Thin-film Model for Discharge Process of Li-O_2 Battery

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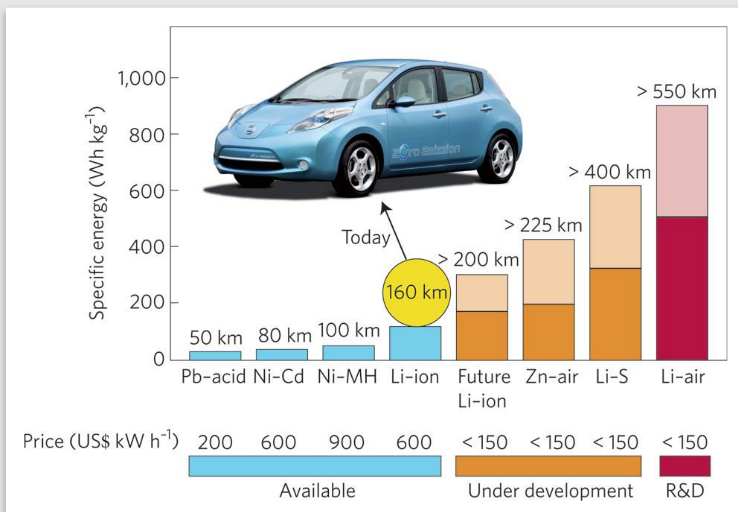
Introduction

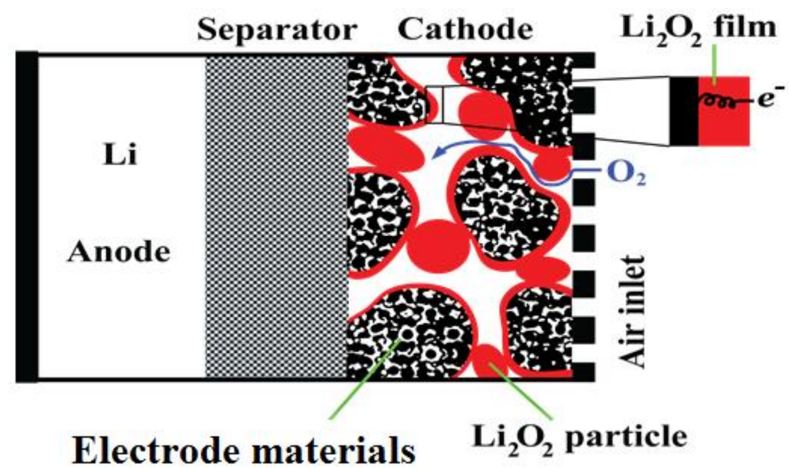
Theoretical Capacity:

$$Q = \frac{nF}{M} = 1165\, mAh/g_{Li_2O_2}$$

n : number of electrons
M: molar mass of active material



P.G. Bruce *et al. Nature Materials* **11**, 19 (2012) .

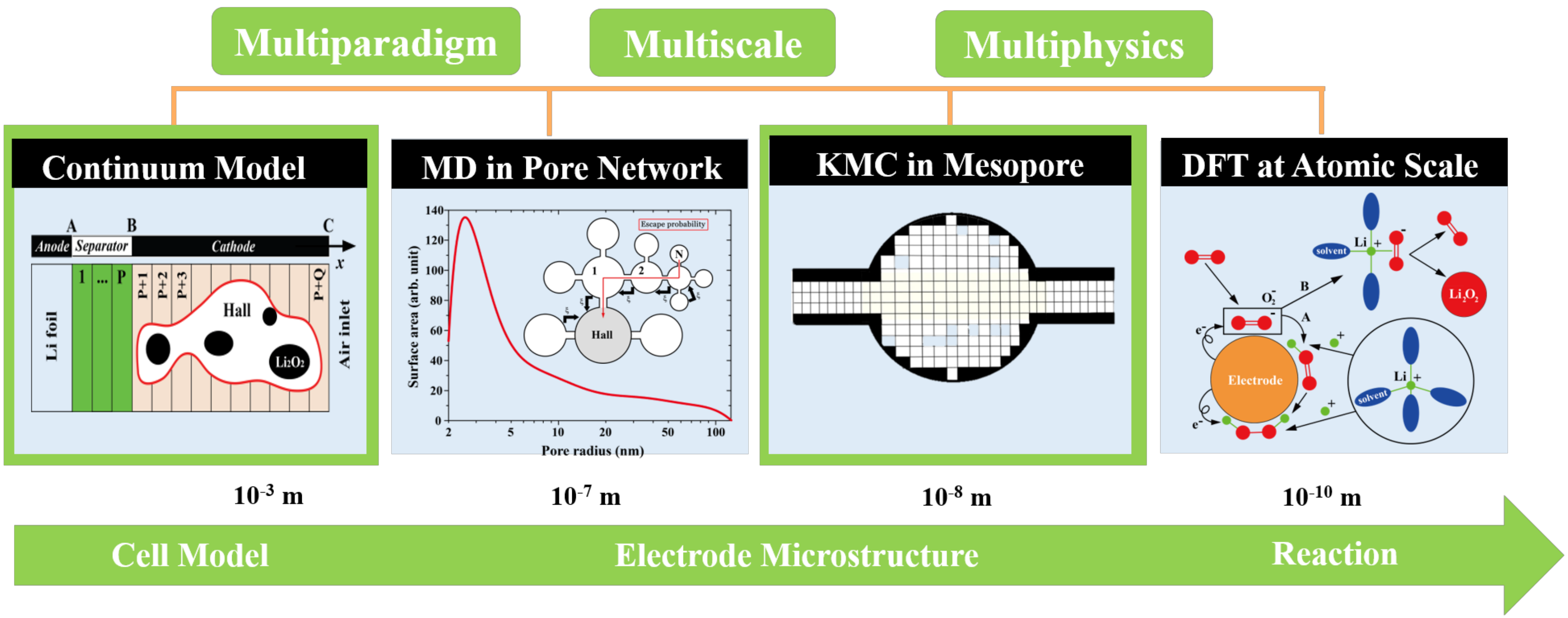


$$2Li^{+} + O_2 + 2e^{-} \xrightarrow{discharge} Li_2O_2$$

Challenges:

- Insufficient O_2 transport
- Low reaction kinetics
- Insulating discharge products
- ....

Multiscale Modeling of Li-air Batteries



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Introduction

Identify the Problem

Translate to Equations

Solve the Equations

Analyze the Results

Introduction

- Identify the Problem
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- Solve the Equations
- Analyze the Results

- Mass Transport
  - Fick's Law of Diffusion
- Electrochemical Reaction
  - Bulter-Volmer Equation
- Electron Tunneling
  - Error Function

Introduction

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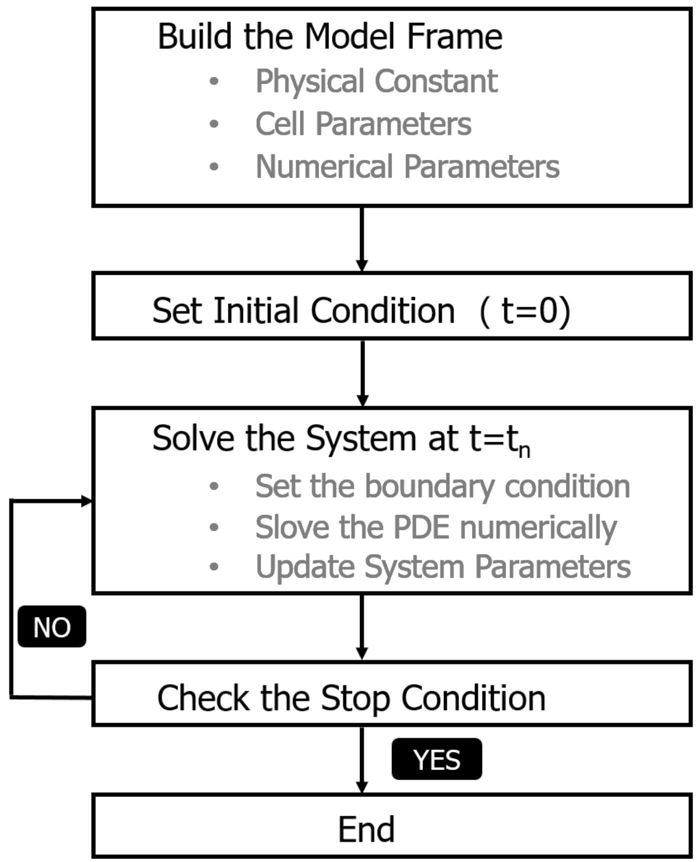
Simulation Flow-Chart



Introduction

Identify the Problem

Translate to Equations

Solve the Equations

Analyze the Results

- Parameter Sensitivity Tests
- Check the consistency of theory
- Compare with Experimental results
- …

Scheme of the Practice

- Part-I Oxygen Diffusion
- Part-II O_2 Transport with Consumption
- Part-III Thin-film model

Part-I Oxygen Diffusion

Fick's First Law

$$J = D\frac{\partial C}{\partial x}$$

Mass Balance Equation

$$\frac{\partial C}{\partial t} = \frac{\partial J}{\partial x} = \frac{\partial}{\partial x}\frac{(D\partial C)}{\partial x}$$

Diffusion in Porous Medium

$$D_e = \frac{\varepsilon}{\tau}D_0 = \varepsilon^{\beta}D_0$$

$$\boxed{\frac{\partial C}{\partial t} = \frac{\partial J}{\partial x} = \frac{\partial}{\partial x}\frac{\left(D_0\varepsilon^{\beta}\partial C\right)}{\partial x}}$$

ε : *porosity of medium*

β : *bruggeman coefficient*

D_0: *bulk diffusion coefficient*

Solve the PDE

Numerical Method

Finite Difference Method

$$\frac{\partial C}{\partial t} = \frac{\partial J}{\partial x} = \frac{\partial}{\partial x}\frac{\left(D_0 \varepsilon^{\beta} \partial C\right)}{\partial x}$$

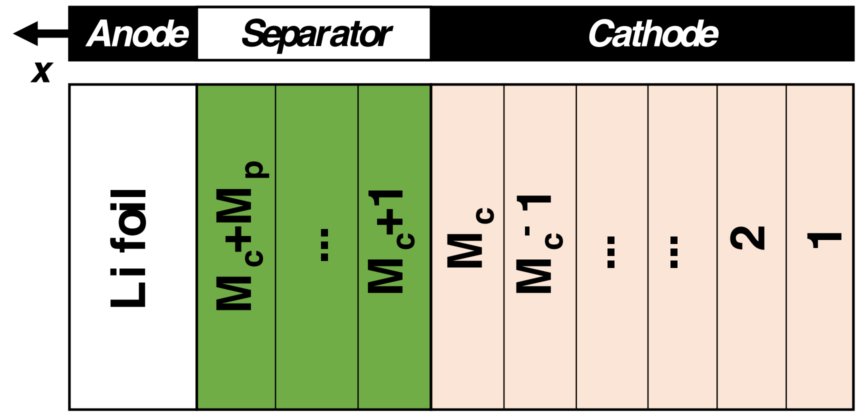
Discretization

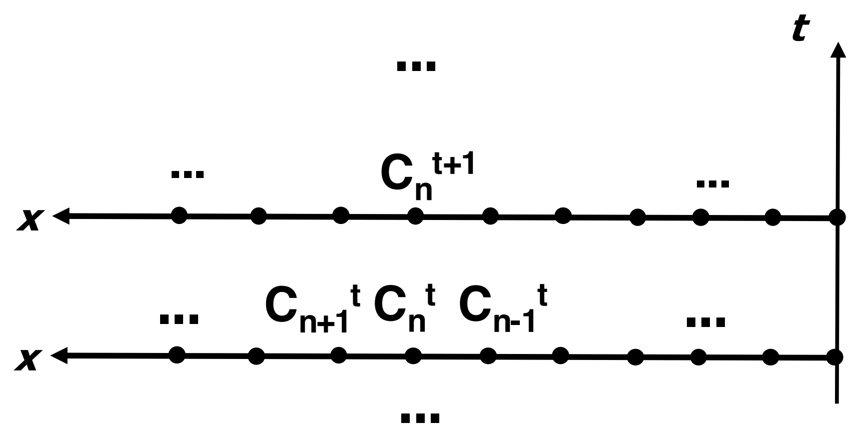
$$\frac{\partial C_n}{\partial t} \cong \frac{C_n^{t+1} - C_n^t}{\Delta t}$$

$$C_{n+1} - C_n \cong \frac{\Delta x}{1!} \cdot \frac{\partial C_n}{\partial x} + \frac{\Delta x^2}{2!} \cdot \frac{\partial^2 C_n}{\partial x^2}$$

$$C_n - C_{n-1} \cong \frac{\Delta x}{1!} \cdot \frac{\partial C_n}{\partial x} - \frac{\Delta x^2}{2!} \cdot \frac{\partial^2 C_n}{\partial x^2}$$

$$\frac{\partial^2 C_n}{\partial x^2} \cong \frac{\Delta t}{\Delta x^2} \left(C_{n+1}^t - 2C_n^t + C_{n-1}^t\right)$$





$$C_n^{t+1} = \frac{\varepsilon^{\beta} D_0 \Delta t}{\Delta x^2}\left(C_{n+1}^t - 2C_n^t + C_{n-1}^t\right) + C_n^t$$

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Initial/Boundary Conditions

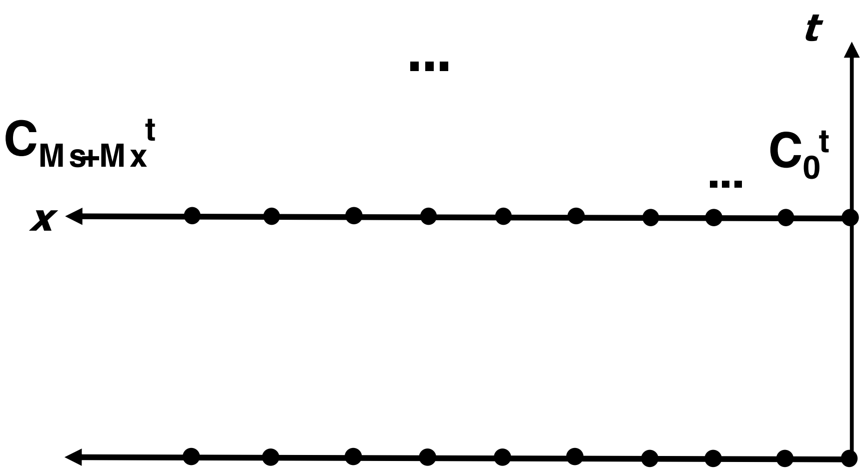
Initial Condition:

$$C(x, t = 0) = 0$$

Boundary Conditions:

$$C(x = 0, t) = Csat$$

$$J(x = M_c + M_s, t) = 0$$




```
%% Initial conditions
C = zeros(1,Mc+Ms); % Saturation concentration of O2

%% Boundary conditions
  % Constant concentration at O2 inlet (x = 0)
  C(1) = (DeCat*dt/dx/dx)*(C_old(2)-2*C_old(1)+C_sat)+C_old(1);
  % 0 flux at anode side (x = Mc+Ms)
  C(Mc+Ms) = (DeSep*dt/dx/dx)*(C_old(Mc+Ms-1)-C_old(Mc+Ms))+C_old(Mc+Ms);
```

Exercise-1

1. Change the value of cathode porosity (poroCat) to 0.6 and 0.9 to see its impacts on the diffusion.

➡ **Link to experiment: cathode structure**

2. Change the value of diffusion coefficient of O_2 (D0) to 5E-9 and 2E-10 to see its impacts on the diffusion.

➡ **Link to experiment: electrolyte property**

3. What else parameters will affect the diffusion? Which components will it have impacts on?

Part II – Transport with Consumption

Discharge Reaction of Li-O_2

$$2Li^{+} + O_2 + 2e^{-} \xrightarrow{discharge} Li_2O_2$$

Mass Balance Equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\frac{\left(D_0 \varepsilon^{\beta} \partial C\right)}{\partial x} + \upsilon$$

```
% Solve the transport
for i = 2:Mc+Ms-1
    C(i) = (DeCat*dt/dx/dx)*(C_old(i+1)-2*C_old(i)+C_old(i-1))+C_old(i)+Source(i)*dt;
end
```

Reaction Kinetics

Bulter-Volmer Equation

$$i = nFk^o\left(\prod c_{f,j}^{s_i}\right) exp\left(\frac{-\alpha nF}{RT}(U - U_o)\right)$$

k^o: *heterogeneous rate constant*

Reaction Rate

$$I = \sum_j I_j = \sum_j nFk^o A_j\left(\prod c_{f,j}^{s_i}\right) exp\left(\frac{-\alpha nF}{RT}(U - U_o)\right)$$

A_j: *active surface area in the* j^{th} *bin*

$$v_j = \frac{I_j}{nF} \longrightarrow$$

```
% Calculate the source term
 KAC = k *a_sp*dx.*C/Cref ;

 KAC_tot = sum(KAC);
 U = U0 - (R*T/(2*alpha*Far))*log(I/KAC_tot);
if KAC_tot ~= 0
 Source = KAC./KAC_tot.*(I/2/Far)/dx;
end
```

Exercise-2

1. Change the value of k^o (k) to 1E-3 and 1E-5 to see its impacts.

➡ **Link to experiment: surface property of cathode materials**

2. Change the value of specific surface area(a_sp) to 1E5 and 1E7 to see its impacts.

➡ **Link to experiment: cathode structure**

3. Which other parameters will affect the results?

Part III – Thin-film Model of LAB

- As an insulator , thickness of Li_2O_2 ↑, reaction kinetics ↓

Active Surface Area

$$A = SP_{tnl} = S\,(1 - \frac{erf(r - r_{lim})}{2})$$

Implement tunneling effects →

```
% Calculate the source term
AcS = GeoS .* theta(deta);
KAC = k .*AcS*dx.*C/Cref ;%KAC
```

Update thickness →

```
%Update the thickness of film
deta = deta + Source * MolarMass /Density / (a_sp *dx);
```

Exercise - 3

1. Compare the discharge curves before and after implementing tunneling effects?

   → Link to experiment: the "sudden death" penonmenon

2. Change the cathode thickness (Lcat) to 1E3 and see its impacts on the result?

3. Can you propose an approach to build the thin-film model when there is a porosity gradient along the cathode?

   → Hint: solve $z = \varepsilon C$ *instead of* C