Introduction to MSMR Archie Yao November 16, 2023

Multi-Species Multi-Reaction Model: Theory and Applications

Learning Objectives:

- Derive OCV model of MSMR
- Application of MSMR to aging

Key Concepts:

Gibbs Free Energy as Maximum Non-expansion work, Chemical Potential, Open-Circuit Voltage, Activity Coefficient, Multi-Species Multi-Reactions, dQdV, dVdQ

Before diving into the Multi-Species Multi-Reaction model, we need to derive several theorems.

The Maximum Non-Expansion Work

Define Gibbs free energy as

$$G = U - TS + pV$$

Gibbs free energy has a clear meaning, which is the maximum nonexpansion work under constant pressure constant temperature (isobaric & isothermo) condition.

The justification is as follows:

$$dG = dU - d(TS) + d(pV)$$

= dW + dQ - TdS - SdT + d(pV) (1)

First equality is because of the definition of Gibbs free energy G = U - TS + pV. The second equality is the first law of thermodynamics dU = dW + dQ. Because of constant temperature, dT = 0. Now, if the whole process is reversible, we have $dW = dW_{rev}$ and $dQ = dQ_{rev} = TdS$, so

$$dG = dW + d(pV) \tag{2}$$

The work dW can be separated into 2 parts: expansion work -pdV, and non-expansion work dW_{ne} (for example electric work, etc.): $dW = dW_{ne} + (-pdV)$. Therefore

$$dG = dW_{ne} + (-pdV) + d(pV)$$

= $dW_{ne} - pdV + pdV + Vdp$ (3)

Under constant pressure, dp = 0, therefore we have $dG = dW_{ne}$.

Gibbs-Duhem equation

We have

$$dG = Vdp - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_n dn_r$$

And by the definition of chemical potential of species i $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i}$, we have $G = \sum_j \mu_j n_j$, therefore

$$dG = \sum_{j} \mu_j dn_j + n_j d\mu_j$$

The two equations must be equal, therefore we have

$$Vdp - SdT = \sum_{j} n_j d\mu_j$$

At constant pressure and constant temperature, this becomes

$$0 = \sum_{j} n_j d\mu_j$$

Chemical Potential As A Function of Pressure

We have

$$dG = dU - d(TS) + d(pV) = TdS - pdV - TdS - SdT + pdV + Vdp$$
$$= Vdp - SdT$$
(4)

Under constant temperature, i.e. dT = 0, we have dG = Vdp. Integrate to have

$$G(p_1) = G(p_0) + \int_{p_0}^{p_1} V dp$$

For ideal gas system, we have pV = nRT, plug-in to have

$$G(p_1) = G(p_0) + nRT \int_{p_0}^{p_1} \frac{1}{p} dp = G(p_0) + nRT \log \frac{p_1}{p_0}$$

i.e. if we define $p^{\diamond} = p_0$, then

$$G(p) = G(p^{\circ}) + nRT \log \frac{p}{p^{\circ}}$$

For a pure system, the molar gibbs free energy is the chemical potential, therefore we have

$$\mu(p) = \mu(p^{\circ}) + RT \log \frac{p}{p^{\circ}}$$

Chemical Potential of Liquids

Denote the pressure of a pure substance A as p_A^* , the chemical potential of pure A (nothing else presents in the system) as μ_A^* .

Now, we assume pure A is contained in a container in two different phases, the liquid phase and gas phase, as Figure 1^1 shows. The equilibrium enforces that

$$\mu_{A,liq}^* = \mu_{A,gas}^* = \mu_A^{\oplus} + RT \log \frac{p_A^*}{p^{\oplus}} \tag{5}$$

We use the superscript * to denote pure substance.

Now, assume that there's another substance B coming in as a solute into A. The chemical potential of A at gas phase changes as a consequence of B coming in:

$$\mu_{A,liq} = \mu_{A,gas} = \mu_A^{\circ} + RT \log \frac{p_A}{p^{\circ}} \tag{6}$$

Using Equation 5 to eliminate μ_A^{\diamond} :

$$\mu_A^{\oplus} = \mu_{A,gas}^* - RT \log \frac{p_A^*}{p^{\oplus}}$$

Plug-in to Equation 6:

$$\mu_{A,liq} = \mu_{A,gas} = \mu_{A,gas}^* + RT \log \frac{p_A}{p_A^*}$$



Figure 1: At equilibrium, the chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of A in the vapour depends on its partial vapour pressure, it follows that the chemical potential of liquid A can be related to its partial vapour pressure.

¹ Peter Atkins, Peter William Atkins, and Julio de Paula. *Atkins' physi*cal chemistry. Oxford university press, 2014 Now, according to Raoult's law, for an ideal solution, we have the ratio of the partial vapour pressure of each component to its vapour pressure as a pure liquid is equal to the mole fraction of itself in the liquid phase (solution):

$$\frac{p_A}{p_A^*} = x_A \tag{7}$$

Therefore we have for a substance A in solution, we have its chemical potential to be

$$\mu_A = \mu_A^* + RT \log x_A \tag{8}$$

Usually, for a real solution, we have instead

$$\mu_A = \mu_A^* + RT \log a_A \tag{9}$$

where a_A is the activity of substance A to account for the non-ideal behavior of real solution compared with ideal solution. The non-ideality is essentially the interaction between molecules, which is neglected in ideal solution.

Change of Gibbs Free Energy of a Reaction

Define the change of a species i in a chemical reaction to be ν_i (i.e. the stoichiometry number). For example, for the intecalation reaction

$$A + 2B \Longrightarrow 3C + 4D \tag{10}$$

We can re-write it as

$$3C + 4D - A - 2B = 0$$
 (11)

Therefore $\nu_A = -1$, $\nu_B = -2$, $\nu_C = 3$, $\nu_D = 4$.

Now, for a reaction that moved along the reaction coordinate for an infinitely small step, we have the change of Gibbs free energy to be

$$\Delta G_r = \sum_i \nu_i \mu_i$$

= $\sum_i \nu_i (\mu_i^* + RT \log x_i)$
= $\sum_i \nu_i \mu_i^* + RT \log \prod_i x_i^{\nu_i}$ (12)

Define $\Delta G_{r,0} = \sum_i \nu_i \mu_i^*$, $Q = \prod_i x_i^{\nu_i}$, we have

$$\Delta G_r = \Delta G_{r,0} + RT \log Q \tag{13}$$

Nernst Equation

Now, we want to relate the maximum non-expansion work of a system outputs to concentration (mole fraction) of reaction species. Let's say we have a battery. According to the meaning of Gibbs free energy to be the maximum non-expansion work (proved in earlier sections), we have

$$\Delta G_r = -nFU$$

where U is the open-circuit voltage, n is the number of electron transferred. According to Equation 13, we have

$$U = -\frac{1}{nF} \Delta G_r$$

= $-\frac{\Delta G_{r,0}}{nF} - \frac{RT}{nF} \log Q$ (14)

Define $U_0 = -\frac{\Delta G_{r,0}}{nF}$, we have the Nernst Equation as

$$U = U_0 - \frac{RT}{nF} \log Q \tag{15}$$

For the intercalation reaction Li⁺ + HM==Li–HM, we have $Q = \frac{c_{Li-HM}}{c_{HM}}$, therefore we have

$$U = U_0 + \frac{RT}{F} \log \frac{c_{HM}}{c_{Li-HM}} = U_0 + \frac{RT}{F} \log \frac{1-x}{x}$$

where x is the filling fraction of Li.

Description of OCV in the framework of multi-species multi-reaction

When deriving

$$U = U_0 + \frac{RT}{F} \log \frac{c_{HM}}{c_{Li-HM}} = U_0 + \frac{RT}{F} \log \frac{1-x}{x}$$

we assumed ideality, i.e. non-interaction between atoms. To account for the non-ideality (which usually has great impact), we need to use activity coefficient instead of concentration or molar fraction:

$$U = U_0 + \frac{RT}{F} \log \frac{a_{HM}}{a_{Li-HM}}$$

Verbugge et al ², in their Multi-species multi-reaction (MSMR) model, suggested that instead of using activity, we can instead use an adjustable parameter ω to account for the non-ideality and still use the mole fraction,

$$U = U_0 + \omega \frac{RT}{F} \log \frac{c_{HM}}{c_{Li-HM}} = U_0 + \omega \frac{RT}{F} \log \frac{1-x}{x}$$

Correspondingly, we can also write Li filling fraction x as a function of U:

$$x = \frac{1}{1 + \exp \frac{F}{\omega RT}(U - U_0)}$$

² Mark Verbrugge, Daniel Baker, Brian Koch, Xingcheng Xiao, and Wentian Gu. Thermodynamic model for substitutional materials: application to lithiated graphite, spinel manganese oxide, iron phosphate, and layered nickelmanganese-cobalt oxide. *Journal of The Electrochemical Society*, 164(11): E3243, 2017 The key insight of MSMR is that for an intercalation reaction of battery electrodes Li + HM = Li - HM, it is assumed that there are *n* different collections of Li-intercalation sites (i.e. the so-called "Multi-species") in the host material (electrode) HM, and for each collections of sites, the reaction (i.e. the so-called "Multi-reaction") is

$$Li + HM_i = Li - HM_i$$

for each of these n reactions, according to the previous derivation, we have

$$U = U_0 + \frac{RT}{F} \log \frac{a_{HM_j}}{a_{Li-HM_j}}, \ \forall j \in [1, 2, ...n]$$

and as Verbugge et al suggested, instead of using activity of HM_j and $Li - HM_j$, we use ω_j instead to quantify the non-ideality of reaction j:

$$U_j = U_{0j} + \omega_j \frac{RT}{F} \log \frac{c_{HM_j}}{c_{Li-HM_j}} = U_{0j} + \omega_j \frac{RT}{F} \log \frac{X_j - x_j}{x_j}$$

where x_j means the filling fraction of Li within the j-th collection of sites, X_j is the fraction of j-th collection of sites within all Li sites. Obviously $0 \le x_j \le X_j$, and $\sum_j X_j = 1$. The total filling fraction of the host material HM, i.e. Li_xHM , is given by $x = \sum x_j$. Equilibrium enforces

 $U_j = U, \ \forall j \in [1, 2, \dots n]$

. Therefore for the whole electrode, we have

$$x = \sum x_j = \sum_j \frac{X_j}{1 + \exp \frac{F}{\omega_j RT} (U - U_{0j})}$$

Instead of expressing OCV U as a function of x, the MSMR OCV model expresses x as a function of U.

A beauty of this OCV expression is that it captures the multi-phase behavior of phase-changing electrode materials through the multi species and multiple collection of sites. As an example, let us look at the MSMR OCV model for graphite, shown in Figure 2. The model parameters are shown in Table 1.

j	$U_{0j}(V)$	X_j	ω_j
1	0.08843	0.43336	0.08611
2	0.12799	0.23963	0.08009
3	0.14331	0.15018	0.72469
4	0.16984	0.05462	2.53277
5	0.21446	0.06744	0.09470
6	0.36325	0.05476	5.97354





Figure 2: Open-circuit potential for the various reactions j of lithiated graphite. Reactions 1, 2, and 5 have two-phase character and substantially flat ocv



Figure 3: Experimental measured OCV value of graphite. There are 3 plateaus at 0.214V, 0.128V and 0.088V respectively.

is shown in figure 3. Note that reaction 1, 2, and 5 (all of which have ω_j value less than 0.1) have flat OCV curves, which correspond to the 3 miscibility gaps of lithiated graphite at 0.214V, 0.128V and 0.088V respectively. Other reactions show more variation in $x_j(U)$, consistent with single-phase behavior.

The MSMR model is implemented in open-sourced software PyBaMM.

The Thermodynamic Origin of ω_i

 ω_i as activity

Nernst equation states that

$$U_j = U_{0j} + \frac{RT}{F} \log \frac{a_{HM_j}}{a_{Li-HM_j}}$$

The MSMR OCV model states that

$$U_j = U_{0j} + \omega_j \frac{RT}{F} \log \frac{x_{HM_j}}{x_{Li-HM_j}} = U_{0j} + \frac{RT}{F} \log \frac{x_{HM_j}^{\omega_j}}{x_{Li-HM_j}^{\omega_j}}$$

Therefore we have

$$a_{HM_j} = x_{HM_j}^{\omega_j}$$
$$a_{Li-HM_j} = x_{Li-HM_j}^{\omega_j}$$

As stated in the previous section, ω_j is another way to quantify the non-ideality, besides activity.

If we define activity coefficient γ_j as $a_j = \gamma_j x_j$, then we have

$$\gamma_{HM_j} = x_{HM_j}^{\omega_j - 1}$$
$$\gamma_{Li - HM_j} = x_{Li - HM_j}^{\omega_j - 1}$$

Therefore, the following expressions of chemical potential of species j are equal under the MSMR framework:

$$\mu_j = \mu_{j0} + RT \log a_j = \mu_{j0} + \omega_j RT \log x_j$$

Single or Double Phase

For each collection of sites, we can write the Gibbs free energy for the collection of site as

$$G_{j} = x_{j}\mu_{Li-HM_{j}} + (X_{j} - x_{j})\mu_{HM_{j}}$$

$$= x_{j}(\mu_{Li-HM_{j}}^{0} + RT \log a_{Li-HM_{j}}) + (X_{j} - x_{j})(\mu_{HM_{j}}^{0} + RT \log a_{HM_{j}})$$

$$= x_{j}(\mu_{Li-HM_{j}}^{0} + \omega_{j}RT \log x_{j}) + (X_{j} - x_{j})(\mu_{HM_{j}}^{0} + \omega_{j}RT \log(X_{j} - x_{j})))$$

$$= x_{j}(\omega_{j}\mu_{Li-HM_{j}}^{0} + \omega_{j}RT \log x_{j}) + (X_{j} - x_{j})(\omega_{j}\mu_{HM_{j}}^{0} + \omega_{j}RT \log(X_{j} - x_{j})) + (1 - \omega_{j})(x_{j}\mu_{Li-HM_{j}}^{0} + (X_{j} - x_{j})\mu_{HM_{j}}^{0})$$

$$= \omega_{j}G_{j}^{ideal} + (1 - \omega_{j})(x_{j}\mu_{Li-HM_{j}}^{0} + (X_{j} - x_{j})\mu_{HM_{j}}^{0})$$
(16)

³ PyBaMM Develop Team. Multi-Species Multi-Reaction model. https://github.com/ pybamm-team/PyBaMM/blob/ d88b7ddcfa6f563100d92c11cdc97b50f261629b/ docs/source/examples/notebooks/ models/MSMR.ipynb#L38. Accessed: 2023-11-15 When $\omega_j = 1$, the collection of site is an ideal, single-phase system. When $\omega_j = 0$, the collection of site is a two-phase system, with the free energy dependent only on the chemical potentials of the two pure species, $\mu^0_{HM_j}$ and $\mu^0_{Li-HM_j}$, no compositional dependence is seen. However, it should be noted that ω_j , in principle, is still a fitted parameter, it can have value larger than 1 (as seen in the parameter value for graphite), when no clear physical meaning is known.

Description of Diffusion in the Framework of Multi-Species Multi-Reaction

What lies at the central of diffusion model is $\nabla \mu$, which is then connected to flux as $J = -\frac{D}{RT}x\nabla\mu$ (where x is the concentration, not coordinate) as Fick's law describes, then finally mass conservation $\frac{\partial x}{\partial t} = -\nabla \cdot J$. In this section, we will derive $\nabla \mu$. Fick's law can actually also be derived with atomistic pictures, see refs⁴.

Define the chemical potential of lithiated host material Li - HM as μ , the chemical potential of filled sites within j-th collection of sites as μ_{Li-HM_j} , the chemical potential of unlithiated host material HM as μ_{HM} , the chemical potential of unfilled sites within j-th collection of sites as μ_{HM_j} , the change of total lithium filling fraction as dx, the change of lithium filling fraction of j-th collection of site as dx_j . We have

$$\mu dx = \sum_{j} \mu_{Li-HM_{j}} dx_{j}$$
$$dx_{HM} = -dx$$
$$dx_{HM_{j}} = -dx_{j}$$
$$\mu_{HM} dx_{HM} = \sum_{j} \mu_{HM_{j}} dx_{HM_{j}}$$
$$\mu_{HM} dx = \sum_{j} \mu_{HM_{j}} dx_{j}$$
$$\mu_{HM} = \sum_{j} \mu_{HM_{j}} \frac{dx_{j}}{dx} = \sum_{j} \mu_{HM_{j}} \frac{dx_{j}}{\frac{dU}{dU}}$$
$$\mu = \sum_{j} \mu_{Li-HM_{j}} \frac{dx_{j}}{dx}$$

Then we plug-in the expression of μ and μ_{HM} , and will have

$$\mu - \mu_{HM} = \sum_{j} (\mu_{Li-HM_j} - \mu_{HM_j}) \frac{dx_j}{dx}$$

Remember for each reaction $Li + HM_i = Li - HM_i$ we have

$$-FU = \mu_{Li-HM_j} - \mu_{Li} - \mu_{HM_j}$$

⁴Ling Zhang. Lecture 3: Diffusion: Fick's first law. https://my.eng.utah. edu/~lzang/images/lecture-3.pdf. Accessed: 2023-11-15 i.e.

$$\mu_{Li} - FU = \mu_{Li - HM_j} - \mu_{HM_j}$$

plug-in to have

$$\mu - \mu_{HM} = \sum_{j} (\mu_{Li} - FU) \frac{dx_j}{dx}$$
$$= (\mu_{Li} - FU) \sum_{j} \frac{dx_j}{dx}$$
$$= (\mu_{Li} - FU)$$
(17)

.1 . .

Therefore

$$\mu - \mu_{HM} = (\mu_{Li} - FU)$$

and subsequently

$$d\mu - d\mu_{HM} = -FdU \tag{18}$$

. From Gibbs-Duhem euqation and under constant temperature and pressure, we have

$$xd\mu + (1-x)d\mu_{HM} = 0$$

therefore

$$d\mu_{HM} = -\frac{x}{1-x}d\mu$$

plug-in to Equation 18, we have

$$d\mu + \frac{x}{1-x}d\mu = \frac{1}{1-x}d\mu = -FdU$$

therefore for a coordinate system r, we have

$$\nabla \mu = \frac{d\mu}{dr} = -F(1-x)\frac{dU}{dr} = -F(1-x)\frac{dU}{dx}\frac{dx}{dr} = -F(1-x)\frac{dU}{dx}\nabla x$$

Note that here x is the concentration (usually expressed as c in literature), r is the coordination, d operates on x and ∇ operates on r. Now plug-in the expression of $\nabla \mu$ to Fick's law, we have

$$\frac{\partial x}{\partial t} = -\nabla \cdot J$$

$$= -\nabla \cdot \left(-\frac{D}{RT}x\nabla\mu\right)$$

$$= -\nabla \cdot \left(D\frac{F}{RT}x(1-x)\frac{dU}{dx}\nabla x\right)$$
(19)

Application of MSMR: Aging Analysis

Before walking through an application of MSMR, we shall first get some background knowledge which helps us understand things better.

The voltage changes associated with a change in electrode balance and/or a change in the electrode signature (e.g. phase change) are in



Figure 4: Open circuit potential and differential voltage curves of comparing optimized computed (orange) to experimental (blue) data for fresh cells (a), (b), cells that have been aged over 300 cycles (c), (d), and cells that have been aged over 600 cycles (e), (f), with their reported mean absolute values. Overall, DV can detect minor differences, while such difference is hard to find in V vs Q plots.

most cases small, e.g. a few mV, and are therefore difficult to visualise and quantify on the classic voltage (V) vs. capacity (Q) curve in which the voltage range typically spans approximately 2 V, see Figure 4 for example ⁵. Therefore you want some plots more sensitive to these changes. The incremental capacity (IC) analysis, or dQ/dV (or equivalently dx/dU), as shown in Figure 5 (b), and the differential voltage analysis, or dV/dQ (or equivalently dU/dx), as shown in Figure 5(c), are two powerful tools. It can be seen that for the dQ/dV curve, the peaks indicates phase changes. For dV/dQ curves, peaks indicate solid solutions.

The best part of dV/dQ curves is they are additive. For a battery, its open-circuit voltage is

$$V = U_{pos}(Q_{pos}) - U_{neg}(Q_{neg})$$

where $Q_{pos} = Q_{pos,ref} + Q$ is the amount of charge in positive electrode, $Q_{neg} = Q_{neg,ref} - Q$ is the amount of charge in negative electrode, Q is the total amount of usable charge capacity (which might change after many cycles, i.e. aging). Therefore,

$$\frac{dV}{dQ} = \frac{\partial U_{pos}}{\partial Q_{pos}} \frac{\partial Q_{pos}}{\partial Q} - \frac{\partial U_{neg}}{\partial Q_{neg}} \frac{\partial Q_{neg}}{\partial Q} = \frac{dU_{pos}}{dQ_{pos}} + \frac{dU_{neg}}{dQ_{neg}}$$

which means the dV/dQ curve of the whole cell is weighted sum of dV/dQ (e.g. dU/dx) curves of individual electrodes.

In the MSMR framework, the dx/dU (i.e. dQ/dV) is

$$\frac{dx_j}{dU} = -\frac{X_j}{\omega_j} \frac{f \exp f(U - U_{0j}/\omega_j)}{(1 + \exp f(U - U_{0j}/\omega_j))^2}$$
$$\frac{dx}{dU} = \sum_j \frac{dx_j}{dU}$$

Capacity loss can be associated with changes in the solid state insertion electrodes and/or faradaic inefficiencies on one electrode or the other. Most forms of degradation lead to slippage in the electrodes, meaning that the utilization window over which the electrodes are cycling shifts as the battery is being degraded. In differential voltage data, these phenomena can lead to an changes in peak heights in the differential voltage and peak location shifts along the voltage axis associated with voltage slippage.

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⁵ Anup Barai, Kotub Uddin, Matthieu Dubarry, Limhi Somerville, Andrew McGordon, Paul Jennings, and Ira Bloom. A comparison of methodologies for the non-invasive characterisation of commercial li-ion cells. *Progress in Energy and Combustion Science*, 72:1–31, 2019; and Victor W Hu and Daniel T Schwartz. Low error estimation of halfcell thermodynamic parameters from whole-cell li-ion battery experiments: Physics-based model formulation, experimental demonstration, and an open software tool. *Journal of The Electrochemical Society*, 169(3):030539, 2022



Figure 5: Relationship between (a) voltage curve and derivative curves (b) IC and (c) DV



Figure 6: Relationship between (a) voltage curve and (b) DV



Figure 7: Example of qualitative application of EVS for accelerated aging. Protocols A, B, and C are different hypothetic protocols (i.e. different currents, temperatures, SoC ranges...). IC helps detecting different degradation mechanisms.

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