

## Supplementary Information

# Surface Diffusion Manifestation in Electrodeposition of Metal Anodes

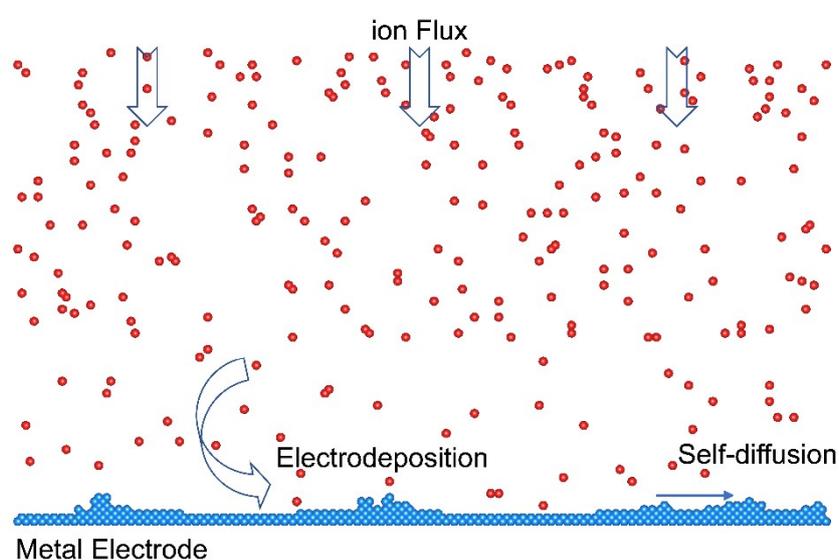
*Bairav S. Vishnugopi, Feng Hao, Ankit Verma and Partha P. Mukherjee\**

School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907, USA

\*Correspondence: pmukherjee@purdue.edu

## 1. Coarse-grained mesoscale model

A coarse-grained meso-scale model has been employed to study the dynamic evolution of the electrochemical system.<sup>1,2</sup> The Kinetic Monte Carlo (KMC)<sup>3</sup> modeling approach incorporates three fundamental mechanisms: metal ion transport in the electrolyte; ion reduction and deposition on the electrode surface; and surface self-diffusion of deposited atoms. A schematic illustrating these three competing mechanisms is shown in Fig. S1.



**Fig. S1.** Schematic of metal electrodeposition, including ion transport, deposition on the metal electrode, and surface self-diffusion. Red circles represent ions in the electrolyte, while blue circles represent deposited atoms on metal electrode.

For each of these processes, a rate constant (as described in the manuscript) is first computed at every lattice site in the domain. The three rate constants -  $k_T$  (ion transport rate),  $k_R$  (electrochemical reaction rate) and  $k_D$  (surface diffusion rate) are then used to calculate a corresponding total rate constant as follows:

For the transport of metal ions in the electrolyte,

$$k_1 = \sum_{i=1}^{N_1} k_T^i \quad (\text{S1})$$

Here,  $N_1$  is the number of metal ions in the electrolyte and  $k_1$  is the total ion transport rate.

For the electrochemical reaction of metal ions,

$$k_2 = \sum_{i=1}^{N_2} k_R^i \quad (\text{S2})$$

Here,  $N_2$  is the number of metal ions at the electrode-electrolyte interface and  $k_2$  is the total electrochemical reaction rate.

For surface diffusion of M atoms,

$$k_3 = \sum_{i=1}^{N_3} k_D^i \quad (\text{S3})$$

Here,  $N_3$  is the number of deposited atoms on the electrode and  $k_3$  is the total surface diffusion rate.

Based on  $k_1$ ,  $k_2$  and  $k_3$ , a total rate constant is then obtained as follows:

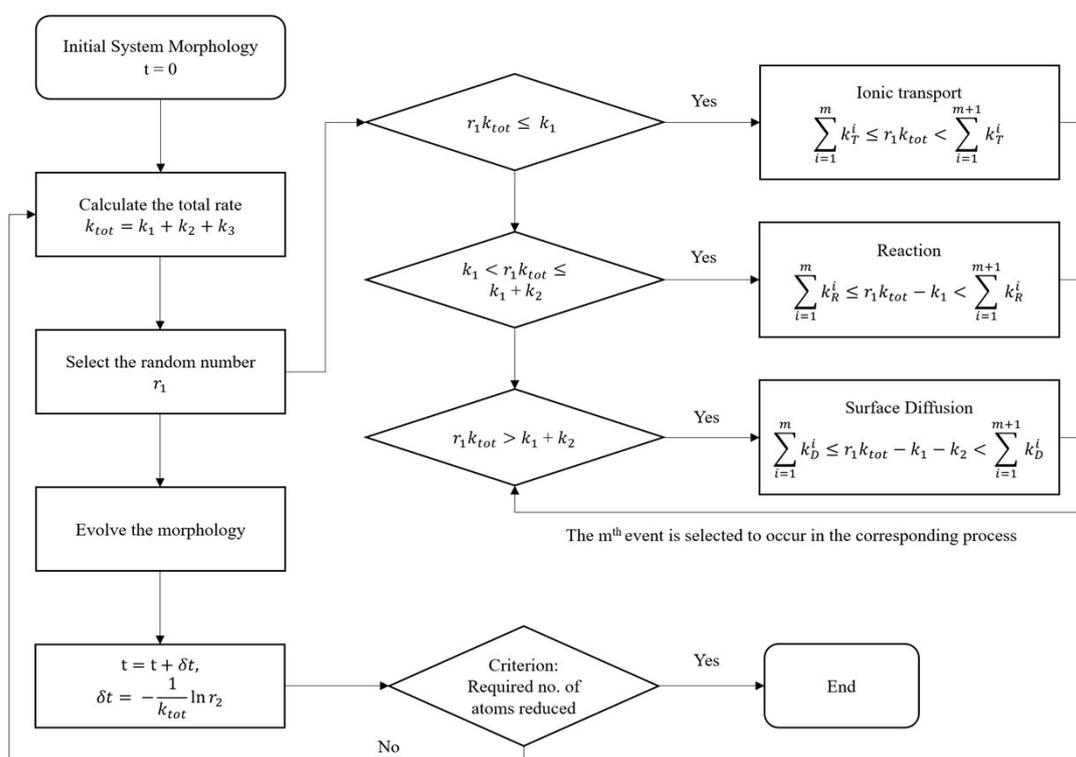
$$k_{tot} = \sum_{i=1}^3 k_i \quad (\text{S4})$$

A random number  $r_1$ , between 0 to 1 is chosen and multiplied with  $k_{tot}$ . Following this, we scan through all the events and select the first event for which the total rate of previously scanned events is larger than  $r_1 k_{tot}$ . The electrochemical system then evolves based on this selected event.

The time step is calculated using a random number  $r_2$ :

$$\delta t = -\frac{1}{k_{tot}} \ln r_2 \quad (\text{S5})$$

A flowchart describing the algorithm used for the dynamic evolution of the electrochemical system is illustrated in Fig. S2.



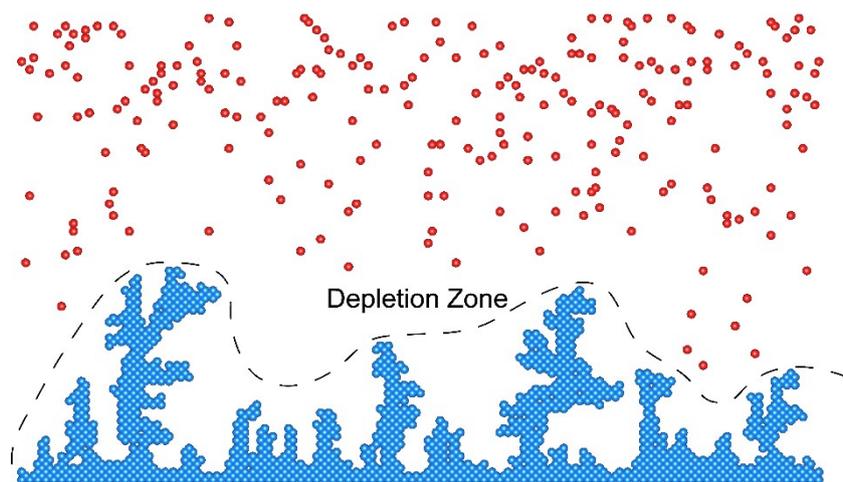
**Fig. S2.** Schematic of the KMC procedure for the dynamic evolution of the electrochemical system

Parameters used in the coarse-grained KMC model have been summarized below in Table S1.

**Table S1.** Parameters used in the model.

Parameters		Values	Units
$\eta$	Local overpotential	0.3-0.5	V
$i_0$	Exchange current density	5	mA cm <sup>-2</sup>
$\alpha$ ( $\beta$ )	Charge transfer coefficients	0.7 (0.3)	
$E_{a1}, E_{a2}, E_{a3}$	Self-diffusion barrier heights	0.01-0.8	eV
$a$	Lattice size	3.5	Å
$R$	Gas constant	8.314	J mol <sup>-1</sup> K <sup>-1</sup>
$F$	Faraday constant	96,487	C mol <sup>-1</sup>
$N_a$	Avogadro constant	$6.022 \times 10^{23}$	mol <sup>-1</sup>
$k_b$	Boltzmann constant	$1.38 \times 10^{-23}$	m <sup>2</sup> kg s <sup>-2</sup> K <sup>-1</sup>
$T$	Operating temperature	300	K
$\nu$	Jump frequency	$2 \times 10^{12}$	s <sup>-1</sup>

Employing the aforementioned algorithm and modelling parameters that have been summarized above, formation of a fractal growth morphology, along with the presence of an ion depletion zone at the reaction front is illustrated in Fig. S3.



**Fig. S3.** Schematic of ion depletion at the reaction front (denoted by the dashed line) during a dendritic growth mode

**References:**

1. F. Hao, A. Verma and P. P. Mukherjee, *ACS applied materials & interfaces*, 2018, **10**, 26320-26327.
2. F. Hao, A. Verma and P. P. Mukherjee, *Journal of Materials Chemistry A*, 2018, **6**, 19664-19671.
3. A. F. Voter, in *Radiation effects in solids*, Springer2007, pp. 1-23.