Supporting Information

Modeling for Homogeneous Mg Electrodeposition on Mg Metal Negative Electrode in Rechargeable Mg batteries

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Governing equations

The equations used in the simulation that were not shown in the paper are presented here. The diffusion of Mg^{2+} ions in the positive electrode can be described by the following equation:

$$\frac{\partial c_s}{\partial t} = -\nabla(-D_s \nabla c_s) \tag{S-1}$$

where c_s is the concentration of Mg^{2+} ions in the positive electrode, and D_s is the diffusion coefficient of Mg^{2+} ions in the positive electrode. Thermal balance is expressed as follows:

$$\rho C_p \frac{\partial T}{\partial t} + \nabla q = Q_{jh} + Q_{chem} + Q_m \tag{S-2}$$

where ρ is the density, q is the heat flux, C_p is the constant pressure heat capacity, Q_{jh} is the joule heat, Q_{chem} is the heat due to electrochemical reactions, and Q_m is the heat due to mixing. The bulk values of the diffusion coefficient were modified using the Bruggeman relationship for the positive electrode and the separator.

$$D_{sep} = \varepsilon_{sep}^{1.5} D \tag{S-3}$$

$$D_{pos} = \varepsilon_{pos}^{1.5} D \tag{S-4}$$

where D_{sep} and D_{pos} are the diffusion coefficients in the separator and positive electrode, respectively, and ε_{sep} and ε_{pos} are tortuosity and porosity, respectively.

Generalization using a dimensionless number

Figure S1 shows the Mg^{2+} ion concentration after charging at position 1 shown in Figure 4 with different diffusion coefficients varying from 7.5×10^{-11} to 7.5×10^{-9} m^2 s^{-1}. As shown in the figure, the differences in the concentrations at positions 1, 2, and 3 are due to their different distances from the Mg^{2+} ion source, which is the active material of the positive electrode. In Figure S1, the values of a dimensionless number A, defined by equation S1, to quantify the suppression of the ion concentration depletion, are also plotted together with the ion concentration after charging. A is defined according to

$$A = \frac{c_0 D F}{i l} \tag{S1}$$

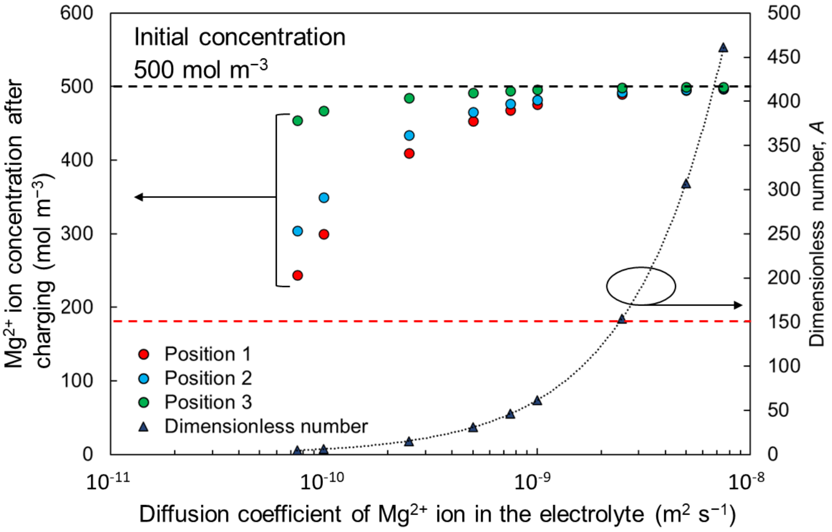

Figure S1. Mg^{2+} ion concentration and corresponding dimensionless number A after charging with different diffusion coefficients of Mg^{2+} ions in the electrolyte solution at positions 1, 2, and 3. The red broken line represents the dimensionless number value of 150 below which the difference in the concentration of Mg^{2+} ions inside and outside the well-type structure is less than 25 mol m^{-3}.

where c_0 is the initial concentration inside the well-type structure, D is the ion diffusion coefficient in the electrolyte solution, i is the current density on the electrode surface and l is the depth of the well-type structure. A decreasing value of A corresponds to an increased concentration of the Mg^{2+} ions inside the well-type structure, which is favorable for suppressing inhomogeneous Mg electrodeposition. For example, in Figure S1, the red broken line represents the A value of 150 below which the difference in the concentration of Mg^{2+} ions inside and outside the well-type structure is less than 25 mol m^{-3}. It should be noted that this threshold value of $A = 150$ was empirically determined. Above $A = 150$, the concentration at the bottom of the well-type structure, where the concentration decreases the most, retains 95% or more of the initial concentration (500 mol m^{-3} in this simulation) after charging. Below $A = 150$, an apparent concentration gradient appears. Although this definition is derived from simulation results, it provides a useful criterion for assessing diffusion-limited regimes.

Here, the depth of the well-type structure l is used as the representative length for the dimensionless number rather than the cubic root of volume $V^{\frac{1}{3}}$ based on the following considerations. In this study, the uniform Mg deposition was observed at a higher diffusion coefficient and a lower current density, which means the dimensionless parameter A should be higher to obtain a uniform Mg electrodeposition. As shown in Figure S2, the Mg^{2+} ion concentration in the well increases with decreasing the well depth l, which is favorable for a uniform Mg electrodeposition and corresponds to the increase in the dimensionless parameter A. In contrast, the Mg^{2+} ion concentration in the well decreases but the dimensionless parameter A increases with decreasing $V^{1/3}$, which is the opposite direction change in A. The above is the reason why the well depth l was chosen as the characteristic length in the definition of the dimensionless parameter A partly because diffusion into the well-type structure is primarily governed by longitudinal transport along the depth direction, which dominates the ion supply limitation.

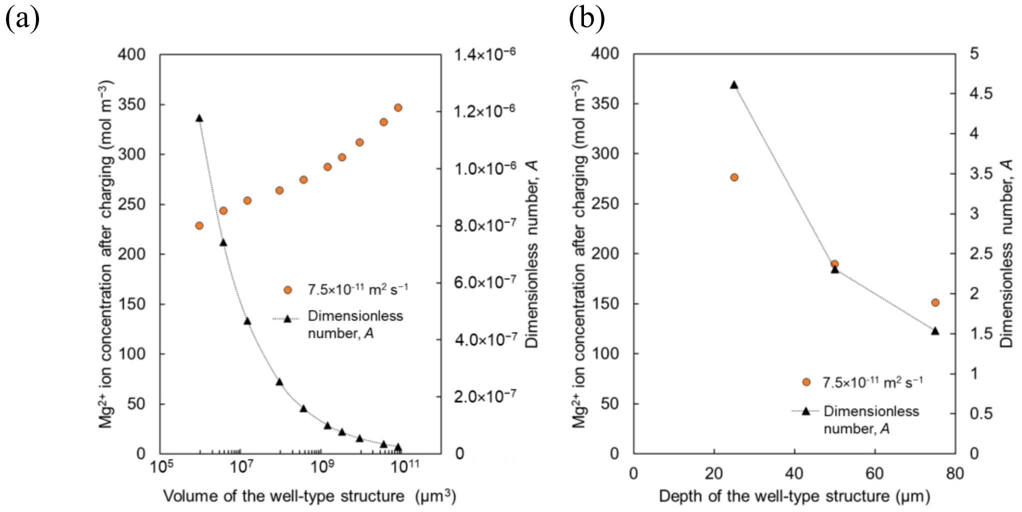

Figure S2. Mg^{2+} ion concentration at position 1 in Figure 4 after charging up to 2.2 V plotted together with the dimensionless number A as a function of (a) the volume of the well-type structure, (b) the depth of the well-type structure. The diffusion coefficient in the electrolyte is set to 7.5×10^{-11} m^2 s^{-1}.