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<div align="center">Module 5 and 6 Concept Repository</div>

Module 5

- Thermodynamics, kinetics, and transports are important definitions in understanding the input and response of electrochemical systems. Driving forces for an electrochemical system are determined by the thermodynamic properties of the electrodes and electrolytes. The response to the driving force depends on kinetic rate parameters. Finally, transported mass and electron transfer through electrolyte and electrodes combines with reaction kinetics to produce the total resistance.
- Ionic conductivity generally increases with increasing temperature and rates of an electrochemical reaction are linked to conservation of charge and electroneutrality which requires same number of cations and anions where $\sum z_i c_i = 0$ where I is the number of species in the solution, c_i is the concentration and z_i is charge number. The rate of reaction is related to current where $m_i = -s_i M_i It/nF$ where m_i is the mass of the species i produced by a reaction with a stochiometric coefficient s_i and n electrons are transferred, M_i is the molar mass, I is current and t is time. The stochiometric coefficient is determined by the equation $\sum s_i M_i^{z_i} \leftrightarrow ne^-$. Through analysis the behavior of electrochemical systems, they are more determined by current density, current per unit area, than total current. Polarization is the departure of equilibrium conditions due to the passage of current whereas over potential refers to the magnitude of potential drop causes by resistance to the passage of current.
- Thermodynamic properties of an electrochemical reaction are called electrochemical potentials where energy change for a reaction is given by the change is the Gibbs free energy for each half cell reaction where $\Delta G = (\sum s_i \mu_i)_{left} - (\sum s_i \mu_i)_{right}$ where μ_i is the electrochemical potential of species i and s_i is the stoichiometric coefficient. The equilibrium or open-circuit potential is the potential which no current flows. The equilibrium potential is denoted by U and related to the Gibbs free energy by $\Delta G = -nFU$. However, temperature to an extent still can cause the reaction to occur. Therefore the electrochemical potential can be related tot molality m_i and activity coefficient γ_i where $\mu_i = \mu_i^\theta + RT\ln m_i \gamma_i$ where μ_i^θ is independent of concentration. Assuming activity coeffiecnts equal to 1 the Gibbs free energy for each half cell reaction recuces to the Nerst equation where $U = U^\theta - RT/nF\ln(\Pi m_i s_i)_{right} + RT/nF\ln(\Pi m_i s_i)_{left}$ which relates equilibrium potential to concentrations of reactants and products. The electrochemical potential can by controlled electrically by applying external power tot perturb the equilibrium and driving a reaction relative to another electrode or reference state. Galvanic cells cause a driving force by connecting positive and negative electrodes while electrolytic cells, a positive potential is applied to the positive electrode to force the reaction in the anodic

direction, or a negative potential is applied to a negative electrode to drive the reaction in the cathodic direction. The surface overpotential η_s is the difference in potential between the two electrodes being the driving force for the reaction. The rate of reaction is related to the surface overpotential by the Bulter-Volmer equation which has the form $i = i_0[\exp(\alpha_a F\eta_s/RT) - \exp(-\alpha_c F\eta_s/RT)]$ where i is current density and i_0 is the exchange current density or rate constant. α_a and α_c are the apparent transfer coefficients of the anode and cathode that relate how an applied potential favors one direction of reaction over the other where a positive η_s prodcues a positive anodic current, α_a and α_c usually have values between 0.2 and 2 and large i_0 is often a fast or reversible reaction. The relationship between current density and surface overpotential can be shown on a Tafel plot and for larger values of η_s i $i= i_0\exp(\alpha_a F\eta_s/RT)$ or $i= -i_0\exp(-\alpha_c F\eta_s/RT)$. The potential difference creates transport through flow of electrons where the driving force is the electric field related to gradient in potential. This is related to current density by electronic conductivity $\sigma_{conductor}$ or $\kappa_{electrolytes}$ and gradient in potential which is similar for a solution of ions. Ions in a electrolyte move in response to the electric field (migration), concertation gradients (diffusion), and bulk fluid motion(convection) related to concentration and velocity and tranference.

- The potential difference across a cell will depend on four component the equilibrium potential U, the surface, the ohmic potential drop, and concentration overpotential where at higher currents ohmic effects dominate.
- Heat generation is reversible if the net entropy "or number of states a system can exist in" of a system is constant whereas irreversible heating increases net entropy. The total heat transfer or lumped-parameter models of battery temperature dynamics is $d/dt[mc_pT] = Q_{irr} + Q_{rev} - Q_{ht}(hA(T-T_{inf}))$ (of convention, conduction, and radiation but can be assumed as h is constant and all heat is convection). The irreversible heating in a battery is $Q_{irr} = I^2R$ in a simple equivalent-circuit battery model and $Q_{irr}= I^2R+(x_2/R_1C_1) +(x_3/R_2C_2)$ based on ohm's law. Reversible heating in a battery is $Q_{rev} = IT\mu$ where I is current, T is temperature, and μ the entropy coefficient which is a measure of reversible heating where $\mu=dOCV/dT$.
- For temperatures changes the Arrhenius equation tells us basic performance characteristics double where $c= c^*\exp(-E_a/RT)$ where E_a is the activation energy and c is a physical constant governing a reaction rate.
- Ohm's law can be extended to a continuum model where x+dx, the current density j changes through position x through and electrolytic medium and is dependent on intercalation rate w between solid and solution and φ is potential. Without intercalation V=IR and with $d\varphi/dx=1/kj$ and k is conductivity. With intercalation $k\, d^2\varphi/dx^2= J'$ where J' is reduction current density per unit volume. Applying Fick's law of diffusion for the electronic phase $dc/dt=D\, d^2c/dx^2 + J'$ where c is concentration
- Putting all these various components of a battery together in an isothermal model is the Doyle-Fuller-Newman Lithium-Ion battery model which can be enhanced for temperature dynamics.

Module 6

- The DFN model is a partial differential algebraic equation (COMPLEX)
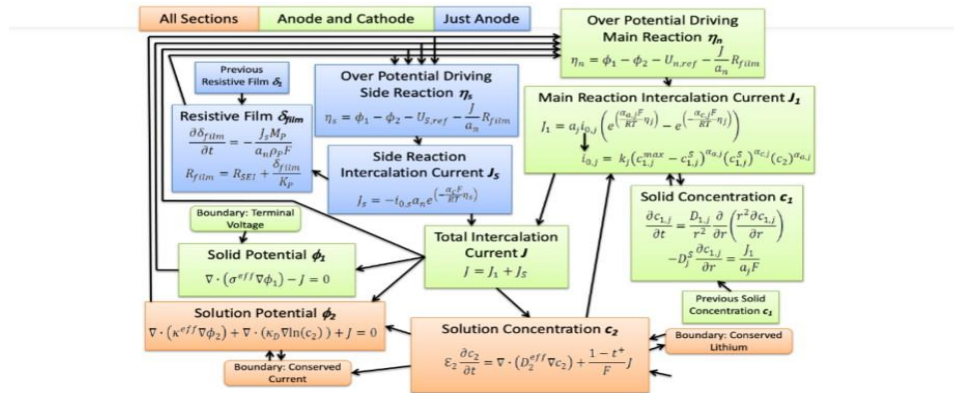
- High fidelity and complexity models are Porous 2-dimensional models such as the DFN model and those grounded in molecular dynamics. Low fidelity and low complexity are equivalent circuit models. Somewhere in between are single particle models where a single particle with radius r represents the anode and cathode and between these two is a static behavior or a PDE for electrolyte behavior without solid component (enhanced). The tradeoff between fidelity and complexity is best approached with enhanced single particle model SPM where a temperature enhanced SPM can approach the accuracy of a DFN with lower computational complexity. Much simpler than DFN and more accurate than ECM.
- Models can be reduced through reducing equations and index reduction (PDAE to PDE by removing algebraic constraints). Model discretization can happen in the time domain and frequency domain and converts PDE to ODE.
- Discretization can occur through finite differences, finite elements, orthogonal projection methods(galerkin), and PADE approximation and they can be reduced all to a ECM through linearization.
- In PADE approximation, for a battery governed by an infinite dimensional PDE, then the transfer function will be infinite dimensional (exponential like time delay) and can be forced to look like a finite dimensional solution. For a time delay e^{-st^*}, the transfer function is approximately $1/t^*s+1$ and $y'= 1/t^*(u-y)$ and is a first order finite dimensional ODE for the infinite dimensions of a time delay. (LOOK AT Joel Journal of electrochemical society PAPER). A second order SPM can reduce complexity. The more order the higher the accuracy for a PADE approximation. The DFM model can be reduced all the way to an equivalent circuit model where Capaciatance and Resistance can be related to spherical diffusion.
- For a temperature -dependent SPM a model of temperature dynamic is needed and a model of single particle behavior on temperature through Arrhenius equation or experiments and can be PADE approximate by finite dimensional transfer function.