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Supplementary Information

Cationic Shield Mediated Electrodeposition Stability in Metal Electrodes

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1. Coarse-grained mesoscale model

Three processes are considered in the system: the transport of additive M^+ and metal N^+ in the electrolyte, the reaction of N^+ ions with electrons at the electrolyte-electrode interface, and the surface diffusion of N atoms on the electrode. The kinetic Monte Carlo (KMC) algorithm is used to describe the electrochemical behaviors.[1]

Three types of rates: the ionic transport rate k_T (k_{TM} for M^+ ions and k_{TM} for N^+ ions), the reaction rate k_I, and the surface self-diffusion rate k_D. First, these rates will be calculated at each lattice site.

For the ionic transport,

$$k_1 = \sum_{j_1=1}^{N_{11}} k_{TM}^{j_1} + \sum_{j_2=1}^{N_{12}} k_{TN}^{j_2}, \tag{S1}$$

where k_1 is the total transport rate, and N_{11} and N_{12} are the numbers of M^+ ions and N^+ ions in the electrolyte, respectively.

For the reaction,

$$k_2 = \sum_{j=1}^{N_2} k_I^j, \tag{S2}$$

where k_2 is the total electrochemical reaction rate, and N_3 is the number of N^+ ions on the electrode.

For the surface self-diffusion,

$$k_3 = \sum_{j=1}^{N_3} k_D^j, \tag{S3}$$

where k_3 is the total surface diffusion rate, and N_3 is the number of N atoms on the electrode of metallic N.

Then, the total rate is obtained as

$$k_{tot} = \sum_{j=1}^{3} k_j. \tag{S4}$$

Set a random number r_1, ranging from 0 to 1, multiplies it by k_{tot}, and steps through all the events, stopping at the first event for which the total rate of previously scanned events is large than $r_1 k_{tot}$.[1] Subsequently, this event is selected to evolve the system. Using a random number r_2, the time step is given as

$$\delta t = -\frac{1}{k_{tot}} \ln r_2. \tag{S5}$$

Meanwhile, new N ions are added to the system to compensate for the consumption of N^+ ions on the electrode. Fig. S1 illustrates the specific flow for the dynamical evolution during electrodeposition.

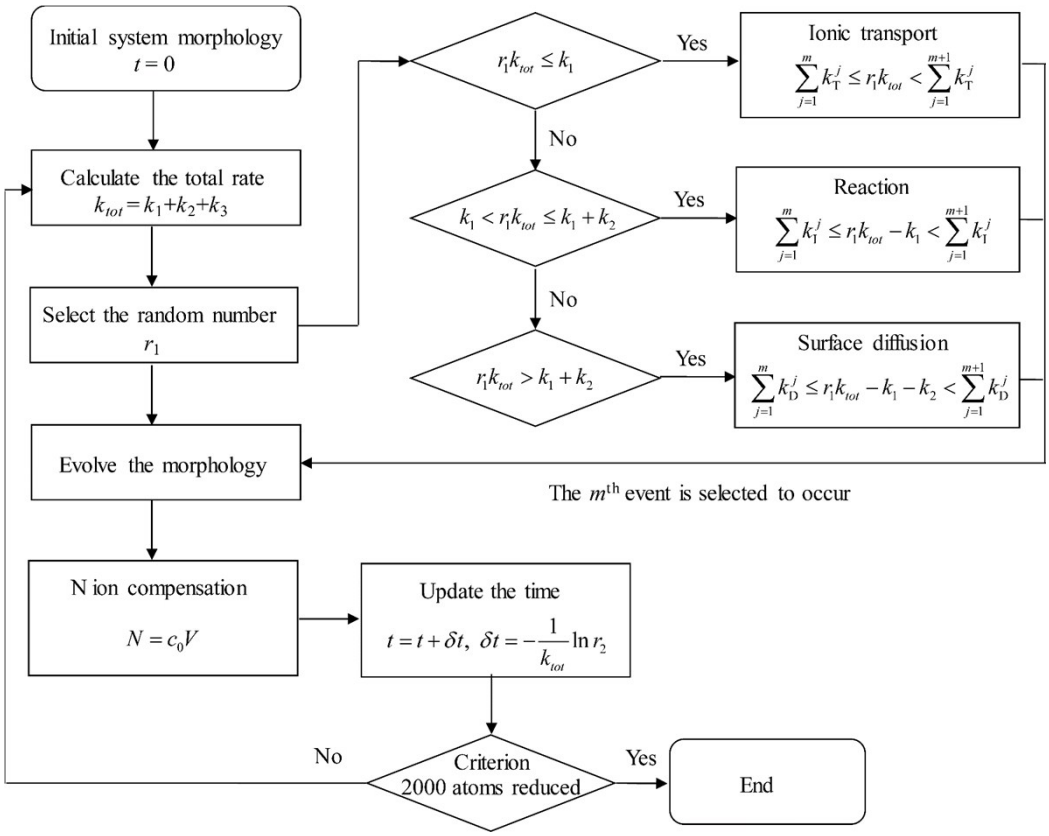

Fig. S1. KMC procedure of the electrodeposition of metallic N.

The following assumption is made to model the cationic shielding effect, as illustrated in Fig. S2. For M^+ ions in the electrolyte, the transport rate is k_{TM}. For the M^+ ions on the dendrite surface, the transport rate is set to k_{TM}^s

$$k_{TM}^s = \left(1 - \frac{y - y_0}{H} C\right) k_{TM},\ y \geq y_0. \quad If\ k_{TM}^s < 0,\ set\ k_{TM}^s = 0. \tag{S6}$$

Here, y is the height of a M+ ion adsorbed to the dendrite, y_0 is the average height of the deposited metal, H is the system height, and C is a constant, which is set to be 10 in the model. Eq. 6 is used to mimic the adsorption of M^+ ions to the dendrite. For the M^+ ions on the dendrite surface (when $y > y_0$), k_{TM}^s linearly decreases in the y direction, and thus, the dendrite tip is the most favored site for the adsorption of M^+ ions.

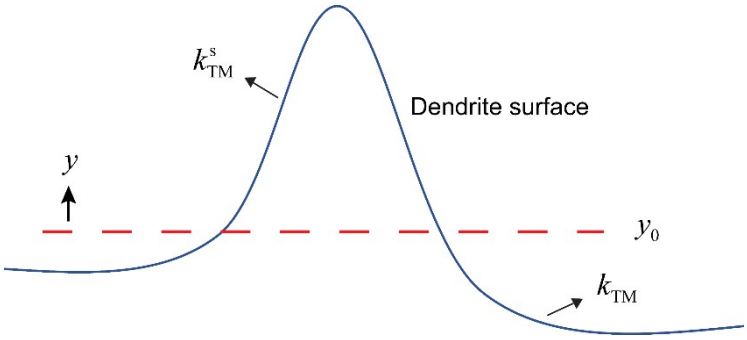

Fig. S2 The transport rate of additive M^+ ions on the dendrite surface.

Based on the parameters reported by Jäckle *et al.* and our group,[2, 3] electrodeposition morphologies of Li, Na, Mg, and Al are illustrated in Fig. S3 (other parameters used are the same as those in Fig. 2(a) in the manuscript). Dendrites of Mg and Al are relatively lower because of their relatively low surface diffusion barriers, which facilitate the movement of surface atoms from the dendrites to adjacent regions.

Furthermore, the cationic shield (CS) effect can suppress dendrite growth for Li, Na, Mg, and Al.

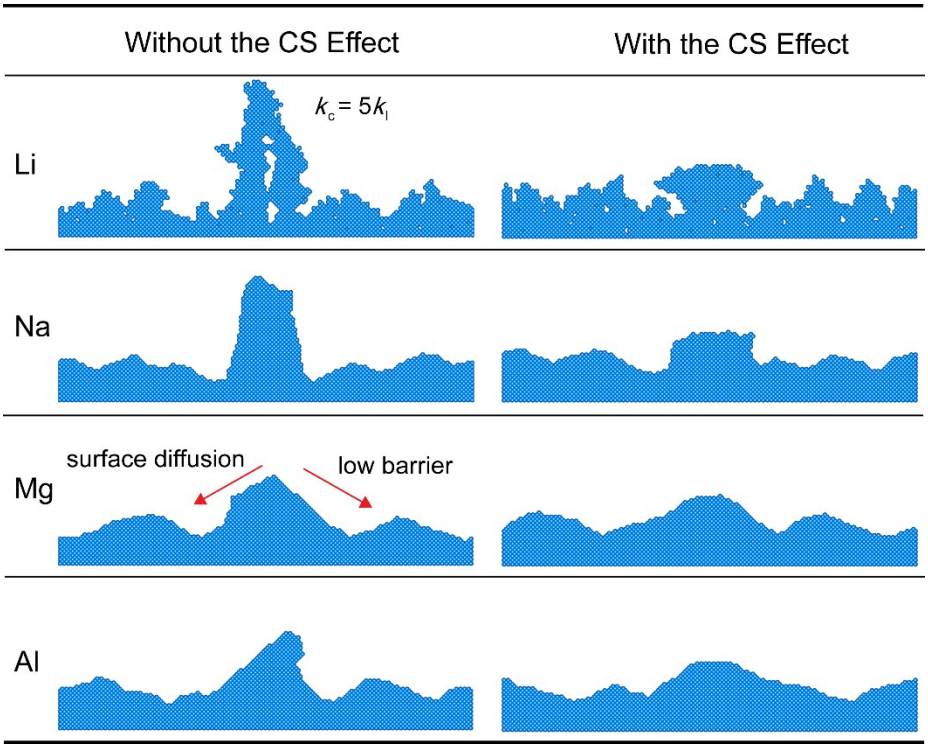

Fig. S3. CS effect on the electrodeposition morphologies of Li, Na, Mg, and Al.

Fig. S4 illustrates the dendrite growth for the case where Bi = 1500 and E_a = 0.3 eV. The gray circles are N^+ ion, and the red circles are M^+ ions. It can be seen that the use of M^+ ions makes the dendrite growth relatively uniform.

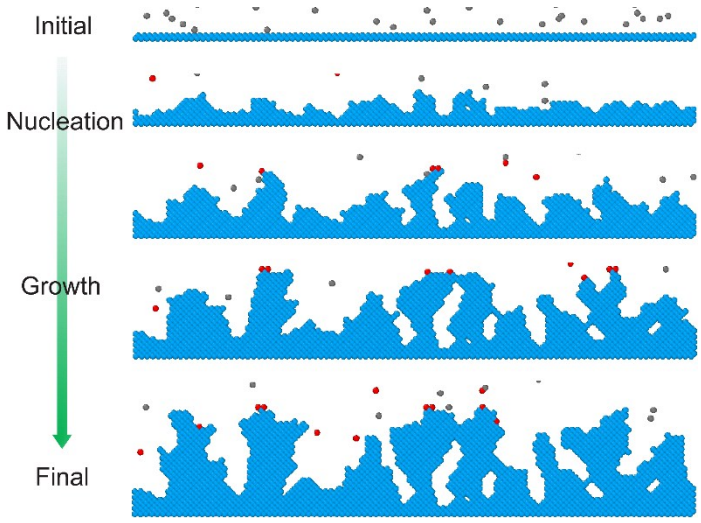

Fig. S4. Dendrite growth for the case where Bi = 1500 and E_a = 0.3 eV, and the gray and red circles represent metal N^+ and additive M^+ ions, respectively.

Reference

1. A. F. Voter, *Introduction to the Kinetic Monte Carlo Method, in Radiation Effects in Solids, edited by K. E. Sickafus and E. A. Kotomin, NATO Science Series, vol 235. Springer, Dordrecht.*, 2005.
2. M. Jäckle, K. Helmbrecht, M. Smits, D. Stottmeister and A. Groß, *Energy Environ. Sci.*, 2018, **11**, 3400-3407.
3. F. Hao, A. Verma and P. P. Mukherjee, *Energy Storage Mater.*, 2019, **20**, 1-6.