice that the potential of the copper wire does not matter. Therefore, we can use any different metal to connect the electrodes.

Gauss Law is

$$q = \epsilon_0 \oint \varepsilon\,\mathrm{d}S \tag{20}$$

describes the electric field strength around a surface. When there is no current flowing on a conductive material, the electric field strength must be zero. Inside a conducting material, there can't be any electric field. If we apply a charge, then

the charges must reside on the surface. The surface, in actual practical since, is less than a nanometer. In semiconductors, that surface layer is less than a 100 nanometers depending on the doping level. In electrolytes, the charge carriers are less than 100 nanometers since the charge carriers are the ions. Re-read the Gaus part

Now, realistically, a metal may be surrounded by an electrolyte, so as the radius from the center increases, the electric potential changes; it changes drammatically at the interface. The $\epsilon \propto \nabla\phi$, so ϵ is massive at the interface; this gigantic electric field enables electrochemical reactions.

For molten salt with MH, the electrochemical and chemical potentials are identical, hence

$$\bar{\mu}^{\mathrm{MH}}_{\mathrm{MH}} = \bar{\mu}^{\mathrm{MH}}_{\mathrm{M^+}} + \bar{\mu}^{\mathrm{MH}}_{\mathrm{H^-}} = \mu^{\mathrm{MH}}_{\mathrm{M^+}} + \mu^{\mathrm{MH}}_{\mathrm{H^-}} = \mu^{\mathrm{MH}}_{\mathrm{MH}} \tag{21}$$

3 Ionic Conductance and Junction Potentials

An ideal non-polarizable electrode should be used at the reference electrode, such as Ag/AgCl. This is great because this electrode ensures that its species concentration in the solution remains unchanged. The electrolyte is to provide ionic transfer, which balances the charge. Electrolytes are electronically insulated. The measured voltage across the circuit is measured as

$$E = E_{\mathrm{rxn}} + iR_{\mathrm{total}} + E_j.$$

The E_j is the junction potential.

There are three electrode systems for difficult cases; this separates the voltage reference point and the current flow point. The reference electrode is a circuit with very high impedence. The current goes through the auxilary or counter electrode (CE). This type of circuit removes the iR contribution on the measured voltage. The CE does have iR contribution, but that is not measured.

We'll mainly look at two-electrode cells.

Electrolytes are often salts, acids, or bases with 0.1 to 1 molality. Examples: sodium chloride, calcium chloride, sodium sulfate, sulfuric acid, and sodium hydroxide. The pH is simply the log scale of the proton concentration

$$\mathrm{pH} = -\log[\mathrm{H^+}] = 14 - \log[\mathrm{OH^-}]. \tag{22}$$

Both ions move in these cases.

For non water solvent, something such as tetrabutylammonium perchlorate or $\mathrm{Li^+P_6{}^-}$. The latter is used in lithium-ion batteries. Water can accomodate about 1.24V; for lithium ion batteries, organic solvents are used to get the higher voltage.

There are solid electrolytes; these are single-ion electrolytes typically. Nafion is the standard membrane that separates fuel cell oxidizers: this is a poylmer with a negative charge, hence only allows proton conduction. Poly Ethylene Oxide (PEO) is typically neutral, and can be used to transfer ions for lithium

salts. There are ceramic materials for electrolytes such as yttria-stabilized-zirchonia which transfers oxygen. Electrodes in batteries are already solid; the electrolyte can be selected. YSZ is also used as oxygen sensors. Glasses can be cation conductors. Then there are molten salt and ionic liquids (ionic liquids are those that are liquid at room temperature unlike molten salts); every species in this is charged.

Our reference electrode typically is close to the reference electrode. For cases where we want to separate the anode and cathode side, a membrane holder would be used to hold a membrane, or a glass frit could be used. The working and reference electrode would be in one chamber. The membrane is common in fuel cells to keep hydrogen and oxygen gas separated. A salt bridge can literally be a tube literally bridging it.

Example: $\mathrm{Zn/Zn^{2+}}$,$\mathrm{Cu^{2+}}$ / Cu. Here, the zinc electrode and copper ion would directly react, hence a junction would be needed. The junction potential is

$$E = (\phi^{Cu'} - \phi^{\beta}) + (\phi^{\beta} - \phi^{\alpha}) + (\phi^{\alpha} - \phi^{Zn})$$

where the $\phi^{\beta} - \phi^{\alpha}$ is the junction potential. It is small, but for production it is a lot.

Suppose on the left side we have 0.01 M HCl and on right we have 0.1 M HCl. If the junction allowed ion transfer, there would be diffusion and they would equilibriate. Protons move faster than the chloride ions; this causes positive charge on the left side of the membrane, and negative charge on the right side of the electrode. This causes chlorine to catch up. The charge difference on either side of the membrane creates an electric field on the junction. This causes the junction potential. This example is a type 1 junction: separated on same electrolyte of different concentration.

Type 2 junction is one that separates same concentration, and one ion of them is identical.

Type 3 junctions are all other junctions and are more complicated to treat.

The resistance is the inverse of conductance, later being measured in siemers. Resistance is the resistivity multiplied with distance travelled over area, $R = \rho l/A$. The conductivity multiplied by the area over length, $L = \sigma \cdot A/l$. Therefore, $\sigma = 1/\rho$. Each species has its own conductivity. The conductivity in total is the sum of all the conductivities of a species that carries the charge.

The conductivity can also be defined as the mobility of the charged species given an applied field strength on the velocity, multiplied

$$k_i = u_i \cdot c_i \cdot |z_i| \cdot F \tag{23}$$

where $u_i = v_i/\epsilon$.

For a sphere, the drag force is given as

$$F_{\text{drag}} = 6\pi\eta r_i u_i \tag{24}$$

and the electric force is

$$F_{\text{el}} = |z_i| \cdot e \cdot \epsilon \tag{25}$$

This yields

$$u_i = \frac{v_i}{\epsilon} = \frac{|z_i|e}{6\pi\mu r} \tag{26}$$

Diffusion coefficients are used when discussing mobility, which brings us to the Stokes-Einstein equation:

$$D_i = \frac{k_B T}{6\pi\eta r_i} \tag{27}$$

where k_B is the Boltzman constant. This can also be rearranged as

$$u_i = \frac{|z_i| \cdot F \cdot D_i}{RT} \tag{28}$$

and this also yields the Nernst-Einstein equation

$$k_i = \frac{C_i D_i |z_i|^2 F^2}{RT} \tag{29}$$

Notice that charge quadratically increases the conductivity. The charge equivalent concentration is the charge of the species multiplied with their concentration.

$$\frac{k}{C_{eq}} = \Lambda = \frac{k_+}{C_{eq}} + \frac{k_-}{C_{eq}} = \lambda_+ + \lambda_- \tag{30}$$

After a certain concentration, solutes start interacting weath other and binding. To get more conductivity, one way is to get a highly soluble compound, and get one with higher equivalent conductivity. This also yields $\lambda_\pm = F \cdot u_\pm$, and $\Lambda = F(u_+ + u_-)$.

The proton has incredibly high mobility and conductivity equivalent; this is also true for hydroxide (which is interesting because the latter is 17 times heavier). This makes water very special, where each protons can hop, and also the hydroxide. Interestingly, lithium is super low for conductivity. This is because of the solvation shell. There will be water molecules encapsulating the lithium; the whole thing will travel. This generates a larger *hydrodynamic* radius: the apparant radius that the ion has based on its mobility. Also, lithium attracts more ions than sodium and potassium, hence lithium's solvation shell is much bigger.

For the halides, they have effectively identical hydrodynamic radius. An iron cyanide hexagonal complex just moves on its own.

The transference number is the fraction of the charge that the cation or anion carries. This is given as

$$t_i = \frac{k_i}{k} \tag{31}$$

where i is the particular ion. The transference number of all of the ions should yield 1. We can rewrite this as

$$t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j \cdot C_j} = \frac{u_i}{\sum_j u_j} \tag{32}$$

Example. $\mathrm{Pt}\,/\,\mathrm{H_2}\,/\,\mathrm{H^+}$ 0.1 M ,$\mathrm{Cl^-}\,/\,\mathrm{H^+}$ 1 M, $\mathrm{Cl^-}\,/\,\mathrm{H_2}\,/\,\mathrm{Pt}$. Here, the half reactions are the same, except that the concentration is different, hence there is an oxidation side and a reduction side. The redox potential is

$$E_{\text{red/ox}} = E^0 - \frac{RT}{nF} \ln\left(\frac{1}{a_{\mathrm{H^+}}^2}\right)$$

and the voltage measured is just the difference. For every 5 electrons, there are 5 moles of protons and 2.5 moles of hydrogen being transferred. Now, if the transference of the hydrogen is 0.8 and chlorine is 0.2, then 1 hydrogen/chlorine ion pain would get transferred for every 5 moles of electron. For these type 1 junctions (where we have identical electrolysis but different concentrations), the junction potential is

$$E_j = (t_+ - t_-)\frac{RT}{F} \ln\left(\frac{a_\alpha}{a_\beta}\right). \tag{33}$$

For type 2 junctions, there is the Lewis-Sargent Relation

$$E_j = \pm\frac{RT}{F} \ln\left(\frac{\Lambda_\beta}{\Lambda_\alpha}\right) \tag{34}$$

Two ways to reduce the junction potential for type 1 is to either make the concentration be similar (which defeats the point of the cell), or making the cation and anion have similar transference numbers.

For type 2, junction potential can be made 0 by making the conductance be identical for both sides only.

For both type 1 and type 2 scenarios, a salt bridge can simply override this. A salt bridge creates two junctions which cancels each other. The first junction has the equal and opposite potential of the second, hence there is cancellation. The magnitude of this potential is dominated by the phase with the largest concentration. The concentration of the salt bridge must be much higher than both electrolyte concentrations. This works in practice, especially with higher concentration: this stops at 1 mV, which is the point where we would not care.

Single ion exchangers are materials that only allow one ionic species to move. For example, cation exchange membrane, which allows cations to move; anion exchange membrane, which allows anions to move only.

For example, for a CEM with left side having higher concentration, the positive ions will move to the right. This charge difference creates an electric field. This is done in, for example, an oxygen sensor, where movement of a known oxygen ion concentration creates a voltage drop. Same is true for pH sensors that use a glass membrane doped with sodium and calcium.

4 Electrode Kinetics

In electrochemistry, current can be used to determine the rate of a reaction, given in coulombs per second. Q denotes charge. Charge of 1 mole of electrons is the Faraday constant. Converting this into the consumption of hydrogen for

example, we have a rate. Consumption of hydrogen is the measure of current for the moles of electrons given based on the reaction. In general, if n is the number of moles of electrons and i is the current:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{i}{n \cdot F} \tag{35}$$

The voltage is proportional to this. The rate of electron transfer is dependent on several things, one of them being the charge transfer process: transferring electron from electrode to active species. This is commonly called charge transfer kinetics. There's also an effect of mass transfer, particularly on the surface. The concentration at the surface drops due to conversion of active species, and diffusion $\partial_N = -D\frac{\partial c}{\partial x}$ brings in new fresh species. These processes of mass transfer, chemical reaction, charge transfer, have an inherent resistance. The potential drop due to these resistances is

$$i(R_{\mathrm{ct}} + R_{\mathrm{rxn}} + R_{\mathrm{MT}}$$

which allows us to calculate the over potential:

$$\Delta E_{\mathrm{ct}} + \Delta E_{\mathrm{rxn}} + \delta E_{\mathrm{MT}} \tag{36}$$

Note that this *only* happens if there is current flow. Consequently, sensors are often unaffected since they measure voltage, but is important for fuel cells.

In lithium ion batteries, there's a mass transfer associated with the solid state in the graphite, then a charge transfer at the electrode, then a liquid electrolyte mass transfer, and more. Consequently, voltage from battery is lower while current is being drawn.

In electrode kinetics, let there be a rate constant k_f for A to B, and k_b for the reverse. The rate is $v_f = k_f \cdot [A]$ and $v_b = k_b \cdot [B]$. The rate constant is given as

$$k = A \exp\left(-\frac{E_A}{RT}\right). \tag{37}$$

The reaction is at equilibrium when the conversion processes happen at the same rate. The net reaction rate is $v_{\mathrm{net}} = v_f - v_b$. At equilibrium, this is zero.

In Chemistry, we look at the activation energy: the difference in energy between the transition state and the base state, described as $\Delta G^{\ddagger}$:

$$k = A \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{38}$$

The difference between transition state energy is

$$\Delta G^{0}_{\mathrm{rxn}} = \Delta G^{\ddagger}_{b} - \Delta G^{\ddagger}_{f} \tag{39}$$

and now can be used to yield

$$\frac{k_b}{k_f} \exp\left(-\frac{\Delta G^{0}_{\mathrm{rxn}}}{RT}\right) = \frac{[A]}{[B]} = k_{\mathrm{eq}} \tag{40}$$

In electrochemistry, we have oxidation or reduction which can be forward or backward; oxidation is anodic direction, and reduction is cathodic direction. The actual reactions happen at the electrode surface.

c is the concentration, and subscript would denote the species oxidization or reduction.

$$v_f = k_f \cdot c_o(x=0,t) = \frac{i_c}{n \cdot F \cdot A} \tag{41}$$

where i_c is cathodic current, and we normalize this to the surface area. The backward reaction is, similarly, $v_b = k_b \cdot c_r(x=0,t) = \frac{i_a}{n \cdot F \cdot A}$. Both forward and backward are happening at the same time in equilibrium, and what we measure is the net.

$$v_{\text{net}} = v_f - v_b = \frac{i}{n \cdot F \cdot A} \tag{42}$$

We can only measure the net current

$$i = i_c - i_a = n \cdot F \cdot A(k_f c_o(0,t) - k_b c_r(0,t)) \tag{43}$$

We can measure and control voltage, and current is related to this. If we have an arbitrary equation $\mathrm{O} + \mathrm{e}^- \overset{\text{red}}{\rightleftharpoons} \mathrm{R}$.

The energy level of an electron in metals is given as the Fermi level. The electrode's electron has a higher Fermi level with negative potential, or lower using positive potential. If the potential goes beyond the potential of the species, electron transfer happens. A positive potential lowers the graph in 'Applied Potential vs Energy States and Barriers' graph. This creates a difference in the $\Delta G^\ddagger$ between anodic and cathodic directions, and consequently makes the v_{net} be on-zero. Applying positive potential to the cathode lowers the anode's free energy and reaction coordinate curve, which creates a bigger $\Delta G_c^\ddagger$, which drives the reaction more in the anodic reaction.

The transition state energy change is given as

$$(1-\alpha) \times -F(E - E^0) \tag{44}$$

where E is the applied potential and E^0 is the standard potential, assuming positives. α is the transfer coefficient between 0 and 1. See the slides for this one!

$$\Delta G_a^\ddagger = \Delta G_{o,a}^\ddagger - (1-\alpha) \cdot F(E - E^0) \tag{45}$$

and

$$\Delta G_c^\ddagger = \Delta G_{o,c}^\ddagger + \alpha \cdot F(E - E^0) \tag{46}$$

The new forward rate constant, when a potential is applied, is

$$k_f = \underbrace{A_f \exp\left(-\frac{\Delta G_{0,c}^\ddagger}{RT}\right)}_{k^0} \cdot \exp\left(-\alpha \frac{F}{RT}(E - E^0)\right) \tag{47}$$

where k^0 is the standard rate constant. Similarly,

$$k_b = \underbrace{A_b \exp\left(-\frac{\Delta G^{\ddagger}_{0,a}}{RT}\right)}_{k^0} \cdot \exp\left((1-\alpha)\frac{F}{RT}(E-E^0)\right) \tag{48}$$

Note that

$$f = \frac{F}{RT}. \tag{49}$$

We can now write the current, again, in a different way:

$$\boxed{i = F \cdot A \cdot k^0 \left[c_0(0,t)\exp(-\alpha f(E-E^0)) - c_r(0,t)\exp((1-\alpha)f(E-E^0))\right]} \tag{50}$$

This is the Butler-Volmer equation that connects current to the applied potential; everything else is a feature of the reaction. This inherently also includes mass transport if it is already included in $c_\square$.

When the slope of the free energy and reaction coordinate curve is the same, then $\alpha = 0.5$. Typically, most reactions are $0.3 \leq \alpha \leq 0.7$. If it is unknown, start with assuming that $\alpha = 0.5$. Mass transfer often dominates, so experimentally hard to find. For large applied potential, α does not change.

If there's no current flowing, the surface has homogenous concentration, and we can use the bulk concentration. This allows us to get

$$\frac{C_o^*}{C_r^*} = \exp\left(\frac{F}{RT}(E_{\text{eq}} - E^0)\right) \tag{51}$$

The equilibrium potential measured is different from standard conditions, and is given by the Nernst equation. Hence, rewriting this as the Nernst equation, we have

$$E_{\text{eq}} = E^0 - \frac{RT}{nF}\ln\left(\frac{C_r^*}{C_o^*}\right) \tag{52}$$

The current is zero when the exchange current is identical for forward and backtward. Combining this with Nernst, we get the exchange current to be

$$i_0 = F \cdot A \cdot k^0 \cdot {C_o^*}^{1-\alpha} \cdot {C_r^*}^{\alpha} \tag{53}$$

The standard rate constant k^0 can vary from $\times 10^{-1}$ and $\times 10^{-9}$. The exchange current density is simply

$$j_0 = \frac{i_0}{A}. \tag{54}$$

Again re-writing the Nernst

$$\left(\frac{{C_o^*}^{\alpha}}{C_r^*}\right) = \exp(\alpha f(E_{eq} - E^0)) \tag{55}$$

we can find the measured current to be

$$i = i_0\left[\frac{C_o(0,t)}{C_o^*}\exp(-\alpha f\eta) - \frac{C_r(0,t)}{C_r^*}\exp((1-\alpha)f\eta)\right] \tag{56}$$

where $\eta = E - E_{eq}$ is the overpotential. This only works if the concentration of either is *not* zero.

Negative over potential is reduction direction (?).

A very high α or very low one would make this be like a diode.

For homework, consider what could happen based on what is there. This includes water. For question 1. Use the first page. Sort the standard potentials in any order. Then, in increasing voltage, see which happens such that all the species make sense.

For question 2, use Nernst when concentration is different.

5 Electrode Kinetics, Intro to Mass Transfer

The Butler-Volmer equation takes place at the electrode surface region. Electrode kinetics is more commonly known as charge-transfer kinetics. Mass transfer (MT) part is typically done via diffusion, though convection and migration can also take place.

The Butler-Volmer assumes a certain energy threshold to cross. There is an ahrenius equation

$$K = A \exp(-\frac{E_a}{RT})$$

If the barrier is same both ways in direction, i.e., k_f and k_b are same, then it is at equilibrium. Applying a positive potential lowers the potential at the cathod*ic* direction. The difference in Gibbs free energy as a result of lowering the potential is

$$\Delta G_c = n \cdot F \cdot (E - E^0)$$

This only changes the energy on one side. This makes the activation energy higher, hence forward reaction is less likely, but backward is easier. For $\alpha = 0.5$, half the ΔG_c is used to increase forward reaction difficulty, and half to increase backward reaction ease.

The forward and backward reactions are given as

$$k_f = k^0 \exp\left(-\alpha \frac{F}{RT}(E - E_0)\right)$$
$$k_b = k^0 \exp\left((1-\alpha) \frac{F}{RT}(E - E_0)\right)$$

where k^0 is the standard rate constant. This is the same in both directions because the pre-factor is the frequency of attempts needed to overcome the energy barrier.

The first exponent term controls the cathodic current (higher is more cathodic current), and the latter controls anodic current (higher is more anodic current). These surface concentrations impacts the mass transfer effect. The mass transfer is present through the concentration terms.

If the overpotential is zero $\eta = 0$, then the system is at equilibrium, and there should be no net current.

The exchange current is given as

$$i_0 = n \cdot FAk^0 \cdot C_0^{*(1-\alpha)} C_R^{\alpha} \tag{57}$$

At equilibrium, the bulk and surface concentration are identical. There is no over-potential if the product or reactant is missing; then we'd just use regular rate equation.

For systems without mass transfer effect, the $C_x(0,t)/C_x^*$ term is simply 1.

When $|\eta|$ is large, just the anodic or cathodic will dominate; however, in the center, both are in effect. The smaller k^0 is, the smaller j_0 is. There is also relationship with bulk concentrations. The see appreciable current, a lot of over potential has to be applied, unless there is high concentration of the species.

If we had hydrogen fuel cell extracting energy, then we have to pay a huge voltage penalty if j_0 is low; similarly, with j_0 low, a lot more energy has to be applied to supply energy. j_0 is too low without platinum for hydrogen fuel cells, that's why platinum is used.

If x is small, then $\exp(x)$ can be linearized as $1 + x$. This allows us to get the linear relationship for small η:

$$i = -\frac{i_0 F}{RT}\eta \tag{58}$$

which is practically Ohms law:

$$R_{ct} = \frac{RT}{Fi_0}. \tag{59}$$

The slope of a j vs η graph basically describes the $-j_0F/(RT)$. This is for a very small η!

If we had a very large overpotential, e.g. a very cathodic $\eta << 0$, then the anodic direction goes to 0, but cathodic contribution to the current is much higher, and all the current measured is cathodic. The opposite is also true. The natural log of, say, the cathodic current is

$$\ln(i_c) = \ln(i_0) - \frac{\alpha F}{RT} \cdot \eta. \tag{60}$$

Before Butler-Volmer, it was descovered empirically that

$$\eta = a + b\log(i).$$

The point where $i_a/i_c \leq 1\%$ is given as

$$\frac{\exp((1-\alpha)f\eta)}{\exp(-\alpha f\eta)} = \exp(f\eta) \leq 0.01 \tag{61}$$

In many old school texts, regular log10 was used, and consequently, a factor of 2.3 is used. For very negative over potentials, we get Tafel plots given with the equation

$$\log(|i|) = \log(i_0) + \frac{(1-\alpha)F}{2.3RT}\eta. \tag{62}$$

The standard rate current can be obtained by extending the slope. As Butler-Volmer gets into large overpotential regimes, we get the Tafel plots.

To empirically obtain α, we need to measure i_0 for different bulk concentrations of anodic and cathodic species. This has to be done for small overpotentials and is weirdly known as *electrochemically quasi-reversible*. Alternatively, high overpotentials can be done for small currents; this is weirdly known as *electrochemically irreversible*. For very fast reactions, with high currents, where we run risks of mass transfer issues, we have $i/i_0 \approx 0$, we get the equation

$$\frac{C_0(0,t)}{C_R(0,t)} = \frac{C_0^*}{C_R^*} \exp\left(\frac{F}{RT}\eta\right). \tag{63}$$

which yields a different type of Nernst equation:

$$E = E^0 + \frac{RT}{F} \ln\left(\frac{C_0(0,t)}{C_R(0,t)}\right). \tag{64}$$

which is for surface concentrations.

Manganese can have valence from 0 to 7, hence it is fun to play with in chemistry and electro-chemistry. When mass transfer can't keep up due to charge transfer kinetics becoming very large, we hit the limiting current; this is the mass transfer regime. Mass transfer limit is due to consumed species not diffusing into the electrode fast enough. At a certain point, the concentration at the surface reaches 0 for the stuff being consumed, and consequently, we hit a limiting current. This yields

$$\frac{\mathrm{d}N}{\mathrm{d}t} = v_{rxn} = \frac{i}{nFA}\alpha v_{MT} \tag{65}$$

where v_{MT} generates the limit. The mass transfer flux is given as

$$J_i(x) = \underbrace{-D_i\frac{\partial C_i}{\partial x}}_{\text{diffusion}} - \underbrace{\frac{z_i F}{RT}}_{\text{charge}} D_i C_i \underbrace{\frac{\partial \phi(x)}{\partial x}}_{\text{electric field}} + \underbrace{C_i v(x)}_{\text{velocity}} \tag{66}$$

which is diffusion, migration, and convections' summation. When migration and convection are absent, we have Fick's law

$$v_{\mathrm{MT}} = -D_O \frac{\mathrm{d}C_0}{\mathrm{d}x}\Big|_{x=0} \tag{67}$$

where D_0 is diffusion coefficient. The distance between the intersection of v_{MT} slope line and flat concentration line, and the $x = 0$ position, is the diffusion layer thickness δ_0. This enables us to re-write equation 67 as

$$v_{\mathrm{MT}} = D_O \frac{C_O^* - C_O(x=0)}{\delta_O} \tag{68}$$

where $\frac{D_O}{\delta_O} = m_o \approxeq$ the mass transfer coefficient. For 0 concentration at the surface, we simply get

$$v_{\mathrm{MT}} = m_O \cdot C_O^*. \tag{69}$$

Hence, the mass transfer limiting current (cathodic) is approximately

$$i_e = n \cdot F \cdot A \cdot m_O \cdot C_O^*. \tag{70}$$

As usual, we get another Nernst equation based on the limiting current

$$E = E^0 - \frac{RT}{nF} \ln\left(\frac{m_O}{m_R}\right) + \frac{RT}{nF} \ln\left(\frac{i_{l,c} - i}{i - i_{l,a}}\right) \tag{71}$$

where i is the measured current, and i_l is the limiting current. This allows us to re-write the Butler-Volmer equation including the mass transfer limit:

$$i = i_0 \left(1 - \frac{i}{i_l}\right) [\exp(-\alpha f \eta) - \exp((1-\alpha) f \eta)] \tag{72}$$

If we have small i_0, i.e., we hit the mass transfer limit earlier. For very fast reactions, Tafel doesn't work as a result.

Platinum is used in NHE because it is a catalyst. Anodic and cathodic currents don't transfer anything overall, so no natural losses. Reaction coordinate = is saying the path being proximity to the surface; if i was the molecule, and I was the flat part, I'd have same energy. When I'm close to the electrode, only then can we have reaction. Ideal gas appears because it is molecular thermodynamics. Naught $\square_0$ simply indicates fundamental.

6 BV, Tafel, Linear Approx and MT

Midterm will be on 3/24.

Diffusion is the main mass transfer form. The current that we measure has to equal to the rate of mass transfer when at maximum. The charge transfer component is nearly instantaneous. The mass transfer coefficient is given by

$$m_o = \frac{D_o}{\delta_o} \tag{73}$$

where D_o is dependent on the species, but δ_o can be adjusted by having flow over the surface. The easiest way is rotating disc electrode. The limiting current can be increased by increasing the MT coefficient, or increasing bulk concentration and surface area.

The surface concentration is difficult to measure, but current is easy, and can be used to find the concentration from the Butler-Volmer equation. The slower charge transfer is, the more wavy the i/i_l vs. η curve is, where it takes time to reach the threshold. Mass transfer becomes important when the slope of the i/i_l begins decreasing.

The higher the j_0 there is, the faster the current transfer. Smaller j_0 leads to a longer linear regime in the Tafel plot. If charge transfer is too high, the concentration can be increased to raise the MT. The potential can be written as

$$\eta = \frac{RT}{\alpha F} \ln\frac{i_0}{i_{l,c}} + \frac{RT}{\alpha F} \ln\frac{i_{l,c} - i}{i} \tag{74}$$

iand can plot the log plot of $(i_{l,c}-i)/i$ vs. η on the x-axis. This creates a linear regime in a plot, and can be used if MT complicates Tafel.

For small overpotentials, the current-potential is linear.

For very fast reactions, resistance terms can be used to get

$$\eta = if\left(\frac{1}{i_0}+\frac{1}{i_{l,c}}-\frac{1}{i_{l,a}}\right) \tag{75}$$

Notice that the charge transfer resistance is $R_{\text{CT}} = f/i_O$ and mass transfer resistance is $R_{\text{MT}} = f/i_l$.

The limiting current, in a current-overpotential graph, can be found by looking at when the current becomes steady. The exchange current density, j_0 is found by taking the slope of a Tafel plot, and seeing where the line intersects the j axis.

In a half cell involving $\text{Pt} \,/\, \text{Fe(CN)}_6{}^{-3}\,(2.0\,\text{mM}), \text{Fe(CN)}_6{}^{-4}\,(2.0\,\text{mM}), \text{NaCl}\,(1.0\,\text{M})$ the net electron transfer is 1, since it only occurs between the iron ions. Thi particular system is very reversible.

We can compare the linear equations and the full Butler-Volmer equation to see the error. At low overpotentials, linear equations and Butler-Volmer without MT works great. With slightly higher overpotentials, linear is iffy, Tafel doesn't work, and Butler-Volmer without MT still works. At higher overpotentials, lenar completely fails, Tafel works, and Butler-Volmer without MT works. However, at limiting currents, none works. Only the full Butler-Volmer equation is viable.

Diffusion can never be turned off. Migration can be turned off by removing charged species. Removing convection is easier by not using fluids. Now, we will consider migration and diffusion in the flux. Looking at it in one-direction, we have

$$J_i(x) = -D_i\frac{\partial C_i}{\partial x} - \frac{z_iF}{RT}D_iC_i\frac{\partial \phi(x)}{\partial x}. \tag{76}$$

When charged species move, there is current flow. We need current to flow from one electrode to the other, inside the cell. For charged species, we have

$$i_i = \underbrace{z_iFAD_i\frac{\partial C_i}{\partial x}}_{\text{diffusion}} + \underbrace{\frac{z_i^2F^2A}{RT}D_iC_i\frac{\partial \phi}{\partial x}}_{\text{migration}}. \tag{77}$$

This equation is usable for an uncharged species as well, since the z_i for the uncharged species i is simply zero. The net current is the net charge transfer of all species.

The simplest case, the volta example, has a copper electrode that is being reduced on one side. Here, copper ions deposit on the surface. Another example is copper cyanide ion plating as copper and depositing cyanide ions. The initial ion could be net charged or uncharged.. In these cases, copper diffuses into the electrode, in all cases. For the first, migration happens into the surface, since copper ion in the solution is attracted to the reduction electrode. For copper cyanide $\text{Cu(CN)}_4{}^{2-}$, this migrates away from the cathode since the cathode is

negatively charged. In the case of $Cu(CN)_2$, there is no charge and hence no migration.

As a thought experiment to understand migration vs diffusion. In a case of electrolyzing hydrogen and chlorine ions, the $t_+ = 0.8 = 4 \cdot t_-$. Here, protons move 4 times faster. The re-shufflying is done via migration. By migration, 8 protons move from anode to cathode, and 2 chlorine ions move from cathode to anode. Notice the error with this: there's more hydrogen ion than chlorine ion on the left. Diffusion causes the remainder of the ions to flow. For H^+, $i_{d,H^+} = 2$, and $i_{m,H^+} = 8$. For chlorine, it is $i_{d,Cl^-} = 8$ and i_{m,Cl^-}.

Finding the cransference number of species i in a system involving $Cu(NH_3)_4Cl_2, Cu(NH_3)_2Cl$ is

$$t_{i^+} = \frac{n_i \cdot [i]}{\sum_j n_j [j]} \tag{78}$$

and this would yield a transference number of

$$t_{Cu^{2+}} = \frac{1}{3} \qquad\qquad t_{Cu^{1+}} = \frac{1}{6} t_{Cl^-} = \frac{1}{2}$$

Diffusion covers the rest. Adding $NaClO_4$ in high concentrations forces the copper ions to move by diffusion instead of migration; the $NaClO_4$ is the primary contributor to migration. This *supporting electrolyte* should be inert.

7 Diffusion MT and Potential Step

Paper submission 3 days before presentation. Presentation starts April 16th. 3 pages of text excluding figures and references. Presentation is 12 minutes, followed by question and answer. The content needed in the paper/presentation is

- Motivation—the why?
- General concept—how does it work?
- Challenges—what are the problems?
- One solution/analysis from papers
- Conclusion—where do you see it go?

We should have 1 or 2 research paper that talks about this matter.

In general, in electrochemistry, everything is time dependent. The limiting current includes m_O or m_R, for example, which depends on the diffusion coefficient divided by the boundary layer thickness; these could be steady state, or have time dependence. Typically, bulk features and intrinsic properties don't change too much, but the boundary layer thickness often does change with time.

Mass transfer may not have migration effects if there are supporting electrolytes, which have much higher concentration, which move instead of the active species. Another case for ignoring migration is if the species is neutral.

The δ is distance from electrode to outward until the concentration nears the bulk. The concentration change w.r.t. time is

$$\frac{\partial C(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} = \frac{\partial}{\partial x}\left(D \cdot \frac{\partial C(x,t)}{\partial x}\right) \tag{79}$$

where D typically doesn't change with space for dilute systems, but can for highly concentrated systems. This yields Fick's second law

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} \tag{80}$$

which has to be fulfilled if diffusion is the only mode of transportation of species.

The equation is written differently depending on geometry. Over a 100 years ago, Chemists loved mercury because they could be dropped as spheres and we'd get new electrode. These are typically not used, but UMEs is present in some systems.

Plugging Fick's law for a 1D case where we have the equation

$$i(t) = nFAJ_O(x=0,t)$$

we get

$$i(t) = -n \cdot F \cdot A \cdot D \frac{\partial C_O(t)}{\partial x}\Big|_{x=0} \tag{81}$$

which can be used to know how our current changes with concentration. 1 initial condition and 2 boundary conditions are needed to solve equation 80. These are typically $C_O(x, t=0) = C_O^*$ or 0 if we did not start with this species (for time); for space, it is $\lim_{x\to\infty} C_O(x,t) = C_O^*$, and the surface concentration. The latter is done by controlling the potential. Remember that $\exp(-nf\eta) = \frac{C_O(0,t)}{C_R(0,t)}$. For a large η, the concentration at the surface is 0. Another is to apply a known current, which yields the condition

$$J_O = \frac{i}{nFA} = -D_O \frac{\partial C_O(x,t)}{\partial x}\Big|_{x=0} \tag{82}$$

Fick's 2nd Law of Diffusion 80 can be solved using a Laplace transform. This yields:

$$-C^* + s \cdot \bar{C}(x,s) = D_i \frac{\partial^2 \bar{C}(x,s)}{\partial x^2}$$

which is simplified to

$$\frac{\partial^2 \bar{C}(x,s)}{\partial x^2} - \frac{s}{D}\bar{C}(x,s) = -\frac{C^*}{D}$$

which is just an ODE. Note that $\bar{C}(x,s)$ is the Laplace transform of $C(x,t)$. We can Laplace transform another Laplace transform to make it even easier to solve, and then transform back. By writing this as

$$\boxed{\bar{C}(x,s) = \frac{C^*}{s} + Aexp\left(-\left(\frac{s}{D}\right)^{1/2} x\right)} + \cancel{B\exp\left(x\sqrt{\frac{s}{D}}\right)} \tag{83}$$

where now we can apply the boundary condition $\lim_{x\to\infty}\bar{C}(x,s) = \frac{C^*}{s}$. To satisfy this condition, $B = 0$ otherwise it would blow up. This is the reason for framing the former part of the above equation. It is known as the 'universal solution' for 1D diffusion to the surface. Taking $\bar{C}(0,s) = 0 = \frac{C^*}{s} + A$ yields the equation

$$\bar{C}(x,s) = \frac{C^*}{s} - \frac{C^*}{s}\exp\left(-x\sqrt{\frac{s}{D}}\right).$$

This yields the solution

$$C(x,t) = C^*\text{erf}\left(\frac{x}{2\sqrt{D\cdot t}}\right) \tag{84}$$

The error function enables us to decide the δ , typically when the argument $z = 1$ or 2 for $\text{erf}(z)$. This allows us to have an equation for the boundary layer thickness:

$$\delta = 2z\sqrt{D\cdot t} \tag{85}$$

A typical value for small ions is $D = 1\times 10^{-5}\ \frac{\text{m}^2}{\text{s}}$.

Whole primary cell of a battery is typically 150 microns, whereas aqueous electrolytes have much larger boundary layer.

Current w.r.t. time is given by the Cottrell Equation

$$i(t) = nFAC^*\sqrt{\frac{D}{\pi t}} \tag{86}$$

Cotrell made a lot of money by making the electrostatic precipitator, which helped reduce pollution. He used that money to fund more research. Without convection, the current goes to 0. With convection, we reach a steady state. Note that, in almost all cases, there is still convection. Convection creates a constant boundary layer. As a result, Cotrell says that $\lim_{x\to\infty}C(x,t) = C^*$, but convection causes $C(x_c,t) = C^*$.

8 Potential Steps at UMEs, Quasi-/Irreversible Systems

We should add notes to the equation sheet to help us understand which is used in what. Homework is due on 3/6.

The lecture 9 video covers reversible systems. We'll now do lecture 10. We usually have to pick sampling time. $i_d(t)$ is the maximum current draw that mass transfer allows us. We typically look for $E_{1/2}$ which is where $i_d/2$ happens. When doing these, we typically assume that reduced species is non-existent, though this may not always be the case. For reversible planar system, equation for applied potential (we can control this variable) is

$$E = E^{0'} + \frac{RT}{nF}\ln\left(\frac{C_O(0,t)}{C_R(0,t)}\right) \tag{87}$$

and the concentration w.r.t. time and space is given as

$$C_O(x,t) = C_O^* - \frac{C_O^*}{1+\xi\theta}\text{erfc}\left(\frac{x}{2(D_O t)^{1/2}}\right) \tag{88}$$

and the current is

$$i(t) = \frac{nFAC_O^*}{(1+\xi\theta)} \cdot \sqrt{\frac{D_O}{\pi t}} = \frac{i_d(t)}{1+\xi\theta} \tag{89}$$

and notice that the equation does not have time in the middle part, but it is secretly tucked away in

$$\theta = \frac{C_O(0,t)}{C_R(0,t)}. \tag{90}$$

The half-wave potential is

$$E_{1/2} = E^{0'} + \frac{RT}{nF}\ln\xi^{-1} = E^{0'} + 29.6\,\text{mV} \times \log\left(\frac{D_R}{D_O}\right) \;\; s.t.\; \xi = \sqrt{\frac{D_O}{D_R}}. \tag{91}$$

Reversible, in these cases, means having high electrode kinetics. Typically, something is reversible if the wave slope is greater than 59.1 mV.

When no reduction agent exists, the current is only positive. $E_{1/2}$ is not when reaction starts happening; in fact, reaction happens much earlier.

when we have semi-infinite spheres as the electrodes, the equation now has a non-time-dependent component:

$$i_d(t) = nFADC^*\left[\frac{1}{\sqrt{\pi Dt}} + \frac{1}{r_0}\right] = i_{d,planar} + \frac{nFADC^*}{r_0} \tag{92}$$

This was common for early mercury electrodes. However, now that is not used. Nonetheless, ultra micro electrodes (UMEs) have similar properties, but require an additional correction factor.

$$i_{ss} = 4nFD_O C_O^* r_O. \tag{93}$$

The time range for semi-infinite diffusion on disk UME is

$$\tau = \frac{4Dt}{r_0^2} = frac\delta^2 L_c^2 \tag{94}$$

where δ is the boundary layer.

In laplace transform, s is a type of frequency. The laplace transform of the current w.r.t. time for semi-infinite spherical diffusion indicates the competing contrast between radius vs diffusion boundary layer thickness. For small times, we have $\gamma = 1/\xi$ in the equation

$$\bar{i}(s) = \frac{nFAD_O C_O^*}{1+\xi^2\gamma\theta}\left(\frac{1+r_O\sqrt{s/D_O}}{r_O s}\right) \;\; s.t.\; \gamma = \frac{1+r_O\sqrt{s/D_O}}{1+r_O\sqrt{s/D_R}} \tag{95}$$

9 Double Layer

Ions added to solution to reduce resistance. Now, when charge is applied, charge accumulates on the electrode; say negative on metal. Then, in the solution, positive charges accumulate close to the electrode, and negative are pushed away. If there's no transfer of charge (i.e. no reduction), the collection of ions still happen. This acts like a capacitor since there's separation of ions. The capacitance is characterized by charge per aplied voltage:

$$C = \frac{q}{E}$$

where the unit is farads. It is inversely proportional to distance, and proportional to surface area. Electrochemical capacitors make great super capacitors because you can have very high surface area. We can get *orders of magnitude* capacitance than regular plate capacitors.

Most ions are surrounded by other ions; lithium cations for example has a large solvation cell. The charged surface electrode itself will also have a layer of inner Helmholtz plane: region where there is mostly ions that belong to the solvent. Then there's the outer Helmholtz plane, which is where the larger solvation shell cations exist. Some really large anion can be adsorbed to a negatively charged surface, such as iodide.

The electrostatic potential has a trend: in the bulk, there's no change in potential or electric field; charge would move around to cancel it. In the interfacial region, there must be a continuous transition field. As a circuit, we have

$$E = E_R + E_C = \underbrace{i \cdot R_s}_{\frac{\mathrm{d}q}{\mathrm{d}t}} + \frac{q}{C_d}$$

where we have

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{EC_d - q}{R_s C_d}$$

and by integrating

$$\int_0^q \frac{\mathrm{d}q}{EC_d - q} = \frac{1}{R_s E}\int_0^t \mathrm{d}t \Rightarrow \ln\left(\frac{EC_d - q}{EC_d}\right) = -\frac{t}{R_s C_d} \Rightarrow q = EC_d(1-\exp(-t/R_s C_d))$$

and the current is

$$i(t) = \frac{\mathrm{d}q}{\mathrm{d}t} = \frac{E}{R_s}\exp\left(-\frac{t}{\tau}\right) \tag{96}$$

where $\tau = R_s C_d$. Note that typically resistance for electrochemistry is about 10 Ohms.

A sweep potential is given as

$$E = v \cdot t \tag{97}$$

where v is sweep rate in this case. Given a sweeping potential, the current is

$$\begin{aligned} v \cdot t &= \frac{\mathrm{d}q}{\mathrm{d}t} R_s + \frac{q}{C_d} \\ i &= vC_d \left[1 - \exp\left(-\frac{t}{R_s C_d} \right) \right] \end{aligned}$$

where, at steady state, we have $i_{ss} = v \cdot C_d$ is capacitive current for unit area. Typically, cycles of these are performed, and is called cyclic (sweep) voltametry. This can be used to draw a current-potential graph.

There is a pure bulk α and pure bulk β region formed on left and right sides.The σ is the surface excess of species i. There's an excess of soap molecules at the oil and water layer. In electrochemistry, there's an excess of positive charge on one, negative on other.

$$n_i^\sigma = n_i^S - n_i^R$$

where S is surface or interfacial zone, and R is the bulk. There's a lot of interface areas when we shake bottle of oil and water; it's not happy and want to combined and divide. This is because interfacial areas contribute to higher Gibbs free energy of the system.

Change of Gibbs free energy with amount of species present is the electrochemical potential of a species. The electrochemical potential must be same in all points of contact, but the *amount* of the species must be different. To make electrochemical potential same everywhere, the product of potential and amount of ions should add up to be the same.

Surface energy, or surface tension, is

$$\gamma = \frac{\partial \bar{G}}{\partial A} \tag{98}$$

and allows us to write surface excess equation as

$$\mathrm{d}\bar{G}^\sigma = \mathrm{d}\bar{G}^S - \mathrm{d}\bar{G}^R = \gamma \cdot \mathrm{d}A + \sum_i \bar{\mu}_i \cdot \mathrm{d}n_i^\sigma .$$

Slide 10 of lecture 11 then shows Gibb's Adsorption Isotherm:

$$-d\gamma = \sum \Gamma_i \, \mathrm{d}\bar{\mu}_i \tag{99}$$

We know how to measure surface tension of liquids, and so mercury is nice. Its surface tension changes with applied potential.

The electrocapillary equation is

$$-\mathrm{d}\gamma = \sigma^M \, \mathrm{d}E_- + \Gamma_{K^+\mathrm{H_2O}} \, \mathrm{d}\mu_{\mathrm{H_2O}} \, \mathrm{d}\mu_M \tag{100}$$

and the Γ are the relative surface excess. The $\sigma^M = -F\Gamma_e$ is the excess charge.

$$\sigma^S = -\sigma^M = F(\Gamma_{\mathrm{K^+}} - \Gamma_{\mathrm{Cl^-}})$$

These equations allow measuring when a mercury drop breaks from a tube. This was measured by letting the mercury fall at a constant rate:

$$g \cdot \dot{m} t_{max} = 2\pi r \cdot \gamma.$$

where t_{max} is the longest time taken for the mercury drop to fall. Applying a potential changes the breakup time. The same can be done for salt solutions. Charge density is highest when the surface tension to potential graph has a maxima (0 derivative). This is because, after a point, there's repulsion from like-charges. This leads to

$$C_d = -\frac{\partial \sigma^M}{\partial E} = \frac{\partial}{\partial E}\left(\frac{\partial \gamma}{\partial E}\right).$$

The capacitance depends on how much salt there is. This is very unlike a flat-plate capacitor. At low concentration, the behavior is extremely different.

According to Gouy and Chapman, the ions counteracts electrostatic attraction especially at low concentrations, which causes a diffuse layer. This causes an average distance $\bar{d}$ which is a function of the applied potential and the bulk concentration, and yield

$$C_d = \frac{\epsilon\epsilon_0}{\bar{d}}.$$

With increasing potential, or $E - E_{PZC}$ increase, will decrease $\bar{d}$. To help see these, separate sheets were made parallel to the electrode. The number concentration of species i is given by a Boltzman distribution:

$$n_i = \underbrace{n_i^0}_{\text{bulk}} \exp\left(-\frac{z_i e \phi(x)}{k_b T}\right) \tag{101}$$

and the charge density is given by $p(x) = \sum_i n_i z_i e$. From Poisson, we also know that

$$p(x) = -\epsilon\epsilon_0 \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}.$$

Combining these two, we get the Poisson-Boltzman equation:

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -\frac{e}{\epsilon\epsilon_0}\sum_i n_i^0 z_i \exp\left(-\frac{z_i \cdot e \cdot \phi(x)}{k_b T}\right). \tag{102}$$

The boundary conditions for this is $\phi(x \to \infty) = 0$ and $\left.\frac{\mathrm{d}\phi}{\mathrm{d}x}\right|_{x\to\infty} = 0$.

By using the starting point to be the outer Helmholtz layer, and allow a linear function within the outer Helmholtz plane (dielectric model), we get a combination of a Helmholts capacitor C_H and a Gouy-Chapman capacitor C_d (diffuse). Slide 25 is super important to do the homework.

10 Linear Sweep voltammetry

In linear sweep voltametry, the potential is swept at a $v \cdot t$ rate. This enables us to get a lot more information. The sweep rate iis often in $v =$ mV/s. Initially, the concentration is bulk every where. E_i is just below when reactions start happening. After the potential is increased slightly, the current increases exponentially, and the surface concentration drops; charge transfer dominates in the small potential region. When more potential is applied, the surface concentration drops and mass transfer becomes slower. This creates an inflection of current-potential graph. With a high enough applied potential, surface concentration is effectively zero. The current starts plateauing. Applying even more current will make the diffusion boundary layer thicker, which will make the gradient of concentration-position shallower. This makes the current decrease, because this is the diffusion limited current; the current no longer has anything to do with potential, and only with time. The applied potential is given as $E_{app} = E_i - vt$ which causes the concentration at surface relation to be

$$\frac{C_O(0,t)}{C_R(0,t)} = \exp\left[\frac{nF}{RT}(E_{app} - E^{0'})\right] = f(t) = \exp\left(\frac{nF}{RT}(E_i - E^{0'})\right) \cdot \exp\left(-\frac{nF}{RT}vT\right)$$

where this is written as shorthand $f(t) = \theta \cdot S(\sigma t)$. The solution requires an initial and boundary condition, which assumes semi-infite and balance of flux.

In linear sweep voltammetry, current is proportional to the area, bulk concentration, square root of sweep rate. For non-reversible systems, this may not hold true. The point where $E_{1/2}$ happens is not where the half current is. The half current here is defined at $E_{p/2}$. The peak potential is the half potential added to $n(E - E_{1/2})$ on the table.

Quick sampling ensures double layer capacitance does not apply. The peak current is proportional to square root of sweep rate, whereas capacitive (steady state) current is directly proportional to sweep rate. By identifying capacitive current, we can remove it to find the true peak current. Higher sweep rate increases peak current, but increases capacitive current even faster. Linear sweep voltammetry consequently has to be done slowly, especially if there's capacitive currents.

Reference electrode should be super close to the working electrode, but not on it (will have short circuit).

Higher ohmic resistance shifts all the solution, but not uniformly since higher current is more shifted. When looking at data, see if the shifts were accounted for! Super important! One way to reduce the uncompesated resistance is to make the distance of working electrode and reference electrode. Lowering scan rate also helps. In highly resistive systems, people use micro electrodes; this forces resistances to the sub-millivolt level. For these electrodes, the sweep rate doesn't matter for the UME component, but does for the planar component. For spherical systems, we have to add the ϕ term. For small radius UME and slow sweep rate, the LSV is practically the scampled current voltametry.

Do use impulse. Distance does matter.

11 LSV and current voltagram

Exam is next Tuesday. Homework is due Saturday. The exam will contain everything up to lecture 14. We should know how to use the equation sheet. We won't have to plot anything, but we will have to understand how to use plots we are given. Focus is on electrochemical measurement techniques, Butler-Volmer, sampled current voltametry, potential steps, and using data from these plots to find transfer coefficients, etc. Gouy-Chapman-Stern calculations will be absent, but their concepts should be known. There will be some short answer or multiple choice conceptual questions. We can bring an *annotated* equation sheet, so long as the annotations are hand-written. Use the equation sheet while practicing the exam and homework. Calculators allowed.

Using sampled current voltagram, we can find several things like half wave potential, but have to do multiple trials. Linear sweep allows getting same amount of data in shorter time.

The dimensionless current is given as $\pi^{1/2}\xi(\sigma t)$, where σ is the sweep rate. σ is often given in mV/s, since a V/s is too fast. Qadrupling the sweep rate doubles the peak current. the peak potential happens at a specific potential, for any sweep rate. At half the peak current, we have $E_{p/2}$, and the $E_{1/2}$ is half of that and the E_p if the system is reversible. If the peak current increases with the square root of the sweep rate, it is reversible, and additionally, sweep rate should increase peak current. This is the simplest indicator of reversibility. Reversible reactions, in a way, appear to have no lag. If there's spherical diffusion, there's another dimensionless term, such that the result looks closer to a sampled current voltammetry. Steady state current does not change with sweep rate. Higher sweep rates, as a result, look closer to a regular curve without spherical diffusion. For slow sweep rates, we see more of a curve that looks like a regular sampled current voltametry.

For irreversible reactions, we consider forward reaction only; the overpotential is large enough to not need to consider backward at all in the Butler Volmer. The time dependent rate is

$$k_f = k^0 \exp(-\alpha f(E_i - E^{0'}))\exp(\alpha) + \dots$$

The dimensionless potential is given as

$$\xi(bt) = \frac{\alpha F}{RT}(E - E^{0'} + \ln\left(\frac{\sqrt{\pi D_0 b}}{k^0})\right)$$

where $b = \alpha f v$. Additionally, spherical will invlolve a correction term again. For irreversible reactions, peak current also raises with sweep rate. The peak potential does, however, shift w.r.t. $\sqrt{v}$. It is also proportional to $\sqrt{\alpha}$. Smaller k^0 makes the natural log larger. E_p will be more and more negative, and sweep rate is increased.

Once we enter the irreversible regime, the peak *current* does not have a relation with k^0, but E_p does. Platinum has a high rate constant for proton reduction.

In quasi-reversible, it's harder because this is a transitional stage. Full Butler-Volmer equation has to be used here to get two boundary conditions. Large Λ is reversible. For very small Λ , you have irreversible. In between, there is quasi-reversible. Sweep rate allows us to choose our regime. We can keep increasing our sweep rate: if the $i_p/\sqrt{v}$ is constant, then we are reversible. When it goes to not-constant, it is quasi-reversible. When it goes back to constant, it is in irreversible.

In cyclic voltammetry, the current gets reversed after reaching a threshold. We always want to go beyond the peak. $E_\lambda \geq \frac{35}{n}$ mV. In reverse mode, the peak current is the net current subtracted by the current that would have existed if we let the system continue. This can be done graphically or using extrapolation. The peak potential on either side should have identical gap from the half potential mark; this gap is $\Delta E_p = E_{p,c} - E_{p,a} = \frac{57}{n}$ mV and is *independent* of the sweep rate, if *reversible*. If it is bigger than $60/n$ mV, then it is quasi-reversible.

Note that there's a double layer current. A faster sweep creates a bigger double layer current. When doing cyclic voltammetry very fast, the double layer current makes a bigger flip. The double layer current has to be included. A CV with a boxy shape showcases large double layer current. Double layer builds faster in porous electrodes.

Also, sometimes there may be additional species forming. In this cases, we have to consider the additional current from the first process. During reversal, it's the species that gets produced *later* that gets converted back first.

Look at people who did analytical work.

12 Constant Current Methods

Exam on Tuesday will be proctored by students. We should come earlier than 3:30 PM. We should ideally also bring a ruler. We'll be handing the equation sheet with the exam.

When measuring peak currents in reverse direction, we must account for the vertical shift. If our reaction is fairly symmetric, i.e. $\alpha \approx 0.5$, then $E^{0'}$ is in middle of $E_{p,a}$ and $E_{p,c}$.

CVs help with identifying coupled reaction. For example, right after electron transfer, there might be a chemical reaction:

$$\mathrm{O} \rightleftharpoons \mathrm{R} \longrightarrow \mathrm{R}^*$$

where R^* is the reacted product. If the scan rate is fast in the presence of a permanent chemical reaction, then not much of the product gets permanently reacted. Fe^{3+} is favored over Fe^{2+}, and is an example of this case.

Alternatively, there maybe a

$$\mathrm{O}^* \rightleftharpoons \mathrm{O} \rightleftharpoons \mathrm{R}$$

where the latter is the electrochemical reaction. The amount of O^* and O is dependent on their ratios. If the rate of $\mathrm{O}^* \rightleftharpoons \mathrm{O}$ is fast, i.e. large k_f, then it

is as if $O^* \rightleftarrows O$ does not exist. With slower rate constants, curve is shallower. The reverse direction does not have this problem.

The middle part between the anodic and cathodic peak current of the same rate is the half-wave potential, $E_{1/2}$. The half wave potential will be slightly off from $E^{0'}$.

For reversible systems, the peak-to-peak gap is less than 60 mV. Additionally, for reversible systems, peak current should not change due to sweep rates.

Cyclic voltammetry can be used to determine the standard rate constant. α can be found with peak currents; Tafel works better often.

Not having 2 peaks indicates chemically irreversible reaction.

Pourbaix diagrams shows stabilities of metals and ions w.r.t. to pH and applied potential. Anything that is charged is dissolved in water. If we wanted to turn iron ions into pure iron, it would generate hydrogen first instead.

Chrono-amperometry (CA) is measuring current over time. This is what we did. Potentiostatic is constant applied potential. Chrono-coulometry can be done simultaneously, since charge over time can be measured by taking the integral of the charge. Galvanostatic is where constant current is applied; chrono-potentiometry (CP) is measuring the potential over time. Cyclic voltammetry (LSV) and chrono-potentiometry involve changing potential or current.

To keep current constant, all of the following must be constant:

$$\frac{\partial N_O}{\partial t} = \frac{i}{n \cdot F \cdot A} = J_O(0,t) = D_O \frac{\partial C_O}{\partial x}\Big|_{x=0} = \frac{i}{n \cdot F \cdot A}$$

Surface potential is equal to formal potential when concentration on the surface for C_O and C_R are identical.

The Sand equation is

$$\frac{i \cdot \sqrt{\tau}}{C_O^*} = \frac{n \cdot F \cdot A D_O^{1/2} \pi^2}{2}. \tag{103}$$

For multicomponent system, first reaction still happens while we are in second reaction regime.

More double layer widens the drop of potential.

13 Guest Lecture — Uday Pal

Lithium gets sandwiched between $LiCoO_2$, i.e., allows change storage in lithium batteries; this is the cathode side. The same thing happens in lithium phosphate $LiFePO_4$.

Most inorganic solids are on crystal lattices, and very often have defects (missing atoms, extra sites, foreign items, etc.). We can also dope materials, which generates intentional defects. Couple of rules are still followed:

- Material (solid) is charge neutral, even if the defects are charged.
- Site balance is observed, e.g. with MgO and Al_2O_3

- Mass balance is observed

Defects are main mechanism for ion transport, so useful for us. Vacancies created when atoms come out of their site (Schottky defect). The vacancy has charge. Negative charges denoted by slashes, and positive charges by solid circles. Vacancies of MgO are $\mathrm{V}_{\mathrm{Mg}}^{//}$ and $\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$.

In Frenkel defect, atom goes in between a structure. This creates a vacant site, and also an occupied site. Substitutional is where an atom gets swapped; if it has a different charge than the original, then the net is the resulting charge. Foreign interstitial is where a different atom just occupies in-between space.

Non-stochiometry is when the amount of an atom is slightly different, e.g. TiO_{2-x}, is often due to pressure effects. Concentration of defects given in square brackets.

These are denoted by Kroger-Vink notation.

- Frenkel defect: $\mathrm{Ag}_{\mathrm{Ag}}^{x} \longrightarrow \mathrm{Ag}_{i}^{\bullet} + \mathrm{V}_{\mathrm{Ag}}^{/}$
- Schottky defect: $\text{null} \longrightarrow \mathrm{V}_{\mathrm{Mg}}^{//} + \mathrm{V}_{\mathrm{O}}{}^{\bullet\bullet}$ and $2\,\mathrm{V}_{\mathrm{Al}}^{///} + 3\,\mathrm{V}_{\mathrm{O}}{}^{\bullet\bullet}$
- Substitutional atom: $2\,\mathrm{MgO} \longrightarrow 2\,\mathrm{Mg}_{\mathrm{Al}}^{/} + 2\,\mathrm{O}_{\mathrm{O}}^{/} + \mathrm{V}_{\mathrm{O}}{}^{\bullet\bullet}$

Configuration entropy change is given as

$$\Delta S_c = k \ln \left(\underbrace{\frac{N!}{(N-n)!n!}}_{\text{dislodged atoms}} \cdot \underbrace{\frac{N!}{(N-n)!n!}}_{\text{added atoms}} \right) \tag{104}$$

where n is atoms, and N is lattice and interstitial sites.

There is an equilibrium constant between the vacancies and interstitial sites' concentration, for a given temperature:

$$K = [\mathrm{Ag}_i{}^{\bullet}] \cdot [V_{Ag}^{/}] = \exp\left(-\frac{\Delta G}{kT}\right)$$

Titanium going into an Aluminum site in $\mathrm{Al_2O_3}$ is denoted as $\mathrm{Ti}_{\mathrm{Al}}{}^{\bullet}$. The charge balance equation is addded when utilizing equations for inding vacancies.

Electrons and holes are also generated through defect reactions, for non-stochiometry. By changing oxygen partial pressure, a metrial can be changed from n-type to p-type.

N_C is the number of electrons in the charge carrying band, and N_V is quantity in valence band. By changing oxygen atmosphere pressure, we can change whether a MgO is a n-type, p-type, or ionic conductor.

Oxygen side has higher oxygen partial pressure, and will make Lanthanum conductive.

14 Convective Systems—RDE

We have to submit our outline by April 8. Our schedules will be decided by next week.

Convection enables us to control mass transfer. The fluid could also be gas. Rotaing disk electrode (RDE) and rotating ring disk electrode (RRDE) are two common analytical methods. The mass transport change affects the concentration profile. By changing the concentration profile, we have a change in the current-voltage relationship.

Migration term is eliminated, and convection is included now:

$$J_i = -\underbrace{D_i \nabla C_i}_{\text{diffusion}} - \cancel{\frac{z_i F}{RT} D_i C_i \nabla \Phi} + \underbrace{C_i v}_{\text{convection}}$$

where v is velocity. The migration gets neglected because we intentionally add supporting electrolyte..

Hydrodynamic boundary layer thickness is the distance from the surface at which the velocity reaches 99% of the free-stream velocity:

$$u(y = \delta_h) = 99\% u_\infty$$

In some cases, it may be considered at 80%. The no-slip condition applies in our case as well. The shear stress is given as the product of viscosity and the slope of the profile

$$\tau_s = \mu \frac{\partial u}{\partial y}\Big|_{y=0} \tag{105}$$

and the force is simply

$$F = \tau_s \cdot A_s. \tag{106}$$

When the shear force becomes large, turbulence onsets. We will be considering the regime of

$$\text{Re} < 2000$$

which is laminar. Turbulence is $\text{Re} > 5 \times 10^5$. The Reynold's number is given as

$$\text{Re} = \frac{v \cdot L_c}{\nu} \tag{107}$$

where the kinematic viscosity is

$$\nu \left[\text{cm}^2/\text{s}\right] = \frac{\mu}{\rho} \tag{108}$$

where μ is the *absolute* viscosity.

For purposes of analysis, we will stick to laminar regime. However, in practice, to enhance mixing we would be more interested in the turbulent regime. Note that the length scale is dependent on the geometry.

The continuity equation conserves mass, and in this class, we will assume incompressible fluids; this is realistic for liquids, but not for gasses:

$$\nabla \vec{v} = 0 \tag{109}$$

The Navier Stokes in steady state is

$$F = m \cdot a = \underbrace{\mu \nabla^2 v}_{\text{frictional}} + \underbrace{\cancel{F}}_{\text{body}} - \nabla p = \rho \cdot \frac{\mathrm{d}v}{\mathrm{d}t} = 0 \tag{110}$$

Rotating disks can literally be connected to a drill machine. Carbon brushes are used to touch the metal shaft to maintain electrical conductivity. The y direction is down, the radial direction is outward along the disk from its spin center. A spinning disk radially pushes out fluid in the radial direction, and by the continuity equation, it must be replenished by perpendicular fluid direction. Our cylindrical coordinate derivative is

$$v = \mu_1 v_r + \mu_2 v_y + \mu_3 v_\phi \tag{111}$$

$$\nabla v = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(v_r r^2\right) + \frac{\partial}{\partial y}\left(v_y v^2\right) + \frac{\partial}{\partial \phi} v_\phi\right] \tag{112}$$

$$\tag{113}$$

The no-slip condition leads to

$$v_r(y=0) = 0 = v_y(y=0)$$

but

$$v_\phi(y=0) = \omega \cdot r.$$

In the bulk solution, there is no shear far away, hence

$$v_r(y \to \infty) = 0 = v_\phi(y \to \infty)$$

but for replenishment, there must be

$$v_y(y \to \infty) = -u_0$$

to retain continuity; the negative sign indicates up. This u_0 term is the limiting velocity.

The non-dimensional solution uses the variable

$$\gamma = y\sqrt{\frac{\omega}{\nu}}$$

We can get the velocity profiles as infinite series. In this, the $a = 0.510$ and $b = -0.616$. We mostly care about the first term of the series when close to the surface. Setting this, *near the surface*, we have

$$v_y = -0.51 \cdot \omega^{3/2} \cdot \nu^{-1/2} \cdot y^2 \tag{114}$$

$$v_r = 0.51 \cdot \omega^{3/2} \cdot \nu^{-1/2} \cdot r \cdot y \tag{115}$$

At the surface, the radial component is low for the no-slip, and further away, it is higher, and even further away, it starts diminishing to 0 again.

The hydrodynamic boundary layer thickness is defined as 80% of the limiting velocity u_0. Typically, $u_0 = 0.88447\sqrt{\omega\nu}$.

Convection ensures constant (bulk) concentration at a critical distance. Cylindrical symmetry cancels any $\partial/\partial\phi$ terms. The concentration should not change based on math along the radial direction, hence $\partial/\partial r = 0$.

Large over potential forces surface concentration to be 0 at the surface. The term B holds all the rotational, viscosity, and other terms:

$$C_O^* = \frac{\partial C_O}{\partial y}\Big|_{y=0} 0.8934\,(3B)^{1/3}. \tag{116}$$

The steady state current is given as

$$i = nFAD_o \frac{\partial C_O}{\partial y}\Big|_{y=0} \tag{117}$$

where for large over potentials we have equation 116, where

$$B = \frac{D_0\nu^{1/2}}{0.51\omega^{-3/2}} \tag{118}$$

and this yields the Levich equation

$$i_l = 0.62 \cdot nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O^*. \tag{119}$$

A faster rotation forces the hydrodynamic layer to be smaller, which makes the concentration gradient to be steeper, which makes the limiting current higher. The mass transfer coefficient is equal to

$$m_o = 0.62D_o^{2/3}\omega^{1/2}\nu^{-1/6} \tag{120}$$

and the boundary layer is

$$\delta_0 = 1.61D_o^{1/3}\omega^{-1/2}\nu^{1/6}. \tag{121}$$

Note that this is the *diffusion* boundary layer, which is different from the *hydrodynamic* boundary layer. A ratio can be obtained:

$$\frac{\delta_O}{\delta_h} = \frac{1.61}{3.6}\left(\frac{D_o}{\nu}\right)^{1/3} \approx 5\%. \tag{122}$$

Notice that this is independent of rotation. The Schmidt number is

$$\mathrm{Sc} = D_O/\nu \tag{123}$$

and is the analog to Prandtl number.

The actual current would simply be scaled equation 119:

$$i = i_{l,c}\frac{C_O^* - C_O(y=0)}{C_O^*} \tag{124}$$

and similarly

$$i = i_{l,a} \frac{C_R^* - C_R(y=0)}{C_R^*} \tag{125}$$

which will be *negative*.

We can also find the over-potential using the surface Nernst equation, which gives

$$E = E^{0'} + \frac{RT}{nF} \ln \left(\frac{D_R}{D_O} \right)^{2/3} + \frac{RT}{nF} \ln \left(\frac{i_{l,c} - i}{i - i_{l,a}} \right). \tag{126}$$

Notice how this is similar to the reversible sampled current voltammetry equation. This can also yield a current-potential graph, showing steady-state current. Rotation rate does not appear, but does influence the limiting current. Hence, increasing rotation rate would increase the maximum limiting current, but the half-wave potential $E_{1/2}$ *stays the same*!

If the limiting current is potential to $\sqrt{\omega}$, then this is reversible. If this is not reversible, then we need to know the backward and forward reaction rate to get

$$i = FAk_f C_O^* \left(1 - \frac{i}{i_l} \right) \tag{127}$$

$$k_f = k^0 \exp \left(-\alpha \frac{F}{RT} \left(E - E^{0'} \right) \right) \tag{128}$$

which then can be separated into two terms:

$$\frac{1}{i} = \frac{1}{FAk_f C_O^*} + \frac{1}{0.62FAD_O^{2/3} \sqrt{\omega} \nu^{-1/6} C_O^*} \tag{129}$$

which is the sum of the inverse of the Koutecky current and the Levich-based limiting current:

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_l}$$

For different rotation rates, we can figure out the Koutecky current, with which we can find out the k_f, and then the k^0 and α.

If the current-potential plots with changing ω has non-constant $E_{1/2}$, we know that it is reversible.

Slide 19 will be helpful for the homework.

Quasi-reversible requires using the entire Butler-Volmer equation.

The rotation rate has a lower limit of $\omega > 10\,\mathrm{s}^{-1}$ for water with a radius of $r = 1\,\mathrm{mm}$, and an upper limit to prevent turbulent flow, which leads to

$$\omega < 2 \times 10^5 \frac{\nu}{r^2}.$$

The voltage sweep must be slow to allow steady state to be reached. An indicator of being 'too fast' is there is a decrease in current after a peak.

The benefit of rotating ring-disk electrode allows measuring the products right after the disk's production. This is not as often used.

15 Electrochemical Impedance Spectroscopy

The original version of EIS is the Scanning Electrochemical Microscopy. There is a working electrode immersed in electrolyte. There's a counter electrode nearby, and the resistance of counter electrode gets tared out. A second, very small, working electrode is close to the primary electrode. Stepper motor can move it. Stuff that gets produced on the surface gets un-produced, thereby measuring it. The tip has to be very close e.g., 10s or 100s of microns. For example, this can map a fingerprint electrochemically, since the areas with oils do not have as much electrochemistry. Single microns accuracy possible with small enough tip and close enough distance. This could also measure surface smoothness (bumps, or coatings that are supposed to protect a metal but there are cracks in coatings (the metal can be used as an electrode)). A heterogenous electrode can also employ this effect. Nowadays, people are able to trap a single electrolyte *drop* at the tip, instead of putting the entire thing in a bath (this has a different acronym).

An atomic force microscope can find the surface topography. Making it conductive enables it to act like an electrode. This now can be used to figure out ion-conducting membranes. Can be used to see how many channels are dead-ends vs conducting. Nafion is a flourinated Teflon. Linear sweep voltammetry can be done on this as well.

In impedance spectroscopy, voltage or current is applied, and the other is measured. Here, different frequencies are tested. This allows measuring resistance and capacitance.

If electrochemistry is possible, a Faradaic current should exist; there should also be a double layer or capacitive current (typically written as i_{dl} or i_{ic}). There's a charge transfer resistance, and a double layer capacitance (for small perturbations).

A sinusoidal voltage is applied, $e(t) = E\sin(\omega t)$ where the amplitude is on the order of 10s of milli volts; this is important because this is the linear regime. the relationship between the voltage input and current output is

$$\dot{E} = Z\dot{I} \tag{130}$$

where $Z(\omega)$ is the impedance, which can be separated into

$$Z(\omega) = Z_{\text{re}} - \hat{j}Z_{\text{im}} \tag{131}$$

where we can find the phase angle ϕ as

$$\tan(\phi) = -\frac{Z_{\text{im}}}{Z_{\text{re}}}. \tag{132}$$

The magnitude can be found as

$$|Z| = \sqrt{Z_{\text{re}}^2 + Z_{\text{im}}^2}. \tag{133}$$

We can also write

$$Z = |Z| \cdot \exp(\hat{j} \cdot \phi). \tag{134}$$

The Bode plot is used to visualize this. On the first plot, there is $\log|z|$ on the y-axis, and $\log(\omega)$ on the x-axis. The second plot has ϕ on the y-axis, and $\log(\omega)$-axis. These two plots are typically combined into one.

Another and more common method is the Nyquist plot. The negative of the imaginary impedance is on the y-axis, and real on the x-axis.

For an ohmic resistor, Ohm's law applies: $e = R \cdot i$. A sinusoidal voltage will yield the same frequency and phase current of that input; the amplitude may change.

$$i = \frac{E}{R}\sin(\omega t). \tag{135}$$

There is no imaginary component of the resistor. On a bode plot, the $\log(Z)$ is constant, and the phase is 0. Note that the 0 is at the top on a Bode plot, since most systems have negative phase shift. This appears as a point on the x-axis on the Nyquist plot.

For a capacitor, the equation is

$$q = C \cdot e \tag{136}$$

which states that the charge is the product of the capacitance and potential; the current is the rate of change of potential multiplied with capacitance:

$$i = C\frac{\mathrm{d}e}{\mathrm{d}t} = \omega CE\sin(\omega t + \frac{\pi}{2}). \tag{137}$$

The impedance of this changes with frequency as

$$Z_{\mathrm{cap}} = \frac{1}{\hat{j}\omega C} = -\hat{j}Z_{\mathrm{im}}. \tag{138}$$

In a bode plot, there a negative 90 degree phase shift, and a decreasing impedance magnitude. On a Niquist plot, this is a vertical line: high frequency is close to the x-axis.

Inductors are not electrochemical components, and arrive from the equipment and wiring. The wires have an impedance. The relationship for the potential of an inductor is

$$e = L \cdot \frac{\mathrm{d}i}{\mathrm{d}t} \tag{139}$$

and for an applied sinusoidal voltage, we get

$$i(t) = \frac{E}{L\omega}\sin(\omega t - \pi/2) \tag{140}$$

which has a phase shift of positive 90 degree. The imaginary impedance is

$$Z_{\mathrm{im}} = \omega \cdot L \tag{141}$$

This is only at high frequencies, and the equipment can be improved to mitigate this.

$1\,\mu$F is a typical capacitance for a double layer. In an R-C circuit, the net impedance is their sum (real of resistor, and imaginary of capacitor).

In a R/C (parallel) circuit, the impedance is

$$Z = \frac{R_t}{1 + \hat{j}\omega C_{\text{dl}} R_t} = \frac{R_t}{1 + (\omega R_t C_{\text{dl}})^2} - \hat{j}\frac{\omega C_{\text{dl}} R_t^2}{1 + \omega R_t^2 C_{\text{dl}}^2}$$

where the latter separates real and imaginary. A Nyquist plot would yield a semi-circle with 2 distinct-ends: high frequency end would be at the 0 real impedance. The diameter of the semi-circle is the real resistance.

Z_f is simply R_{ct} since at the small amplitudes, we have linear resistances for faradaic. There's also an electronic resistance due to all the machinary, which is given as R_e. This R_e creates a x-axis shift in the semi-circle. The peak of the circle would now yield

$$f_{\text{RC}} = \frac{1}{2\pi RC} \tag{142}$$

and this is the basic Randles circuit.

Real electrochemistry has 2 electrodes, hence, we can simply include the second electrode in series. Alternatively, this second electrode, the counter electrode, can be made very large in size to reduce impedance. Alternatively, we can have the kinetics very large, such as lithium metal.

The right most typically is the sum of all resistances at high frequencies, in a Nyquist plot. EIS is not a unique identifier, since multiple circuit models can represent the same.

Mass transfer effects can be included in the Randles Equivalent Circuit by writing the Z_f as the sum of the R_{ct} and the Warburg Impedance (mass transfer) Z_w. Slide 20 in the Warburg Impedance, and showcases how the electrochemical potential changes due to changing fluctuation of the species at the surface. For small amplitude voltage, we have a linear relationship mostly:

$$\eta = \frac{RT}{F}\left(\frac{C_O(0,t)}{C_O^*} - \frac{C_R(0,t)}{C_R^*} + \frac{i}{i_0}\right) \tag{143}$$

A larger diffusion coefficient and bulk concentration also leads to smaller Warburg impedance. For cases where we start with no product species, we do have large Warburg Impedance. Also, at high frequencies, very little charge is passed, and very little surface molecules are changed, and hence, matters less at these high frequencies.

For a reversible fast electrode kinetics, the i_0 is small, so R_{ct} is small. The phase angle is close to -45 degrees: this allows distinguishing between ohmic (no phase shift) and capacitive (90 degree phase shift).

The Warburg Impedance branches of in the Nyquist plot, and the extrapolated intercept is (?). This branch is known as the Warburg tail. This tail can enable to learn about the diffusion coefficient, since it is mass transfer controlled. The kinetic control regime can be used to find R_{ct} which can then be used to find i_0 and then k^0.

In real EIS, discrete frequencies are used; the lower frequencies take longer, and thus is done less often. Very low frequencies with unstable systems can end up reducing repeatibility in the same experiment.

We should use as little circuits component as possible. If the experiment is not properly shielded, then we will see positive imaginary impedance.

Ionic resistance is given as R_O which is equal to the electrolyte resistivity divided by the radius of the pores:

$$R_O = \frac{\rho}{\pi r^2} \tag{144}$$

and the impedaance of the cylindrical pore is

$$Z_O = \frac{Z_{eq}}{2\pi r} \tag{145}$$

where Z_{eq} is the interfacial impedance. The circuit is built of several circuits of the same type. This ends up showcasing a fluctuating line on the Nyquist plot.

16 Batteries

The first battery was a collecction of metals stacked together, by Alessandro Volta, around the 1800s. This was constructed from copper and zinc in series, with acid-soaked paper in between (sulfuric acid). Here, the more reactive zinc oxidized into zinc ions. The reduction reaction was $2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2$, and the oxidation was $\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^-$, which has a Nernst potential of 0.76 V. However, there is a slow side reaction in this setup; in modern day, this is called 'self-discharge': $\mathrm{Zn} + 2\,\mathrm{H}^+ \longrightarrow \mathrm{H}_2 + \mathrm{Zn}^{2+}$.

To construct a battery, an energy storing redox material is needed—one being anode and another being cathode. Short-circuit has to be prevented while still offering ion-transport. An electron transport method will be required.

In a typical battery, there is a current collector (CC): these are typically thin foil metals. The anode and cathode material store energy. The separator is typically an expensive porous polypropylene. In total, there is 5 layers.

Primary batteries are non-reversible, and the half reactions are not reversible. These are alkaline cells, lithium-button cells—*not confused to be rechargeable lithium ion!*. The latter is very high energy density.

Secondary batteries are rechargeable. Lead acid batteries have exceeded for a long time. NiCad and NiMH have been almost completely been replaced by lithium-ion batteries.

Lithium's higher energy state is β, which has higher energy than α. $\alpha \to \beta$ is a chemical reaction if we let it happen: heat will be produced due to difference in enthalpy difference. Attempting to utilize this heat is given by the Carnot limit. We can use this electrochemically instead. The difference between Gibbs energy change and heat change is given by

$$\frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \approx 100\% \tag{146}$$

and, almost always, the electrochemical reaction is much more useful in terms of work. Fuel cells are far more efficient than simple combustion.

Batteries typically write its energy as watt-hours, where each watt-hour is 3600 J. Per-volume density is Wh/L typically. Per volume energy density is the true 'density', but colloquially it can also mean 'per mass'. The per mass density is known as gravitometric density, which is Wh/kg. There is also a 'per footprint area', which is basically 'how much space does this literally take on a floor?'. The units for the latter is $\mathrm{Wh/cm^2}$.

Power density is instantaneous measure of input/output. This is different from capacity. A Ragone Plot shows the power density and energy density (both gravitometric)!

Other factors are longevity, safety, scalability, cost, recyclability, and efficiency.

The lead acid battery has the cell

$$\mathrm{PbO_2 \,/\, PbSO_4 \,/\, H^+, SO_4, H_2O \,/\, PbSO_4 \,/\, Pb} \tag{147}$$

where the reduction (discharge direction) is

$$\mathrm{Pb^{4+}O_2 + 4\,H^+ + 2\,e^- + {SO_4}^{2-} \rightleftharpoons PbSO_4} \tag{148}$$

and the oxidation in discharge direction is

$$\mathrm{Pb + {SO_4}^{2-} \rightleftharpoons PbSO_4 + 2\,e^-} \tag{149}$$

The potential per cell is 2.05 (Nernst), but are traditionally in series to be 12V. However, sometimes hydrogen evolves, which has to be prevented (done using a gell nowadays). 20 years ago, it was solution acid, and had to be vented. Lead acid batteries have benefits of being cheap and high power. However, it has issues of toxicity, and struggle with deep discharge (i.e., do not force your lead acid battery to turn your car on if it low on charge).

Typically, when people discuss battery anode/cathode, they are talking about 'discharge'. In almost any battery, the electrolyte reacts with one of the electrodes.

In a alkaline battery, the shiny end parts is the current collector. The negative pole has a pin going inside which is also a current collector. There is a fine zinc powder around the pin. Underneath the case and outside of the zinc, there is manganese oxide $\mathrm{MnO_2}$. There is a separator in between. A 6M potassium hydroxide drives the ion conduction. Here, the reactions are

$$\mathrm{2\,Mn^{4+}O_2 + 2\,H_2O + 2\,e^- \longrightarrow 2\,Mn^{3+}O(OH) + 2\,OH^-} \tag{150}$$

for the reduction (positive electrode) with 0.2 V, and

$$\mathrm{Zn + OH^- \longrightarrow Zn^{2+}\,O + H_2O + 2\,e^-} \tag{151}$$

and has 1.28 V. Net is 1.5V. The Pourbiax diagram shows that, if we are slightly alkaline, the zinc forms a protective oxide, but too much pH will create soluble $\mathrm{{ZnO_2}^{2-}}$ which is corrosive and the bi-product is hydrogen producing side reaction.

To know the charge or capacity, we need to know the mass or volume of all the materials.

For NiCad batteries, there used to be a lot of advantages, but the cost of it and toxicity of Cadmium had it phase out. NiMH were better, but problems with deep discharge and overcharging risk.

In lithium ion batteries, there are several benefits such as low weight. Both graphite and lithium are light, but note that the cobalt in the cathode is not. The cost of lithium ion batteries has gone down more so because of manufacturing techniques. It has a long cycle life.

The potential between the graphite and $LiCoO_2$ is about 4 V, which prevents us from using water: water will electrolyse. Original lithium batteries used TiO_2 which could use water for a small duration, but would have hydrogen side reactions.

One type of storage is dissolution: the host material X takes on lithium ions: this is solid solution (or alloys of all-metalic): $\mathrm{X} + n\,\mathrm{Li}^+ + n\,\mathrm{e}^- \longrightarrow \mathrm{Li}_n\mathrm{X}$. This has a limit of how much lithium can be carried.

Another type is phase change, where a new compound is made: $\mathrm{X} + n\,\mathrm{Li}^+ + n\,\mathrm{e}^- \longrightarrow n\,\mathrm{LiX} + (1\text{-n})\mathrm{X}$. The host literally changes. This has a massive change in amount of lithium.

Current batteries use both of the above techniques.

Decomposition or conversion type is where lithium takes away the oxygen from a metal: $\mathrm{MO} + \mathrm{Li}^+ + \mathrm{e}^- \longrightarrow \mathrm{M} + \mathrm{Li_2O}$. These are advanced anode materials that are not quite available. Problem with this is that mechanically these things tend to break apart due to different materials.

Lithium cobalt oxide was the first useful cathode material. The mechanism is known as 'rocking chair mechanism' because lithium would just re-shuffle with this method. Unlike batteries that need a hydroxide, this meant that a side-product isn't moved around. In lithium cobalt oxide cathode batteries, we cannot exceed more than half of the lithium, otherwise material will decompose. This had 4 V against the lithium metal potential. However, this has safety issues. There is cobalt surrounded octahedral-ly with oxygen. Such shape is edge shared, meaning that the cobalt ions are very close to each other. This bring a lot of cobalt-cobalt interactions, leading to good (enough) conductivity. In between such layers, there are lithium ions, which move in/out. These have to be aligned properly. However, the cobalt is a problem because of human ethics and scarcity. Additionally, under heat, the cobalt oxide releases oxygen which leads to higher temperature and more oxygen and so on: thermal runaway. This can lead to fires.

In Galvanostatic measurements, where we apply current to remove/add the amount of lithium, there is a limited potential. Although it can get up to 4.5V by depleting more lithium, this poses a problem of degradation. Practical range is 3.5 to 4.2 V. If too much lithium taken out, then the cobalt oxide repulses each other; when all is taken out, crystal structure changes due to the large amount of force.

A plateau in a Galvanostatic diagram shows a phase-change, whereas a sloped voltage shows a solid solution.

Modern lithium-ion batteries use NMC: lithium cobalt/nickel/manganese oxide at a ratio of 1:8:1 typically. Such a ratio is called NMC811. This has two advantages: first, the nickel allows more reversible extraction of more lithium without causing instability to the structure; down to a value of 0.35 instead of 0.5. This allows slightly higher voltage, so more power. This does cause a slight issue of more side reaction due to higher voltage.

The cobalt shuffles between Co^{3+} and Co^{4+}, the nickel shuffles between Ni^{2+} and Ni^{4+}; the manganese remains constant as Mn^{4+} and lithium as Li^{+}. Sometimes the nickel (II) might jump into the lithium chain.

Nickel is still expensive and rare.

The next 'big' move in lithium ion batteries is the lithium iron phosphate: $LiFePO_4$. Making this is difficult, but is far cheaper and abundant. A large driving factor of cost reduction is China's manufacturing. This is great for grid storage. This has a low capacity (gravitometric) and lower voltage, but this is not a big problem for the grid. This also has a large longevity. This also has high safety: the oxygen is in the molecule of phosphate itself, which significantly prevents release of this gas. The phosphate is an insulator and consequently, there is only 1D transfer of ions. A lot of material engineering is involved to make this work: one key method is making each unit smaller and smaller. This also helps running it faster. However, this also means it is harder to pack, so this ends up having lower energy density.

It took a long time to figure out the right anode material. Lithium was originally used as the anode, but ended up catching fire. Graphite was the solution. Graphite is just high-quality charcoal. Each ring of 6-carbon has a lithium: $LiC_6 \rightleftharpoons C_6 + Li^+ + e^-$. Lithium graphite goes through multiple phase changes: on the atomic level, it is simply where the lithium 'sits'. The carbon also pretty light-weight. It has double the capacity than NMC. The voltage is also great for lithium plating. However, this creates a problem that, if discharge happens very fast, we could dip below 0 V, and cause plating. This can cause short circuits and fires. Also, volumetric density isn't as good. Graphite is also conductive (so no added material needed).

There is a Stable Interface Layer (SEI) formed at the surface of graphite. At the very reductive potential that this has, the electrolytes would typically degrade; however, the formation of this layer prevents side reactions, which is just a few nanometers. This forms at the first few cycles. This protects graphite from further degradation. The factory does this.

17 Batteries 2

Maier, Angew. Chem 2013 is one of the dryest papers about material thermodynamics. We will be given a sample presentation. We should upload our slides after the presentation into the drive.

An alternative to graphite anode is lithium titanate (LTO): $Li_4Ti_5O_{12}$. The lithium inside this compound have no affect in terms of capacity, but we can add additional lithium (up to 3). On a weight basis, this has half the capacity

of graphite, but on a volumetric basis, it has more. Using this leads us to have lower potential: we lose 1.3 volts down to 2.5 volts. However, this has the benefit of not degrading the electrolyte, and no formation of an SEI layer. This is extremely stable on its own. This consequently enables it to be long lasting. LTO is also very cheap. As a result, this would be great for the grid storage, in addition to the LFP. This is an octahedral compound; adding the additional lithium turns it more of a rock salt structure. This unfortunately makes charging harder since additional lithium reduces diffusivity. This has a phase change effect. This stable voltage yields to difficulty knowing what the amount of charge is. The oxygen ions remain unchanged, and consequently improving stability.

Sloped regions in a voltage-capacity graph shows a solid solution state; the flat parts show a 2 phase.

$$\mu_{\mathrm{Li}} = \bar{m u}_{\mathrm{Li}^+} + \bar{\mu}_{e^-}$$

If we let β be the solid lithium, then for a pure lithium half cell:

$$\begin{aligned} EF &= -\mu_{\mathrm{Li}}^{\alpha} - \mu_{\mathrm{Li}}^{0,\mathrm{Li}} \\ &= \underbrace{-\mu_{\mathrm{Li}}^{\theta,\alpha} + \mu_{\mathrm{Li}}^{0,\mathrm{Li}}}_{\Delta G^0} - RT \ln(a_{\mathrm{Li}}^{\alpha}) \end{aligned}$$

In a lithium-poor compound (de-lithiated), listed here as $\mathrm{Li}_\theta \mathrm{X}$. While lithiating, we add a new phase, called Δ here, which is to nidicate deviation.

$$\overset{\theta}{\mathrm{Li}_\theta \mathrm{X}} + \mathrm{Li}_{1-\Delta} \overset{\Delta}{\mathrm{X}} \equiv \mathrm{Li}_n \, \mathrm{X}$$

The mole fraction is the amount of lithium divided by whatever else is there.

A common tangent is yielding from the equation

$$\mu_{\mathrm{Li}} = \left(\frac{\partial G}{\partial n_{\mathrm{Li}}} \right)_{\mathrm{restconstant}}$$

In equilibrium, for all numbers of lithium,

$$\mu_{\mathrm{Li}}^{\theta} = \mu_{\mathrm{Li}}^{\Delta} = c$$

That is, the potential is constant as long as the stochiometry between the two phases is constant.

The maximum capacity is given as

$$Q_{max} = F \cdot n_x (1 - \theta - \Delta)$$

18 Fuel Cells and Electrolyzers

Fuel cells are considered to have high energy density, but not so good in terms of power, according to the Ragone plot. However, this is slightly misleading since it depends on how the fuel cell is constructed.

Both fuel cell and EV requires electrochemical conversion. In EV, all the electrochemistry is in the battery. In fuel cell, the cell is different from the energy (which is in a different container). This allows more independent control of power (more fuel cell) and energy (bigger tank). The nice thing about fuel cells (hydrogen based) is that the oxygen can be taken from the ambient air. The water produced can just be released to the atmosphere. For fuel cells for the grid, the water might be just collected for re-use for electrolysis.

In a proton exchange membrane fuel cell, the anode side has hydrogen, with some anion, from acid. This has the hydrogen oxidation reaction (HOR). The oxygen reaction is the oxygen reduction reaction (ORR). The standard cell potential is 1.229 V. A membrane separates the two, typically a proton exchange membrane. The proton passes through, and nothing else. These typically have an output of $1\,\mathrm{W/cm^2}$. These are typically run at 80°C to improve efficiency without degradation. The pressure for the gasses is typically 1 to 2 atmospheres.

Additionally, we need to be careful to not let the water pool up on the anode side; that would block oxygen flow.

The opposite is an electrolyzer. The produced oxygen gas can easily be separated from the water.

The thermoneutral cell potential is the voltage needed to put into the system that maintains isothermally. That is, an excess potential is needed to maintain the temperature, given as

$$E_{\mathrm{tn}} = -\frac{\Delta H}{n \cdot F} \tag{152}$$

There is a phase change: from the liquid to gas phase requires more energy, so higher temperature and more energy helps. Already using water vapor helps.

The efficiency of the electrochemical cell is given as

$$\eta_V = \frac{E_{tn}}{V_{cell}} \tag{153}$$

is the voltage efficiency. The current efficiency is typically 100%, since all the current go into producing gas; in batteries, this was not completely the case since there were side reactions.

The electric efficiency is the product of the two:

$$\eta_{el} = \eta_{curr} \cdot \eta_v \tag{154}$$

For electrolysis cell, it is typically 60% to 85%. For fuel cell mode, it is similar. Some of the reason for losses is ohmic, activation loss (makes up most of it)(also known as charge transfer), mass transport. The ohmic resistance is due to the ion resistance. When a lot of current is poured in, the mass transport losses happen mostly at high power settings (and can be mitigated by more flow).

In a cell potential-current plot, the area under the curve is the power; the peak in power is somewhere in the middle.

Hydrogen gas access in a fuel cell is provided for through porosity. The electrolyte offers the means of allowing the hydrogen ions H^+ to go in and out. The conductive electrode allows the means for electrons to be provided.

Typically, it is best to combine all of these together. A catalyst is included to reduce the overpotential. The metal could be the catalyst, but these are very expensive. The electrochemical reactions happens only where all three of these are present, hence, this is called the triple phase boundary. Since the electrochemistry only happens here, we want to maximize the area.

Platinum catalyst nanoparticles (1 to 5 nano meters, or 0.1 to 0.4 $\mathrm{mg/cm^2}$) are used as catalyst. Platinum is very expensive, so even for these small amounts, the price can add up very quickly. These are placed on anoporous carbon support, on the order of 10 to 100 nano meters. Ionomers are mixed in, something like sulfonate ion $\mathrm{SO_3}^-$ is mixed in. This is known as a composite electrode.

On a molecular level, the mechanism depends on the metal used: Tafel step or Heyrovsky step. The volmer step is the same, where $\mathrm{H^+ + e^- \longrightarrow H_{ads}{-}M}$ where the metal adsorbs the hydrogen atom. Another hydrogen ion comes in:

- In Tafel: $\mathrm{2\,H_{ads}\,(M{-}H) \longrightarrow H_2\,(g)}$
- In Heyrovsky: $\mathrm{H_{ads} + H^+ + e^- \longrightarrow H_2\,(g)}$

Each of these individual steps have different activation barriers and rate constants. The latter requires three species coming together, hence it is a slower step, unless you can have a lot of adsorbed ions to accept hydrogen ions. Realistically, these are very similar in terms of rate.

Metals have different crystal planes, and this is important for determining which step is taken. This is seen as two peaks in a cyclic voltammetry.

Platinum and carbon can oxidize for the oxygen side, hence it is not used. Iridium oxide IrO_x is a more stable catalyst, typically applied on a semiconducting metal oxide, such as $\mathrm{TiO_2}$ and $\mathrm{Nb_2O_5}$. The former is much cheaper than the latter. The OER is the slowest reaction that takes place.

In the OER process, the oxygen has to be taken from the water molecule, and combine with another oxygen on the oxygen-metal surface. Another potential process is oxygen reacting with the oxygen of the iridium: this is discovered by using water with isotopic oxygen, but then finding non-isotopic oxygen gas. Knowing these is important because knowing what steps take place helps understand what step takes the most activation energy.

Poly(tetrafluoroethylene) with oligo(hexafluoropropylene oxide)-sulfonate side groups is Nafion: this is essentially Teflon with side sulfonate side groups that allow protein to go through the material. These have pockets of water deviating away from the Teflon (because Teflon hates water); this creates channels for hydrogen ion to pass through. The Teflon also helps prevent water from sticking. However, Nafion is highly toxic due to PFAS.

The bipolar plates have gas channels that help flowing gas. Carbon paper or similar helps gas diffuse from the flow channel. The catalyst layer is few microns thick.

These cells are called gas diffusion electrolysis.

An H-Type cell, instead, does not have as much mixing.

In mixed membrane/electrolyte system, a catholyte can be used, where there a cathode-electrolyte between the two.

Anion exchange membranes, unlike Nafion, has positively charged ions that allow negative ion transport. Bipolar membrane combines the two.

The Keeling Curve is a very accurate. The fluctuation since 1955 is over 30% today. As a result, it makes sense CO2 conversion back down makes sense.

CO2 can be converted into chemicals using electrochemistry. Carbonmonoxide is a very commonly needed chemical. Ethylene is a fundamental building block of lot of other type of molecules.

Converting CO2 to CO is $CO_2 + 2\,e^- + 2\,H^+ \longrightarrow CO + H_2O$ in acidic conditions has Nernst potential of about -0.1 V, while alkaline is $CO_2 + 2\,e^- + 2\,H_2O \longrightarrow CO + 2\,OH^-$ has -0.93 V. However, challenge is that hydrogen gas might form during the process; to prevent hydrogen forming, we want to lower the activity of HER, and increase CO2 reduction activity. Consequently, higher pH is used, which has slower hydrogen evolution. Attempting to purify CO and hydrogen is difficult. Additionally, bicarbonates might form, and react with the electrolyte, and form precipitate. Additionally, there's a low ionic conductivity.

One solution to these problems is to use large cations in the electrolyte: this reduces potential of CO2 and prevent hydrogen gas formation.

19 Student Presentations 1

Silicon anodes can increase in their volume in silicon-anode based lithium-ion batteries. The increase in volume can cause cracking.

Dendritic growth is one of the bigger problems with Lithium-metal batteries. Piercing the separator leads to short-circuiting and fires.

Question