Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Mechanistic Understanding of Electrochemical Plating and Stripping of Metal Electrodes

Deepti Tewari and Partha P. Mukherjee*

School of Mechanical Engineering, Purdue University, West Lafayette, IN 47906, USA

*_Correspondence_: pmukherjee@purdue.edu (Partha P. Mukherjee)

Implementation of Transition events in the Mesoscale Kinetic Monte Carlo (KMC) Algorithm

Three processes that are included in the mesoscale Kinetic Monte Carlo (KMC) model during charging and discharging. Diffusion of metal ion in liquid electrolyte, diffusion of metal atom on the surface and reduction or oxidation for charging or discharging respectively. The probabilities for different processes are assigned to kinetic rates. A two dimensional lattice based KMC model is developed. A rejection free, partition search KMC algorithm is used[1–3]. The computational domain is periodic in horizontal direction. N_x is the number of lattice points in the horizontal direction.

During charging, two set of matrices are maintained and updated. One is the occupancy matrix, which keeps track of the lattice sites that are occupied or empty. The other matrix is the charge matrix which keeps track whether an entity is a metal ion or a metal atom.

During discharging process, three set of matrices are maintained and updated. The occupancy and the charge matrix have the same definition as during the charging process. In addition, a connectivity matrix is created to keep track of metal atoms that are connected to the electrode and metal atoms that are disconnected to the substrate. A metal atom can be oxidized if it is connected to the electrode. Metal atoms not connected to the electrode are counted as dead metal.

For both charge and discharge process, the matrix containing the rate of all the processes is maintained and updated with each transition event.

The KMC algorithm involves the following steps.

Calculate the total rate

(i) The total rate for diffusion of Li ions in electrolyte

$$\Omega_{ion\_diffusion} = \sum_{i=1}^{N} R^{i}_{ion\_diffusion} \qquad \text{(S1)}$$

(ii) The total rate for diffusion of Li atoms on surface

$$\Omega_{surface\_diffusion} = \sum_{i=1}^{N} R^{i}_{surface\_diffusion} \quad \text{(S2)}$$

(iii) Total rate of reduction or oxidation for charging or discharging

$$\Omega_{reduction\ /\ oxidation} = \sum_{i=1}^{N} R^{i}_{reduction\ /\ oxidation} \quad \text{(S3)}$$

N is the number of atoms and ions. Superscript i denotes the rate for a particular atom or an ion.

The total rate is calculated as

$$\Omega_{total} = \Omega_{ion\_diffusion} + \Omega_{surface\_diffusion} + \Omega_{reduction\ /\ oxidation} \quad \text{(S4)}$$

Selection of the transition event

A partial search strategy is used to select the transition event. A random number γ_1 uniformly distributed on (0,1) is generated. If $0 < \gamma_1\Omega_{total} \le \Omega_{ion\_diffusion}$, then ion diffusion is selected. If $\Omega_{ion\_diffusion} < \gamma_1\Omega_{total} \le \Omega_{ion\_diffusion} + \Omega_{surface\_diffusion}$, then surface diffusion is selected. If $\Omega_{ion\_diffusion} + \Omega_{surface\_diffusion} < \gamma_1\Omega_{total} \le \Omega_{total}$, then reduction or oxidation is selected depending on whether it is charging or discharging. Figure S1 depicts this selection of the type of event schematically. In the example shown in Figure 2, diffusion of metal atom on surface is selected.

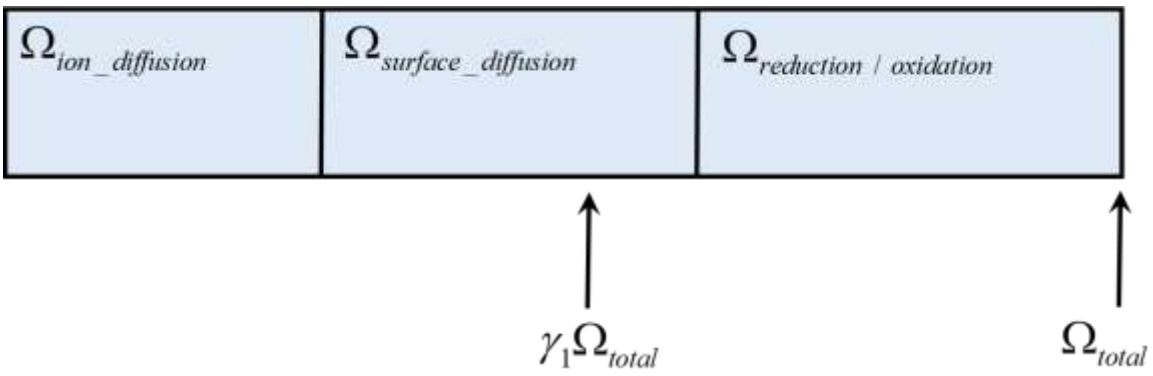


Figure S1: Schematic showing selection of type of the transition event.

The next step is to select the entity (specific ion or atom) for transition. In the example shown in Figure S1, surface diffusion is selected. Figure S3 shows schematically how to select the specific atom that will diffuse. Generate another random number γ_2 uniformly distributed on (0, 1). Surface diffusion of the ith atom is enacted.

$$\sum_{j=1}^{i-1} R^{j}_{surface\_diffusion} < \gamma_2 \Omega_{surface\_diffusion} \leq \sum_{j=1}^{i} R^{j}_{surface\_diffusion} \quad \text{(S5)}$$

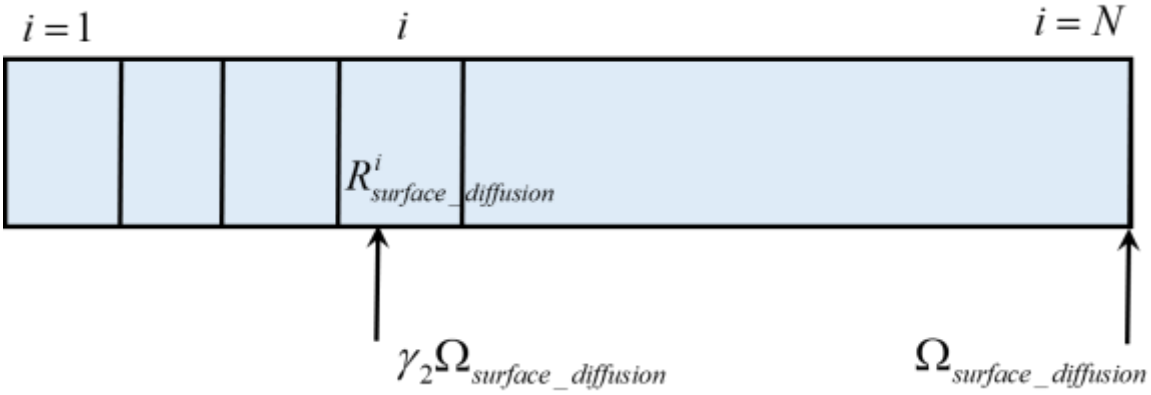


Figure S2: Schematic showing the selection of surface diffusion of the ith atom.

Update structure and time

After the implementation of the transition event, the occupancy and the charge matrix is updated. The rate matrix is updated for the first and second neighbor of the entity (ion or atom) undergoing transition. If a reduction reaction occurs, another ion is introduced such that the number of ions in the KMC computational domain remains constant. Then the occupancy and charge matrix are modified to account for the additional ion. The matrix containing rates is also updated for the additional ion and its first and second neighbors. If an oxidation event occurs during discharging process, the occupancy and charge matrices are updated as well as the rates of first and second

neighbors of the atom that is oxidized. In addition, the connectivity matrix is updated to check if any new group of atoms have become detached from the electrode. Upon oxidation, an ion is removed from the computational domain so the number of ions remain constant throughout the discharge process. When an ion is removed, the occupation and charge matrices are updated. The rate of the first and second neighbor of the removed ion is also updated.

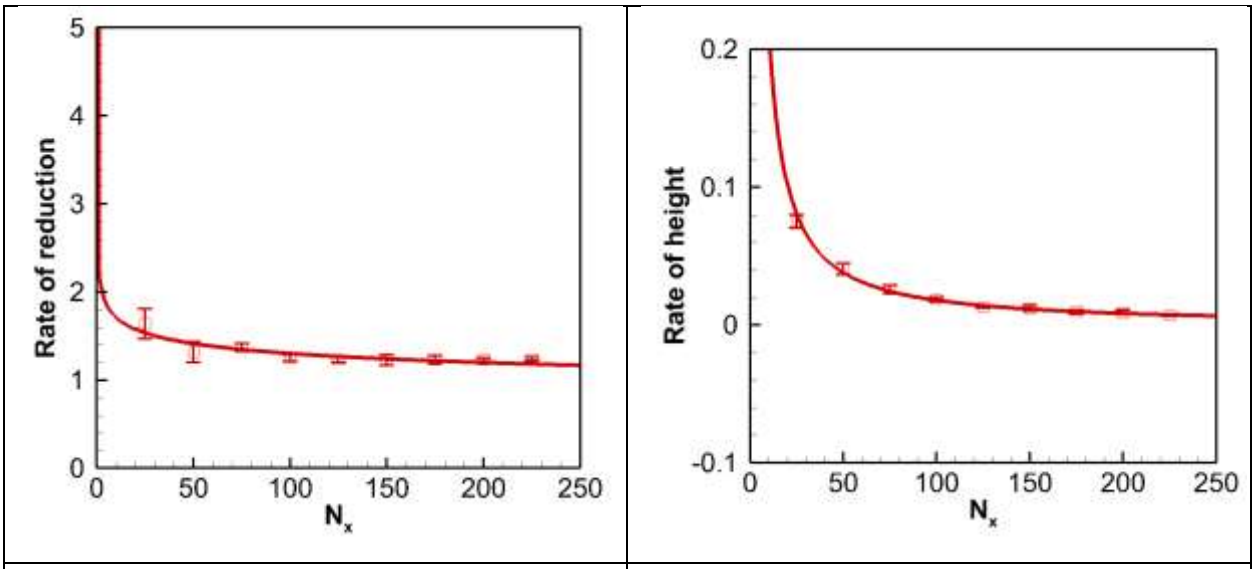
To update time, a random number, γ_3 on (0, 1) is generated. The time increment δt is calculated as,

$$\delta t = \frac{-\ln(\gamma_3)}{\Omega_{tot}} \quad \text{(S6)}$$

Computational Domain

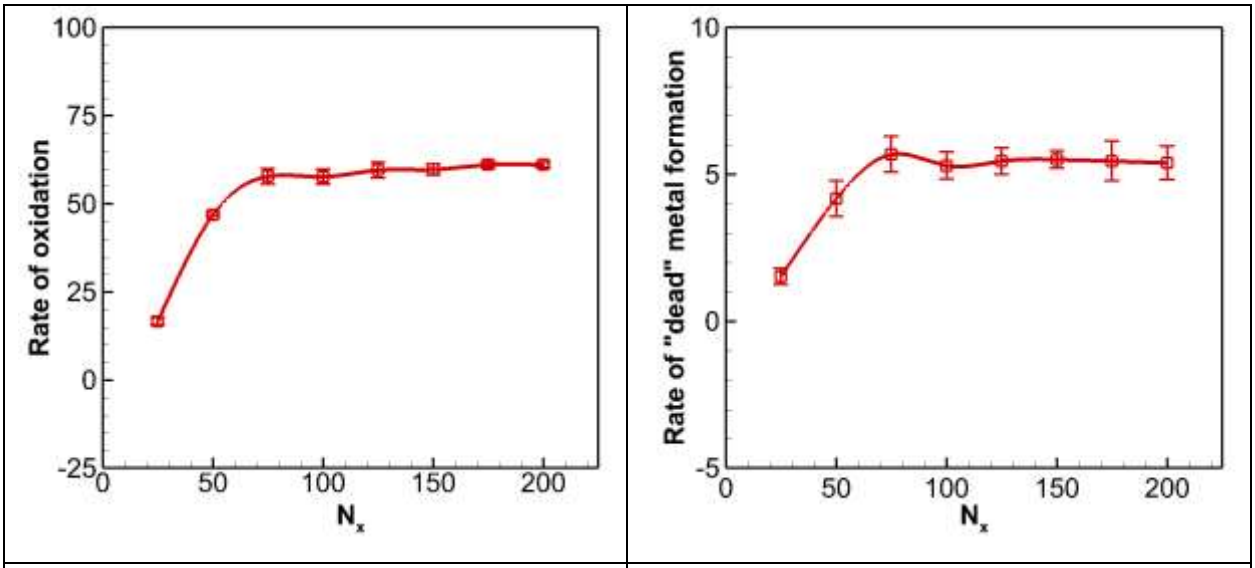
The two dimensional computational domain comprises of lattice grid of ($N_x \times N_y$) sites where N_x is the number of lattice sites in horizontal direction and N_y is the number of lattice sites in vertical direction. To study the effect of domain size, N_y=100 is kept constant while N_x is varied. Figure S3 shows the effect of domain size N_x for charging. Rate of reduction is the average slope of the number of reduction reactions with time. Rate of height is the average slope of height of deposition with time. N_x=175 is used in all KMC simulations based on the results shown in Figure S3.

Figure S4 shows the effect of computational domain during discharging. In Figure S4 (a), the rate of oxidation is the average slope of number of oxidation reactions with time and in Figure S4 (b), the rate of dead metal formation is the average slope of the number of dead metal with time. N_x=175 is used in all KMC simulations.



(a) (b)

Figure S3: Effect of the KMC domain size during charging. (a) Rate of reduction as the number of lattice points in horizontal direction, N_x is increased (b) Rate of height of deposition with N_x. The KMC simulations were performed at P_{red}=0.1, P_e=0.8 and P_f=0.1.



(a) (b)

Figure S4: Effect of the KMC domain size during discharging. (a) Rate of oxidation as the number of lattice points in horizontal direction, N_x is increased (b) Rate of dead metal formation with N_x. The KMC simulations were performed at P_{ox}=0.5, P_e=0.4 and P_f=0.1.

References

(1) Schulze, T. P. Efficient Kinetic Monte Carlo Simulation. *J. Comput. Phys.* **2008**, *227* (4), 2455–2462.

(2) Tewari, D.; Liu, Z.; Balbuena, P. B.; Mukherjee, P. P. Mesoscale Understanding of Lithium Electrodeposition for Intercalation Electrodes. *J. Phys. Chem. C* **2018**, *122*, 21097–21107.

(3) Voter, A. F. Introduction To the Kinetic Monte Carlo Method. In *Radiation Effects in Solids*; 2011; pp 1–23.