Comparing nucleation and growth models for Li_2O_2

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Abstract

The global desire to reduce carbon emissions to avoid global warming has led to support of technology which reduces consumption of fossil fuel. In turn, increased demand for electric vehicles (EV). Energy density and composition are key to new battery technology as they both determine how much material is needed and how expensive building the battery will be. Lithium-ion batteries are the predominant technology used for rechargeable energy storage, but their energy density has capped at around 600 kWh/kgbattery [1]. This energy density is not sufficient to provide for driving range above 310 miles and smaller storage units, which can reduce capital costs. Lithium air (Li-Air) batteries have a theoretical energy density of 3500 kWh/kgLi, and an experimental energy density of around 1200-1800 kWh/kg on their first discharge cycle [1, 2]. The lightweight and inexpensive air cathode makes the technology favorable over other energy storage solutions [3].

While Li-ion batteries store intercalation, which can be modeled through a diffusion process [4], the accumulation of Li_2O_2 happens through particle nucleation and growth. This makes the exposed surface area important. In order to create models which accurately predict the storage capabilities of the battery, an accurate expression for nucleation and growth of particles should be developed. Currently, most papers use equations based on concentration [5, 6], and similar to those used to use in nonelectrochemical systems. For my project, I proposed applying an electrochemical model, typically used for electrodeposition, for nucleation and growth (ENG) [7, 8]. This model could eventually be compared to experimental data and heterogeneous nucleation and growth (HNG).

After attempting to validate the electrochemical model, and discovering the generation of negative areas, despite verification of equations, concentration gradients were added to a prior nucleation and growth model.

1 Electrochemical model:

The model starts by assuming a certain overpotential, and then examining the change in overpotential the nucleation and growth undergoes. All properties were taken from [8], while the equations were taken from [7, 8]. Table 1 shows those properties. First, the current was calculated using the assumption that transport was diffusion limited

$$i = \frac{zec_0}{r}D\left[1 - e^{-f\eta}\right]$$

Where $f = \frac{ze}{k_bT}$, in these equations, z is the charge transfer, r is the radius, η is the overpotential, e is the elementary charge, T is the temperature, and k_b is Boltzmann's constant. The change in radius was modeled by the equation

$$\frac{dr}{dt} = \frac{c_0vD}{r}\left[1 - e^{-f\eta}\right]$$

The voltage drop was calculated using the equation: $\frac{d\eta}{dt} = \frac{i_0 - \frac{2\pi r^2 i}{A}}{C_d + zef\Gamma e^{f\eta}}$ Here, i_0 is the exchange current density, A is the area, C_d is the specific capacitance of the double layer and Γ is the adatom concentrations. All values for the parameters were taken from the original reference.
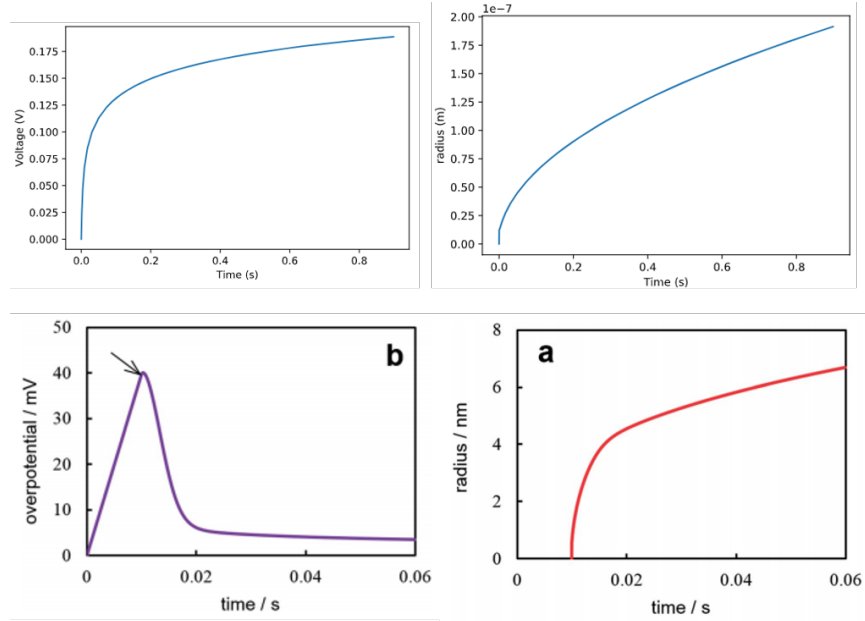
Figure 1: Validation of ENG model compared to data in [7])

Figure 1 shows the model validation, where all parameters are the same compared to the paper values. The voltage spike could not be replicated, despite repeated attempts. Furthermore, in an attempt to determine the reason for this result, the change in area was calculated. Shown in Figure 2, the area is negative for the entire duration of the code. The persistence of negative area values indicates these equations do not sufficiently control for area decreases.

Table 1: Literature properties for the ENG model

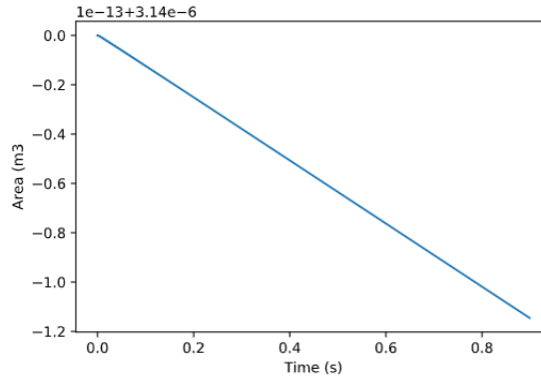| Property	Definition	Value
s	electrode area	3.14E-20 m^3
C_d	double layer capacitence	80 μFcm^{-2}
Γ_0	Adatom concentration	1.2 E13 cm^{-2}
σ	surface tension	1E-5 J cm^{-2}

Figure 2: Area calculations

2   ADDITIONS TO PRIOR HNG MODEL

As the ENG model could not be rendered as functioning, I added a preliminary mass control model to my previous HNG model. Currently that model only contains only growth and assumes a set number of nuclei. The base equation for the change in radius can be derived from the change in mass, which is based on the following [2]:

$$dn/dt = k_f S - k_R A$$

Where:
$$k_R = k_r exp((2/MW)/(RTr_c rit))$$
To express this in a change in radius, the right side of the equation should be multiplied by inverse of the molar volume, and the area expressed in terms of radius.
$$dr/dt = MW/k_f S - k_R 2r^2$$
After starting with an initial concentration, equal to the concentration of the electrolyte salt, two equations were developed: one for the electrolyte phase, and one for the cathode. For the electrolyte phase, it was assumed that Li^+ ions entered the solution at the same rate as the current, which is calculated using the Butler Volmer equation:
$$j = j_0 \left[e^{\frac{\alpha F \eta}{RT}} - e^{\frac{-\beta F \eta}{RT}} \right]$$
This leads to a flux of Li^+ ions
$$N = \frac{I}{F}$$
In the electrolyte, the change in concentration would equal to
$$\frac{\partial c}{\partial t} = -Dc - \frac{i_2 t}{zvF} + \frac{I}{F}$$
Where t is the transport number and v is the number of cations per unit [10]. This formula was partially derived by me, so I'm a little worried I'm double counting somewhere. In the cathode, there will be again diffusion and current related terms, while some amount of L^+ ions will exit depending on radial growth.
$$\frac{dc}{dt} = Dc + \frac{i_2 t}{zvF} - \frac{dr \rho 2\pi r}{dt MW}$$

For this run, the properties were taken from two different papers [11, 12], in Table 2. Figure 3 shows the radial and concentration change before and after the added code. The larger value for the radius shows that higher amounts of concentration is created by additional Li^+ ions in the generation term.

Table 2: Literature Properties used for the HNG model

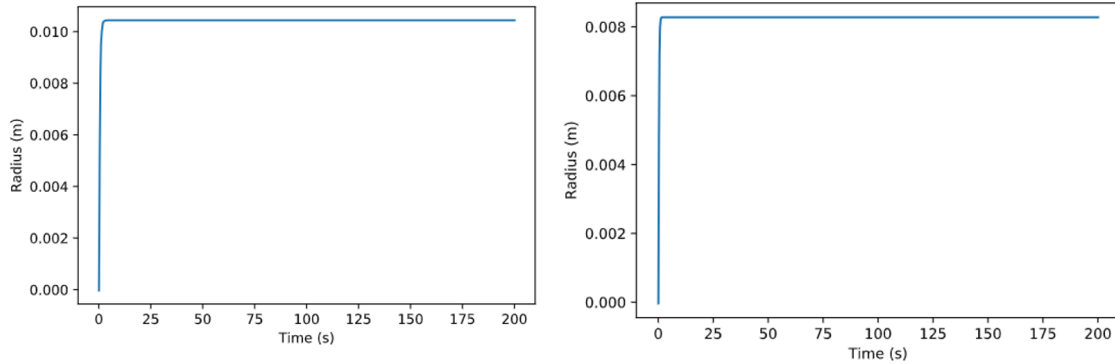| Property	Definition	Value
D [11]	Diffusion coefficient	7.3E-10 $m^2 s^{-1}$
t [11]	transport number	0.15

Figure 3: HNG model run (a) before addition of new equations and (b) after addition of new equations

3 CONCLUSIONS

Both codes require additional work. In prior versions of the ENG code, I had included nucleation, but encountered math errors at certain voltages. This led me to discover the negative areas, I've begun to doubt the efficacy of the EHG modeling. A second eye might be helpful, the radial trends seem similar enough to those presented in the paper, so perhaps there are extra considerations to the voltage that I haven't accounted for. For the HNG model, the flux equations need to be verified and additional elements, such as voltage changes should be added to make the model more realistic.

4 REFERENCES

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When you're a heterogenous interface that's in proximity to both an electron and ion