Li Ion Transport through Holey Graphene: MD Simulations

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SABERS Meeting
11/19/19 – 11/20/19

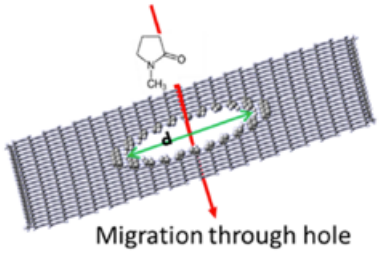


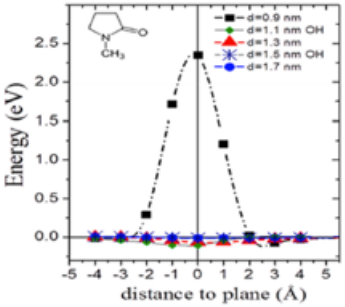
Outline

- Why machine learning in atomistic simulations
- Artificial neural networks (ANNs) in atomistic simulations – physically informed ANNs (PINNs)
- Validation test case simulations
- HPC Implementation of PINN
- Empirical vs ANN vs QM (DFT) simulations benchmark

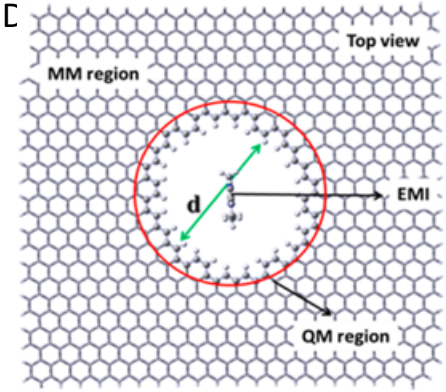
Review of Migration Simulations of Holey Graphene

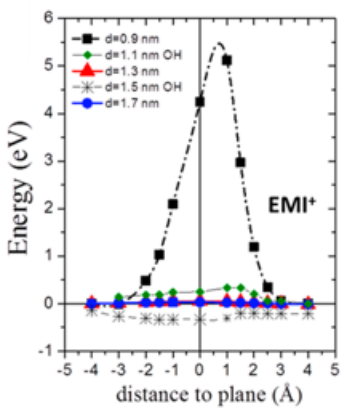
- DFT/MM simulations[1] of N-methyl-2-pyrrolidone (NMP) solvent migrating through holes of holey Graphene (hG)
  - NMP molecules can migrate through holes of R > 1.1 nm
  - Essential for the evaporation of the NMP solvent during the drying process





- D c oles of hG





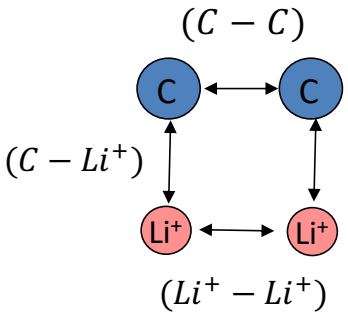
[1]X. Han et al. ACS NANO, 8 (2014) 8255-8265.
[2]1-ethyl-3-methylimidazolium bis(trifluoroethylsulfonyl)-imide (EMI:TFSI)

Migration of Li^+ Ions through Holey Graphene

Preliminary Simulation Results

Li-C_6 Potential

Three types of interactions:



Each one is different and has to be modeled differently

Li-C_6 Potential

N. Chakraborti et al., Journal of Phase Equilibria and Diffusion, Vol. 28 No. 2 (2007) 140-149.
C.M. Shumeyko et al., Scripta Materalia, 102 (2015) 43-46. in supplementary material.

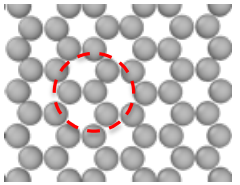
$(C-C)$

$$E = \sum_{i=\{C,Li^+\}} \left(\phi_{2,i} - \phi_{3,i}\right)$$

$$\phi_{2,i(C-C)} = \sum_{j>i} aU_{ij}^{(1)} \qquad \phi_{3,i(C-C-C)} = \sum_{j>i} bU_{ij}^{(2)} \left[1 + \beta^n \left(\sum_{k\neq i,j} W_{ijk}\right)^n\right]^{-1/2n}$$

$$U_{ij}^{(1)} = exp\left(-\lambda_1 r_{ij}\right) \qquad W_{ijk} = f_c(r_{ik})G(\theta_{ijk})$$

$$U_{ij}^{(2)} = exp\left(-\lambda_2 r_{ij}\right) \qquad G(\theta_{ijk}) = 1 + \frac{c_{CCC}^2}{d_{CCC}^2} - \frac{c_{CCC}^2}{d_{CCC}^2 + \left(h_{CCC} - \cos\theta_{ijk}\right)^2}$$



Short range: $r_{C-C} < 2.1\text{Å}$

$a_{CC} = a$ (eV)	$b_{CC} = b$ (eV)	$\lambda_{1,CC} = \lambda_a$	$\lambda_{2,CC} = \lambda_b$	$\beta_{CC}^{nCC} = \beta$	$n_{CC} = n$	$c_{CCC} = c$	$d_{CCC} = d$	$h_{CCC} = h$	R (Å)	D (Å)
1393.6	346.74	3.4879	2.2119	$1.5724E-7$	0.72751	38049	4.3484	-0.57058	1.95	0.15

Medium range: $r_{C-Li} < 10\text{Å}$

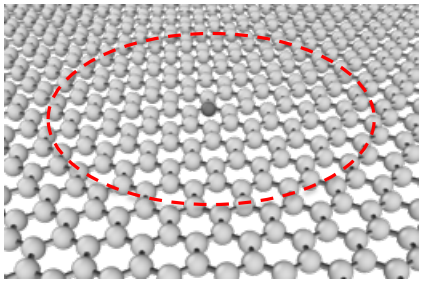
$(C - Li^+)$

$$U_{ij}^{(C-Li^+)} = \frac{A_1}{r_{ij}^{\lambda_1}} exp\left(-\alpha_1 r_{ij}^2\right) - \frac{A_2}{r_{ij}^{\lambda_2}} exp\left(-\alpha_2 r_{ij}^2\right)$$

$(Li^+ - Li^+)$

$$U_{ij}^{(Li^+-Li^+)} = \frac{A_3}{r_{ij}^{\lambda_3}} exp\left(-\alpha_3 r_{ij}\right)$$

Long range: $0 < r_{Li-Li} < \infty$



(eV)		(Å^{-1})
$A_1 = 3.40404268$	$\lambda_1 = 1.71241891$	$\alpha_1 = 0.229357324$
$A_2 = 1.88927008$	$\lambda_2 = 1.16453151$	$\alpha_2 = 0.133259571$
$A_3 = 0.48865113$	$\lambda_3 = 1$	$\alpha_3 = 0.0033331$

Medium range: $r_{C-Li} < 10\text{Å}$

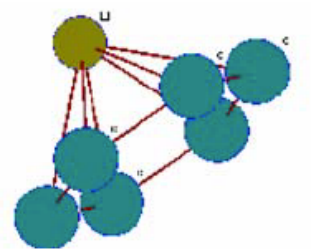
Long range: $0 < r_{Li-Li} < \infty$

Li-C_6 Potential

Verification

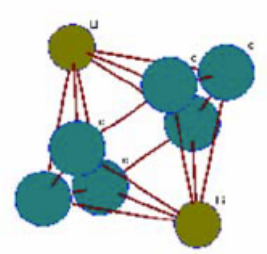
N. Chakraborti et al., Journal of Phase Equilibria and Diffusion, Vol. 28 No. 2 (2007) 140-149.

Testing $(C - C)$ and $(C - Li^+)$ interactions



-37. 144 eV

Testing $(C - C)$, $(C - Li^+)$, and $(Li^+ - Li^+)$ interactions



-44.596 eV

Both energies were reproduced exactly

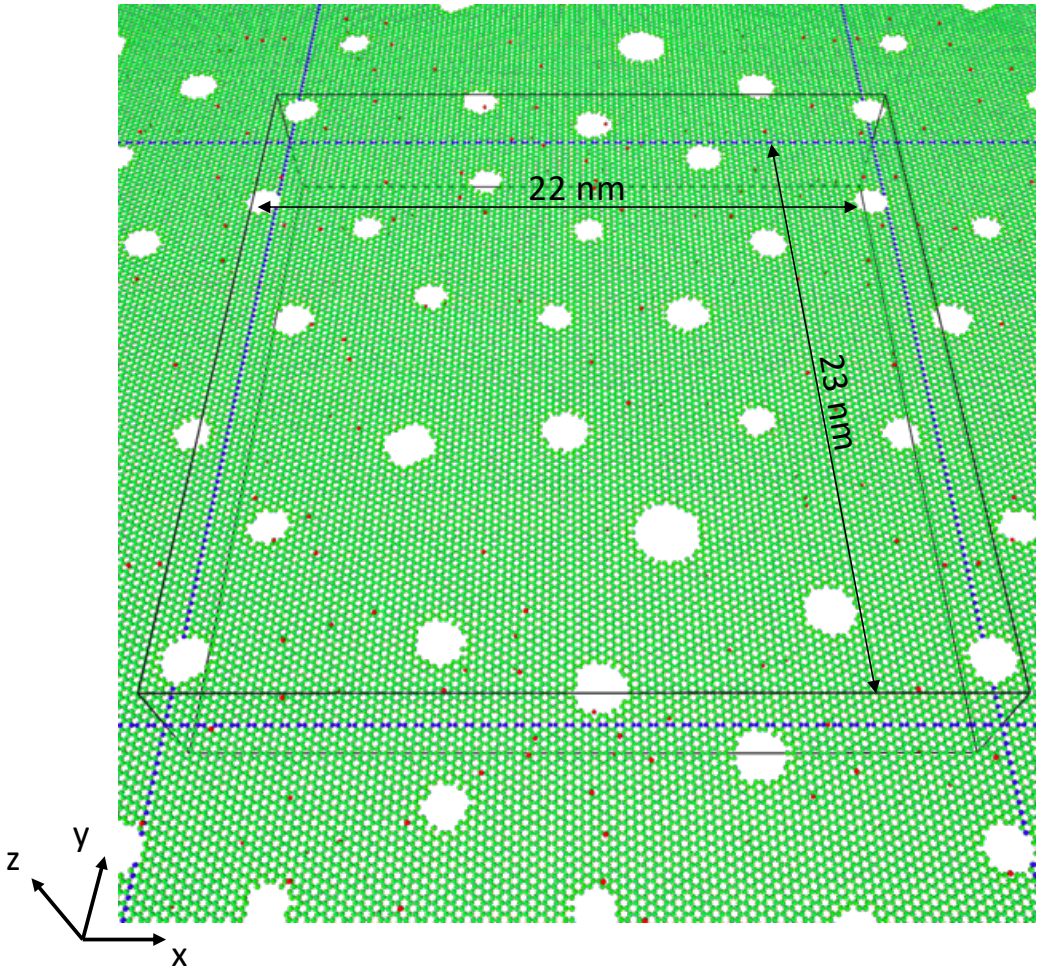
Test Model Simulation

- C atoms (17169)
- C atoms fixed in z
- Li^+ ions (100)

20 random holes of
$R \in (1 \div 3\ nm)$

T = 300 K

Voltage: 0.01 $V/\text{Å}$



Test Model Simulation

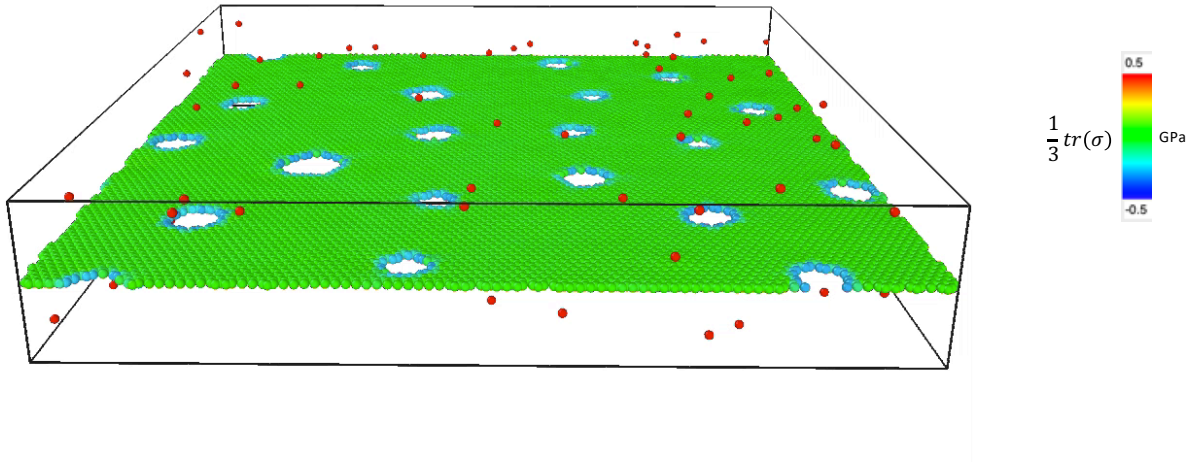
- C atoms (17169)
- Li^+ ions (100)

20 random holes of
$R \in (1 \div 3\ nm)$

T = 300 K

Voltage: 0.01 $V/\text{Å}$

Upper perspective view



Test Model Simulation

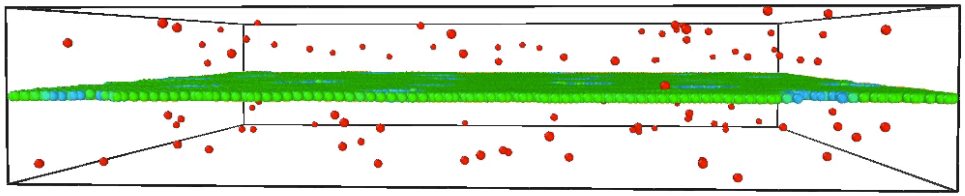
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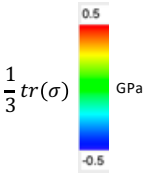
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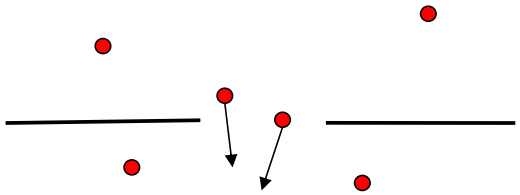
Edge view





Diffusion Mechanism

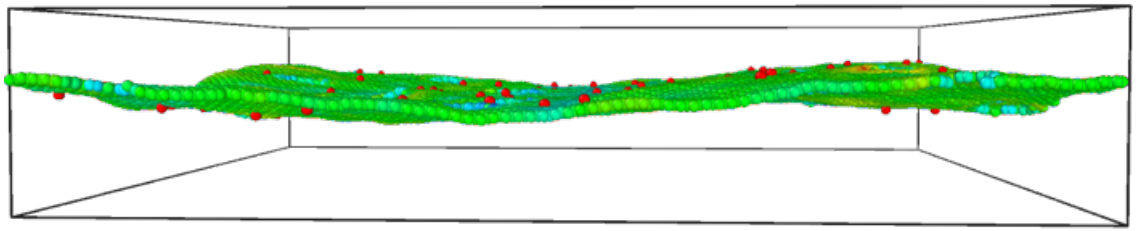
Volume diffusion



Surface diffusion

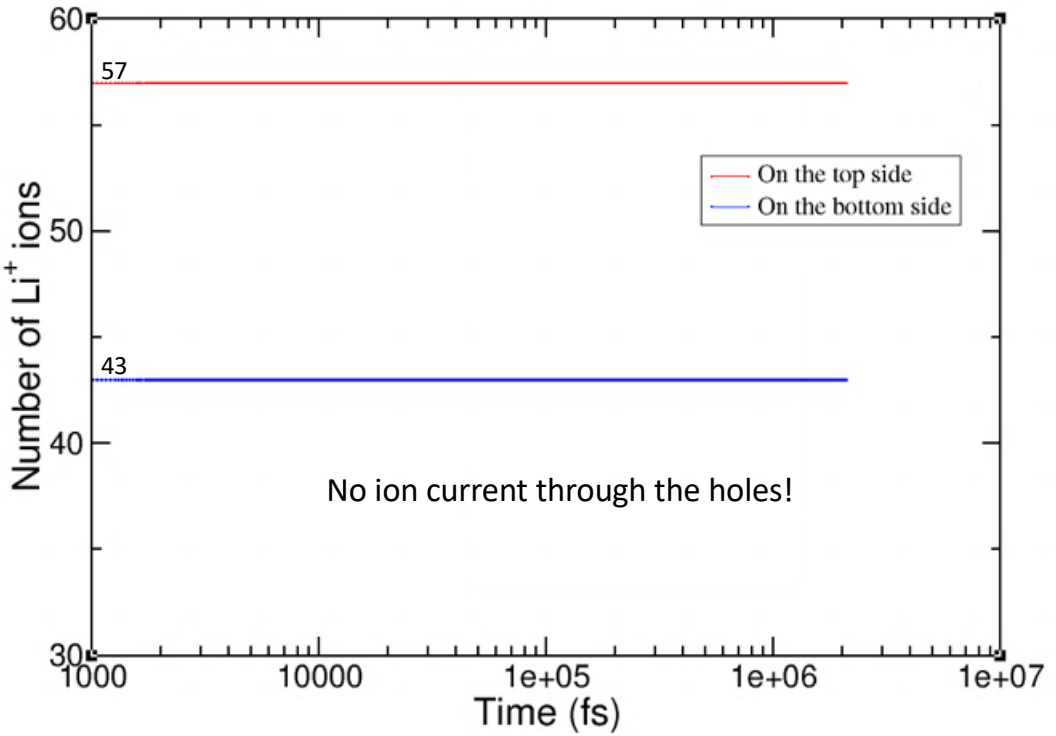


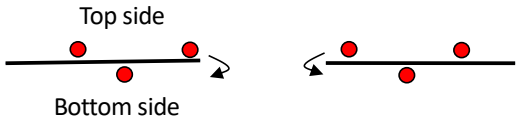
Li+ ions are attracted to the hG and experience surface diffusion



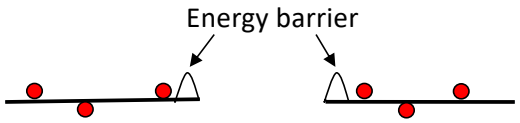
Test Model Simulation

Measuring Li^+ current by counting ions on top and bottom side of the hG layer





Diffusion Mechanism

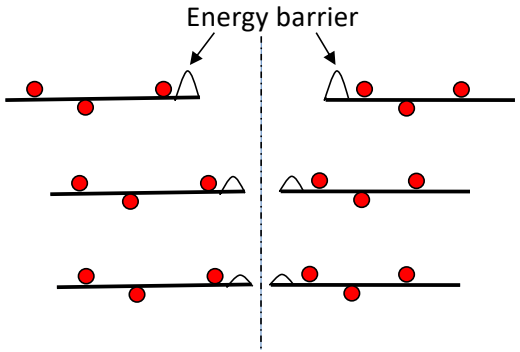


Energy barrier at the edge of the holes prevents hole penetration

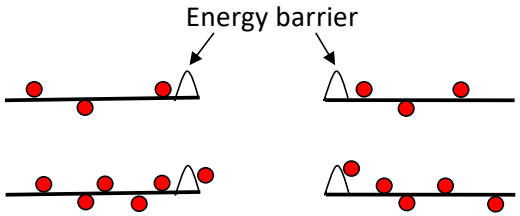
Diffusion Mechanism

Possible solutions

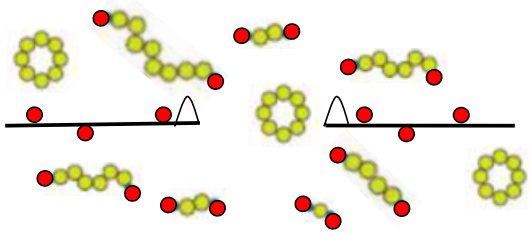
Decrease the hole size



Increase Li^+ concentration



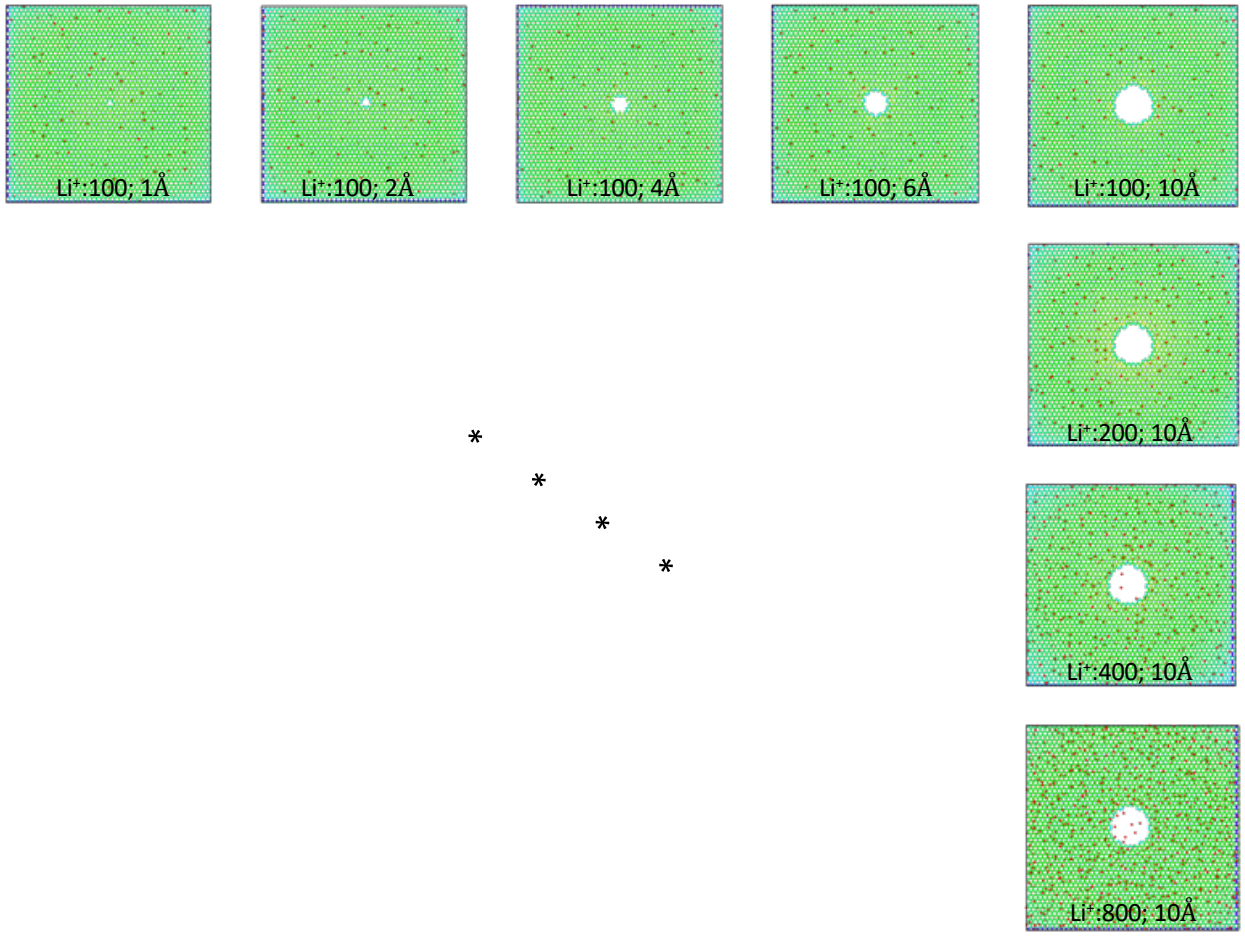
Volume diffusion through the cathode reactant via ion transfer
(currently not in the model)



Systematic Study of Through-Hole Diffusion

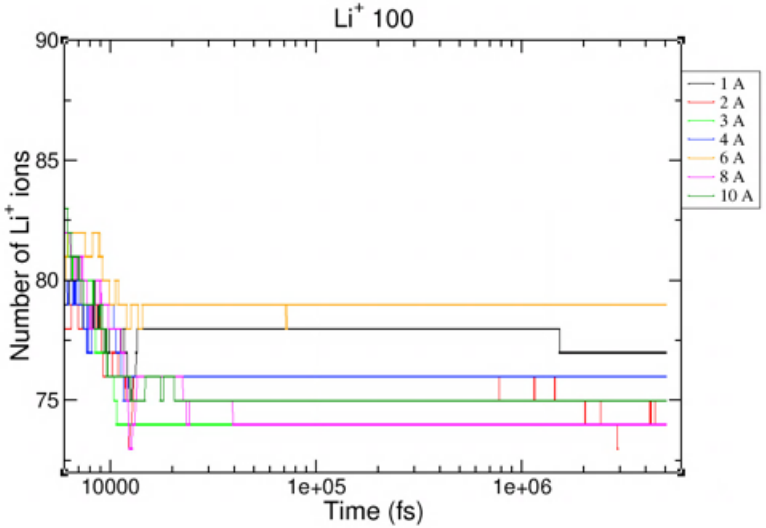
Central hole in a 11x11 nm graphene plate

Hole size (Å): 1, 2, 3, 4, 6, 8, 10; Li^+ ions: 100, 200, 400, 800

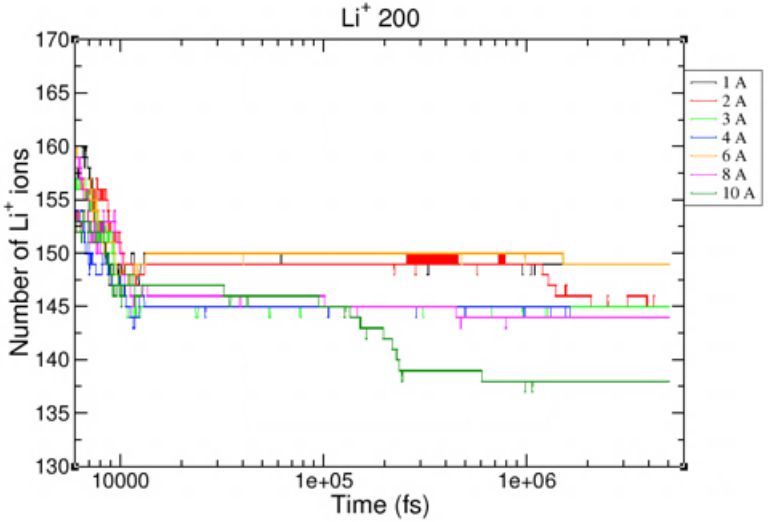


Systematic Study of Through-Hole Diffusion

Central hole in a 11x11 nm graphene plate



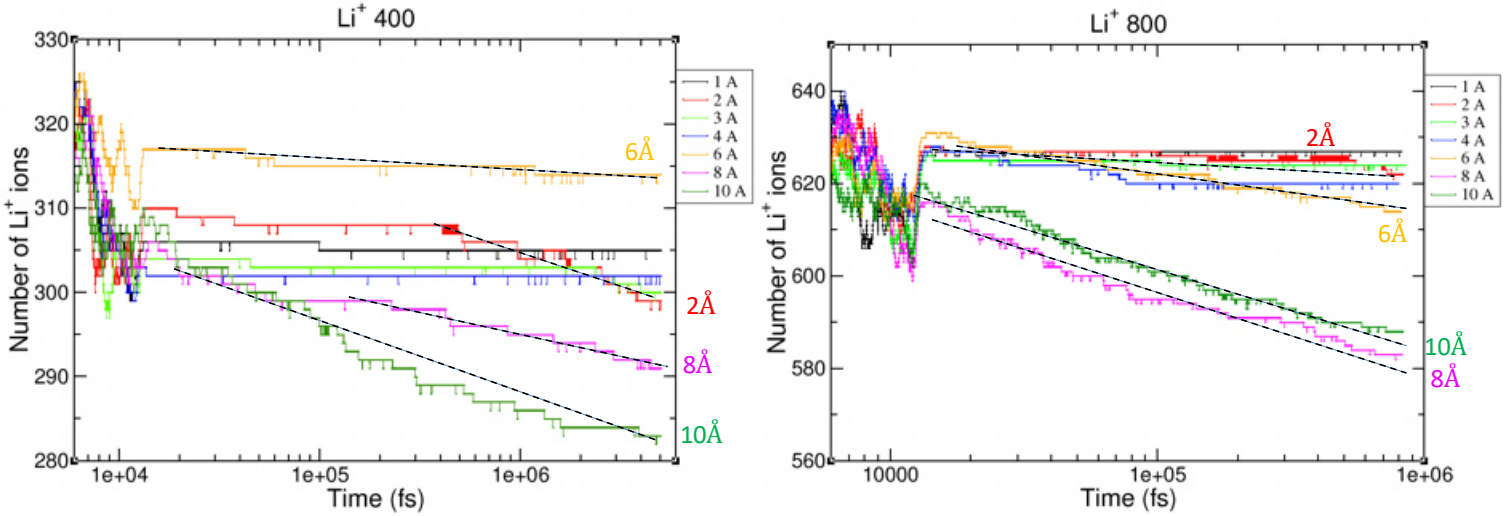
Not enough statistics, but current seems to stop after some relaxation time even for the largest holes (R = 6 - 10 Å)



Increase of the Li^+ concentration seems to trigger periodic current flow (e.g., R = 2 Å, and 10 Å holes)

Systematic Study of Through-Hole Diffusion

Central hole in a 11x11 nm graphene plate



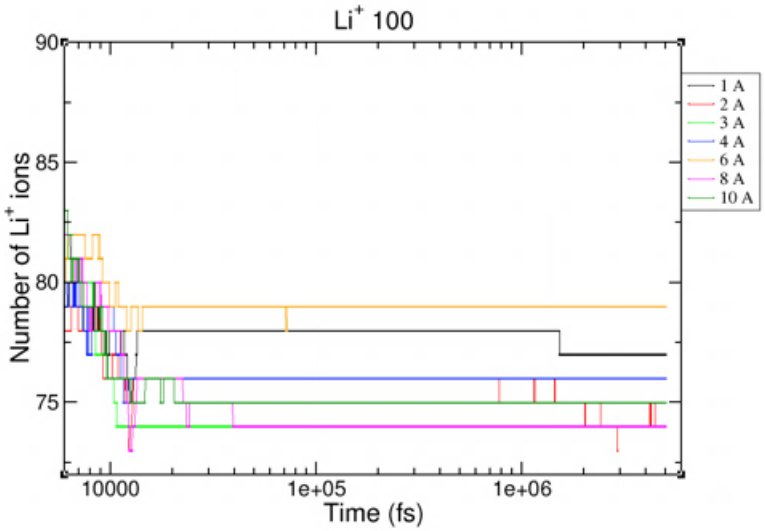
Consistent current is achieved for R = 2, 6, 8, and 10 Å holes

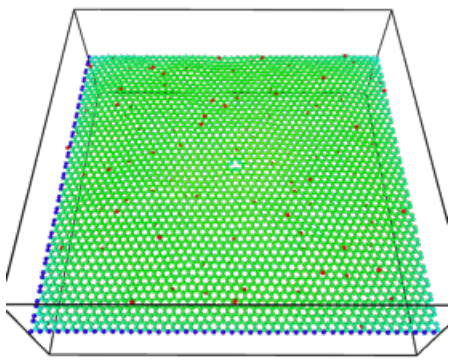
Statistics is too small for reliable analysis

Systematic Study of Through-Hole Diffusion

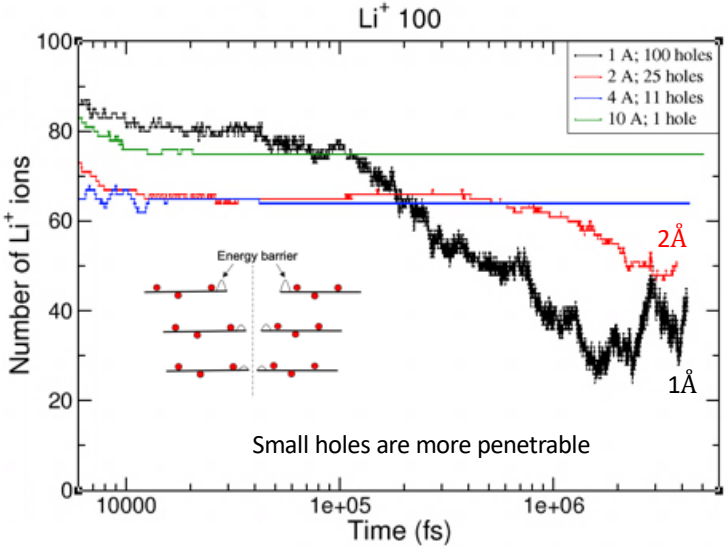
Central hole in a 11x11 nm graphene plate

One hole

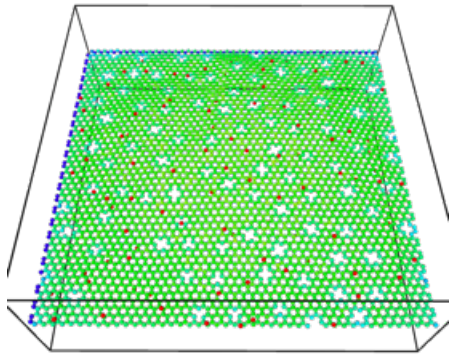




Many holes: equal hole area

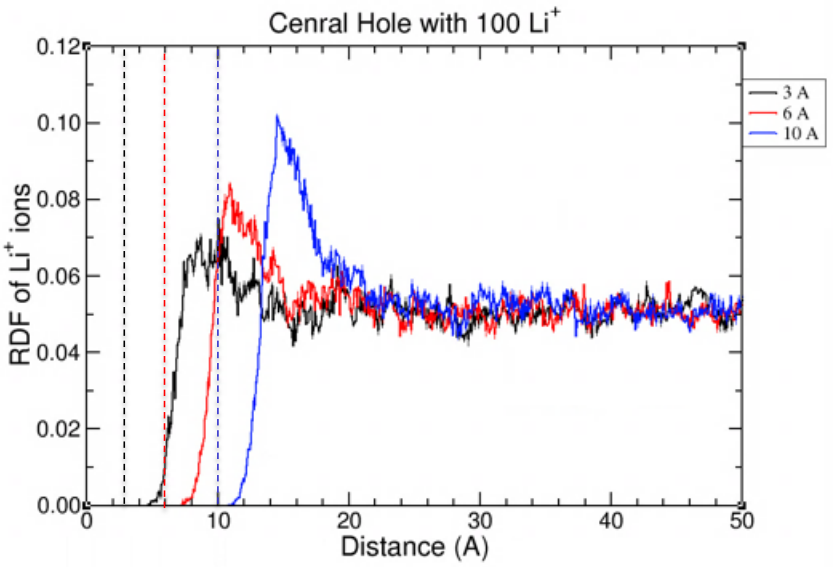


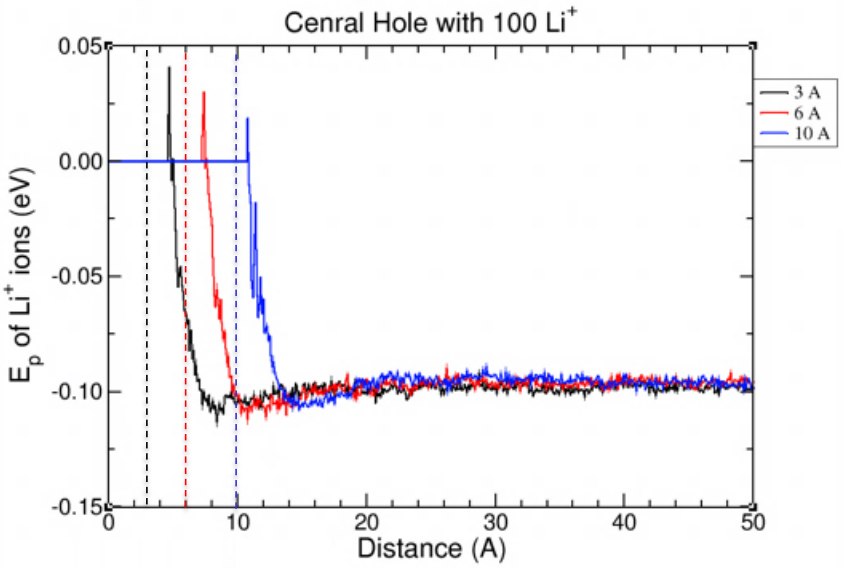
Small holes are more penetrable



Systematic Study of Through-Hole Diffusion

Central hole in a 11x11 nm graphene plate







Summary of the Results

- Li^+ ions are attracted to the graphene surface and experience surface diffusion
- There is an energy barrier for Li^+ ions to pass through the edge of a hole in the holey graphene
- Possible ways to overcome the energy barrier:
  - decrease the hole size (hole diameter < 0.5 nm)
  - increase Li^+ ions concentration on the graphene layer

Research Plan

Milestone 3QFY20:
Development of a molecular dynamics computational model of cathode microstructure, and estimates of the Li ion permeability in the composite cathode. (4/23/2020)
Feasibility: SABERS requires an understanding of cathode ion transport properties as a function of its microstructure.

Work to address the milestone

- Systematic study of Li ion transport through holey graphene layers as a function of hole size and distribution, and strength of the electric current
- Building a molecular dynamics model of cathode microstructure including sulfur, and Li_2S_{n-2} polysulfide molecules between hG layers
- Studying diffusivity of Li ions through the cathode microstructure