

# Computational Modeling of Zn-ion Battery Using Chevrel Cathode

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# 1 Introduction

With the increased use of electronics, the need to store electrical energy has become an essential part of every day life. It is for this reason that the explosion in popularity of rechargeable lithium ion batteries is not hard to explain. It has proven to be a robust technology with high energy densities and cyclability, perfect for handheld devices. However, it is less well suited for mid to large scale application, such as in electric vehicles and grid stabilization given associated safety concerns. Alternative battery chemistries may be more well suited for use in meso scale and macro scale energy storage, which will become increasingly important as renewable energy becomes a growing fraction of our power grids. One promising possible option may be rechargeable magnesium ion or zinc ion batteries. These multivalent ions carry twice the charge per ion as compared to lithium, however they suffer from reduced mobility because of this more highly concentrated charge. To overcome this, and other shortcomings, it has become necessary to gain a deeper understanding of the transport and kinetics involved in these battery systems. It is possible that the anode for Mg ion and Zn ion batteries can be the metals themselves. This would bring with it very high energy and charge densities. It is for this reason that much attention is currently being paid to the electrolyte and cathode materials.

Aurbach et al. (2000) brought rechargeable magnesium ion batteries into reality when it was demonstrated that the chevrel phase ( $\text{Mo}_6\text{S}_8$ ) is capable of accommodating  $\text{Mg}^{2+}$  ions into its crystal lattice with relative ease and fast kinetics. Later, Chen et al. (2014) would collect detailed cycling data on  $\text{Mg}^{2+}$  ion batteries. Kim et al. (2016) took this data and created an impressive computer model around the chevrel cathode of these secondary batteries. The model of Kim et al. made it possible to take a glimpse at what may be happening inside the small particles of the cathode material during charging, giving insight into what the optimal cathode particle size may be as well as transport limitations of the material.

However, Aurbach et al. (2000) did not just inspire research into magnesium ion battery systems. The implication of  $\text{Mg}^{2+}$  as a viable working ion inspired many to look into other multivalent ions. Among these,  $\text{Zn}^{2+}$  has also become increasingly interesting as a battery material. Given that Zn ion batteries have already demonstrated their viability as a primary (non-rechargeable) battery material it is

easy to imagine why Zn ion batteries would seem like a desirable secondary battery component.  $\text{Zn}^{2+}$  could possibly be used as a working ions for secondary batteries. Cycling data of Zn ion batteries has been collected and could be compared to much in the way that Kim et al. (2016) has done. The systems of differential equations used by Kim et al., however, is complicated and is outside the scope that can be encompassed in one semester. In this work the first steps towards modeling the  $\text{Zn}^{2+}$  chevrel cathode system will be taken, shadowing the what has been accomplished by Kim et al., in the hopes of shedding some light on how the transport and kinetics of  $\text{Zn}^{2+}$  intercalation into the chevrel phase differ from and are similar to those of the  $\text{Mg}^{2+}$  system so that the chemistry can be optimized for the used in rechargeable Zinc ion batteries.

## 2 Methods

### 2.1 Newman and Tobias's One Dimensional Electrode

Ultimately, Kim et al. only gives the equations used and does not at all describe the methods used to solve them simultaneously. It is for this reason that the work of this paper starts from the most rudimentary of battery models. Newman and Tobias, in 1962, demonstrated to the electrochemical community how to first model batteries as a porous electrode. Historically, Newman used the BAND method of solving a system of ordinary differential equations, in a steady state battery system. With Python it is no longer necessary to use this method, which requires initial guesses close to the true value, as it requires the linearization of exponential equations. However, the equations that Newman and Tobias proposes still prove to be very useful in the modeling of batteries. They divide the current and potential into two components, the current held by the electrons carried through the solid state cathode and the potential of the this solid state, as well as the current held by the ions carried by the liquid electrolyte and the potential of the electrolyte itself present their relationship as such:

$$i_1 = -\sigma \nabla \phi_1 \quad \text{current through the solid phase (cathode)} \quad (1)$$

$$i_2 = -\kappa \nabla \phi_2 \quad \text{current through the liquid phase (electrolyte)} \quad (2)$$

$$\nabla \cdot i_1 + \nabla \cdot i_2 = 0 \quad \text{charge balance equation} \quad (3)$$

$$\nabla \cdot i_2 = ai_0 \exp[\beta(\phi_1 - \phi_2)] \quad \text{Butler-Volmer Equation} \quad (4)$$

Equations 1 and 2 are essentially modified versions of Ohm's Law. These equations can be simplified into one dimensional functions dependent only on  $x$  (distance from the separator into the cathode) and have the following boundary conditions:

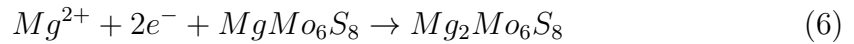
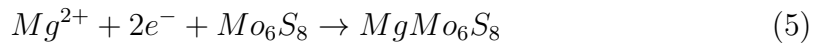
$$\text{At } x = 0, i_2 = i_{app}, i_1 = 0, \phi_2 = 0$$

$$\text{At } x = L, i_2 = 0$$

where  $L$  is the total depth of the cathode. Intuitively, the current must be held entirely in the electrolyte at the very start of the cathode material, and conversely held entirely by the cathode at the full length of the cathode. Also, the potential is arbitrarily set to 0 at  $x = 0$  as that is the reference potential of the system much in the same way that the potential of the Zn ion battery system uses the potential of zinc metal set to zero as its reference potential or the Mg ion battery system sets the potential of magnesium metal to zero.

## 2.2 Modeling Change in Transport and Kinetics for the Two Chevrel Phases

One of the innovations that Kim et al. (2016) introduced into the modeling of the  $Mg^{2+}$  system was the use of a step function. This is a response to the voltage drop that is so characteristic of rechargeable batteries using chevrel cathodes. Using X-ray diffraction Levi et al. (2006) showed that two reactions dominate the Mg ion battery system in the cathode, and that these two reactions happened sequentially. These two reactions being as follows:



The implication of these two reactions happening sequentially has a physical manifestation that become apparent when analyzing the voltage as a function of

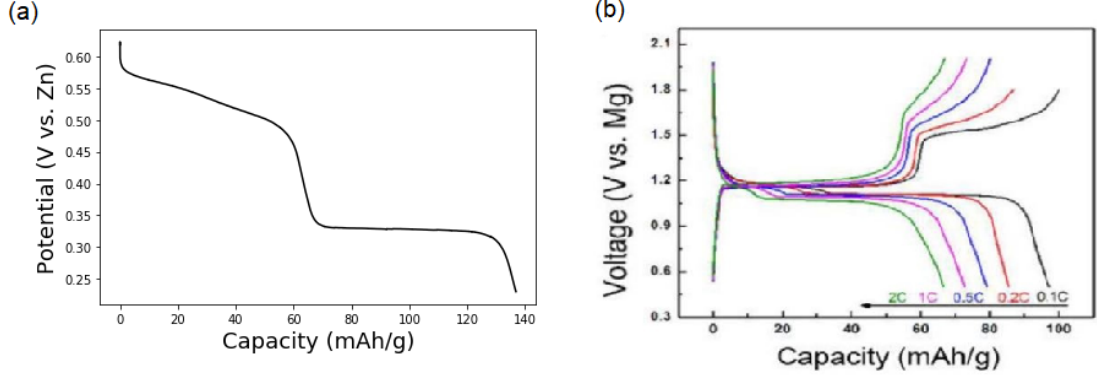


Figure 1: Potential vs. Capacity curves for (a) the Zn ion battery tested here and (b) the Mg ion batteries of Chen et al. at several different rates of discharge. Figure 1 (b) also includes the potential curve for the recharge portion of the cycle. But, in both the Zn and Mg case it can be observed that there are two distinct potentials at which the battery chemistry will discharge at, depending only on the state of charge of the battery.

total voltage. Figure 1 shows discharge curves for both (a) Zn ion and (b) Mg ion batteries. In both cases there is a drop in voltage. But, this is not a drop in voltage that is associated with exhaustion of reactants. The drop in voltage is associated with the transition of the main reaction transitioning from equation 5 to equation 6. Kim et al. captured these physical manifestations using the following equations:

$$D_s = \frac{D_{s,fast} - D_{s,slow}}{2} \tanh[S_D(y - 0.5)] + \frac{D_{s,fast} + D_{s,slow}}{2} \quad (7)$$

$$i_{0,pos} = \frac{i_{0,fast} - i_{0,slow}}{2} \tanh[S_i(y - 0.5)] + \frac{i_{0,fast} + i_{0,slow}}{2} \quad (8)$$

The parameters that seem to be most effected by the transition from equation 5 to equation 6 are the diffusion and kinetics at the electrode surface, in the form of the exchange current density. Intuitively, these parameters would be deeply effected as the state of reduction of the cathode material, and therefore the electron environment will be very different between  $\text{Mo}_6\text{S}_8$  and  $\text{MgMo}_6\text{S}_8$  in regards to its receptiveness to positively charged ions.

## 2.3 Depth of Diffusion into Cathode Material

Kim et al. presents the following equations to be used in their model:

**Charge balance in solid phase:** A modified Ohm's Law, analogous to equation 1.

$$\frac{\partial}{\partial x} \left( -\sigma_{eff} \frac{\partial \phi_s}{\partial x} \right) = -\alpha_v i_n \quad (9)$$

**Charge balance in electrolyte:** A further modified Ohm's Law, analogous to equation 2.

$$\frac{\partial}{\partial t} \left( -\kappa_{eff} \frac{\partial \phi_e}{\partial x} \right) + \frac{2\kappa_{eff}RT(1-t_+^0)}{F} \left( 1 + \frac{\partial \ln f_{+-}}{\partial \ln c_e} \right) \frac{\partial}{\partial x} \left( \frac{\partial c_e}{\partial x} \right) = a_v i_n \quad (10)$$

**Mass balance in electrolyte:** Relating the migration of ions in electrolyte to the current.

$$\frac{\partial \varepsilon_e C_e}{\partial t} = \frac{\partial}{\partial x} \left( D_{e,eff} \frac{\partial C_e}{\partial x} \right) + \frac{1-t_+^0}{F} \alpha_v i_n \quad (11)$$

**Mass balance in solid phase:** This is one of the larger innovations of Kim et al. to take into consideration depth of diffusion into individual particles of cathode material and introduces a third dependent variable.

$$\frac{\partial C_s}{\partial t} = D_s \left( \frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r} \frac{\partial C_s}{\partial r} \right) \quad (12)$$

Unlike the Newman and Tobias model, where the current and the potential are clearly related to each other by their current, the dependence of these equations on one another is related through the nominal current, which is position and time dependent.

Ultimately, Python is not intrinsically capable of handling partial differential equations. It is for this reason that the Method of Lines was used. Partial differential equations that were second order in position (x) or depth (r) were put into the form:

$$\frac{\partial^2 u}{\partial x^2} = \frac{u(x+h) - 2u(x) + u(x-h)}{h^2} \quad (13)$$

and put into the native odeint available in Python to solve for the function that is first order in time. This did come with some large limitations as to would could be solved using this method, and this will be discussed later.

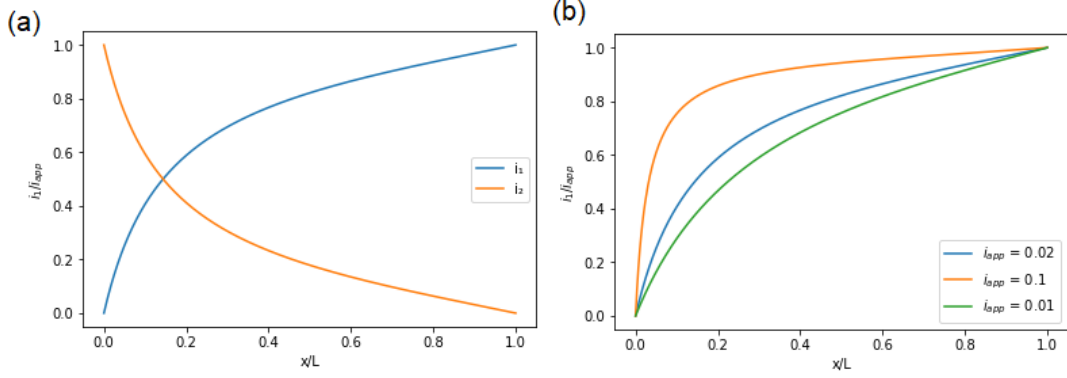


Figure 2: The distribution of the current (a) of different phases can be seen here. The current carried by the solid cathode material ( $i_1$ ) starts at 0 at the very start of the cathode and slowly becomes the sole carrier of current as working ions diffuse into the particles of the cathode material. The opposite is true for the current held by the electrolyte ( $i_2$ ). The rate of discharge of the battery (b) change the distribution of the current through the cathode, which is to be expected

### 3 Results and Discussion

#### 3.1 Newman and Tobias Model

Python's built in boundary value problem solver (`solve_bvp`) proved to be robust enough to solve the simplified one-dimensional model porous electrode model proposed by Newman and Tobias. As discussed earlier, this is a steady state calculation independent of the concentration of the electrolyte. But, these beginning values prove useful for initial calculations, and will be used for some simplified models.

#### 3.2 Kim et al. Model

Solving all the differential equations proposed by Kim et al. is challenging give that the system, overall, is characterized by 3 independent variables ( $x, t, r$ ) and 4 dependent variables ( $C_s, C_e, \phi_s$  and  $\phi_e$ ). It is for this reason that for the scope of this project, the differential equations were solved independently. Despite the inaccuracy associated with solving of the equations independently, some genuine insight may be gleaned from the results. To begin, the nominal current as a



function of time, and position this was done using the Butler-Volmer equation with equation 8. Doing this gives a function for current that is dependent on time and position (intuitively, current is independent of diffusion into the cathode particles).

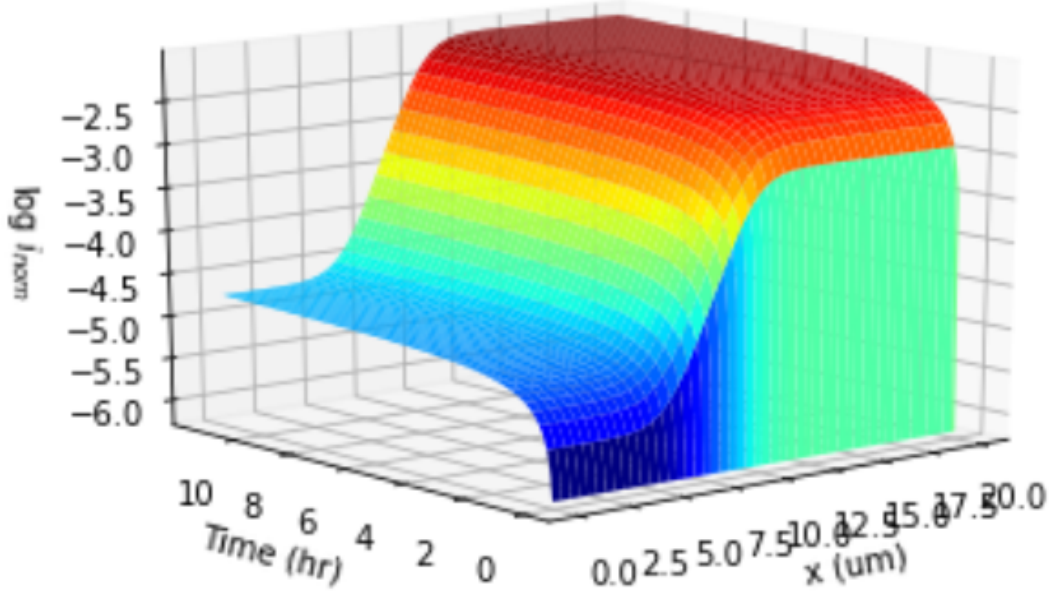


Figure 3: Nominal current as a function of position along the length of the cathode and time of discharge.

It is fortunate that the nominal current seems to be strongly dependent on the position along the cathode and weakly dependent on the time of discharge (which is strongly correlated to the fractional conversion of  $\text{Mo}_6\text{S}_8$  to  $\text{MgMo}_6\text{S}_8$  and onto to  $\text{Mg}_2\text{Mo}_6\text{S}_8$ ). For the remainder of the work, the nominal current ( $i_{\text{nom}}$ ) will be assumed to be only a function of position ( $x$ ). This simplification is very necessary to make the following calculations possible. More on this in the Challenges section.

The most unique characteristic of the model proposed by Kim et al. is the introduction of a third dependent variable, radius. Taking into consideration the diffusion of working ions into the individual particles of the porous cathode, as opposed to considering the porous cathode one large, uniform material, greatly deviates from older models, and is what makes the work of Kim et al. so intriguing.

ing. Equation 12 may not seem dependent on position  $x$ , but it does reflect the concentration of the solid, which is dependent on the potential along the cathode. It is for this reason that this equation would indeed need to be solved simultaneously with the other differential equations. But, for now it is solved independently, and shows the behavior that would be expected.

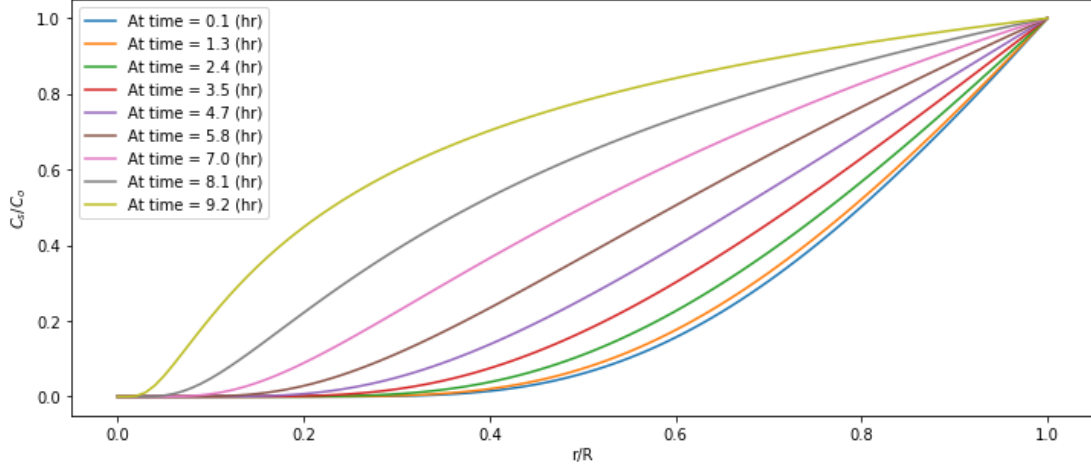


Figure 4: Depth of diffusion of working ion into spherical cathode particles.

Working ions have trouble diffusion entirely into the spherical cathode particles. Even after long time of discharge, the very center of chevrel spheres are resistant to intercalation by working ions. Perhaps this reflects the accumulation of positive charge in the cathode particles (due to cation insertion) causing electrostatic repulsion in at the very center of the particle.

The concentration of the electrolyte could also be solved independently, under the assumption that the voltage is uniform and that the current reaches steady state (which seems to be a decent assumption). Equation 11 was also solved independently using the Method of Lines. For some reasons the results of the solution are a complete inversion of what was to be expected.

The concentration should start at its maximum values and drop from there, and as time passes the concentration should drop throughout the cathode. Essentially, there seems to be problem in correctly applying the boundary conditions as, at  $t = 0$ , if all the values start at the max concentration of working ion in the electrolyte this would correctly reflect what Kim et al. also reported in their

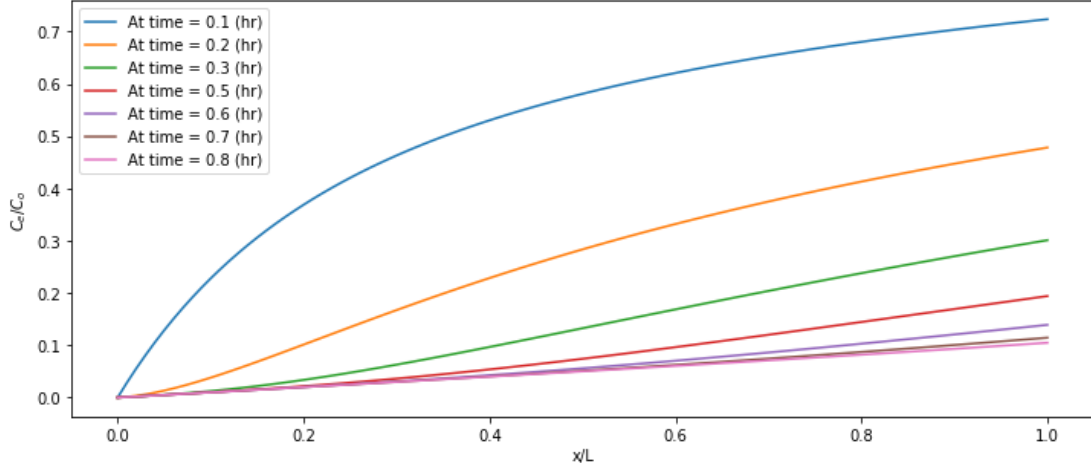


Figure 5: Concentration of working ion through cathode material.

works. Regardless, what is in good agreement, is that the concentration of the electrolyte equilibrates very quickly, which is to be expected as the applied current, and the potential applied reach steady state values almost immediately. Also in good agreement is that the concentration of working ion in the electrolyte at the end of the cathode, drops continuously as discharge continues but reaches a steady non-zero value. One reason there may be trouble in applying the boundary condition is that the model of Kim et al. was written only for the charging phase of a battery cycle, not for the discharge phase. Though, Kim et al. does state that when reversing the current (going from recharging to discharging) there was still good agreement, but clearly the model presented here is not nearly as robust as that of Kim et al.

## 4 Challenges

There were many challenge involved in the modeling of this system. Conceptually, the system is complicated and in some ways hard to understand. Kim et al. shows concentration in the solid as a function of depth into spherical particles and time, but this disregards the position of that particle in the macroscopic cathode. Particles near the separator will probably reach maximum concentration sooner than those at the current collector. An appreciation for the work of Kim et al. was

definitely gained during this project, as it only became increasingly apparently how impressive it is to have modeled such a system.

The greatest challenge of the project was trying find a way to solve partial differential equations that are not separable. At first glance the differential equations presented by Kim et al. did not seem to be inseparable, but time dependent values are actually nested in other values, in most cases the nominal current ( $i_{nom}$ ). The first attempt was to use the source code of the odeint function built into Python to gain access the which index of both independent variables the function is on during solving, i.e. in the solving of equation 11 the dependent variable  $x$  was handled in the *for loop* therefore variables dependent on position could be calculated dynamically, however, since iteration of the independent variable time is handled in the odeint function, it is not possible to dynamically calculate values dependent on time. However, "highjacking" of the odeint function was not possible upon the realization that the actual calculations are run in FORTRAN. That is to say, that the difficulty in solving inseparable partial differential equations is markedly much greater than solving separable ones.

A second attempt involved writing our own odeint, using Euler's that could handle variable amounts of differential inputs. This code is as follows: Being able

```
def my_odeint(function,y0,x):
    y = np.zeros((np.size(x),np.size(y0)))
    y[0,:] = y0
    for i in range(len(x)-1):
        dx = x[i+1]-x[i]
        y[i+1,:]=y[i,:] + np.asarray(function(y[i,:],x[i]))*dx
    return y
```

to use this code in place of odeint, and placing the partial differential equation function inside of it so it would have been possible to know which index of both position ( $x$ ) and time ( $t$ ) the calculation was on, so that values dependent on both (like  $i_{nom}$ ) would have been dynamically calculated for any combination of time and position. But, for some reason using our odeint would lead to no convergence of answers, possibly do to the step size being to large, and any attempt to shrink the step size to gain convergence to a solution would cause run time errors. It is worth noting that our odeint function worked perfectly well in solving problems involving

rabbits and foxes. The next attempt was to use the Runge-Kutta method, however debugging of this code proved time consuming and was not completed before this writing.

Future attempts would involve fitting/optimization, and checking that the calculated dependent values of one independently solved PDE would match those of another PDE, in a sense, while still solving them independent, having the converge to agreed upon values of arrays such as checking to make sure that the value for  $C_e$  between equations 9 and 10 match followed by matching  $i_{nom}$  match between 11 and 9 and in this way "tying" all of the differential equations together while varying fitting parameters.

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