PCCP

Electronic Supplementary Information

Periodic Precipitation Banding of Metal Hydroxides in Agarose Gels via Cyclic-Voltage-Driven Reaction–Transport–Reaction Process

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Additional Figures and Tables

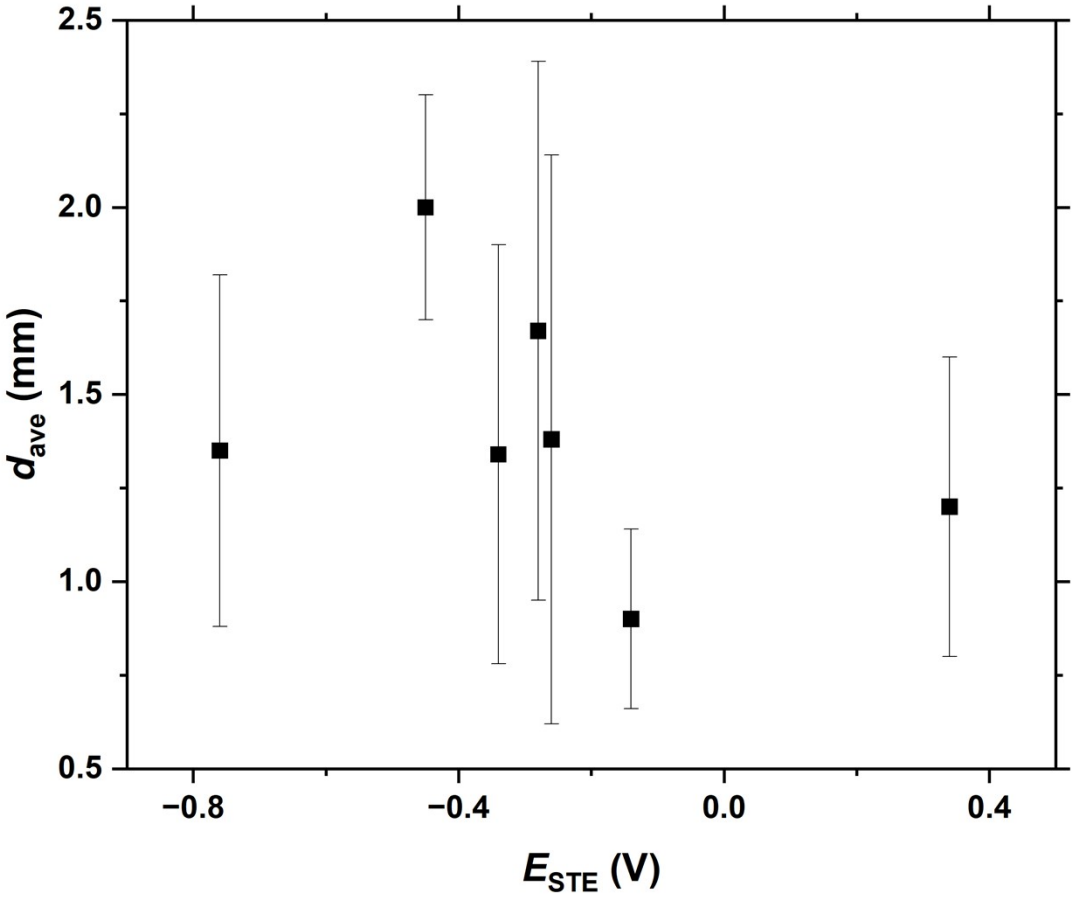

Fig. S1 E_{STE}-dependence of d_{ave} for the Fe, Co, Ni, Cu, Zn, In, and Sn anode RTR systems.

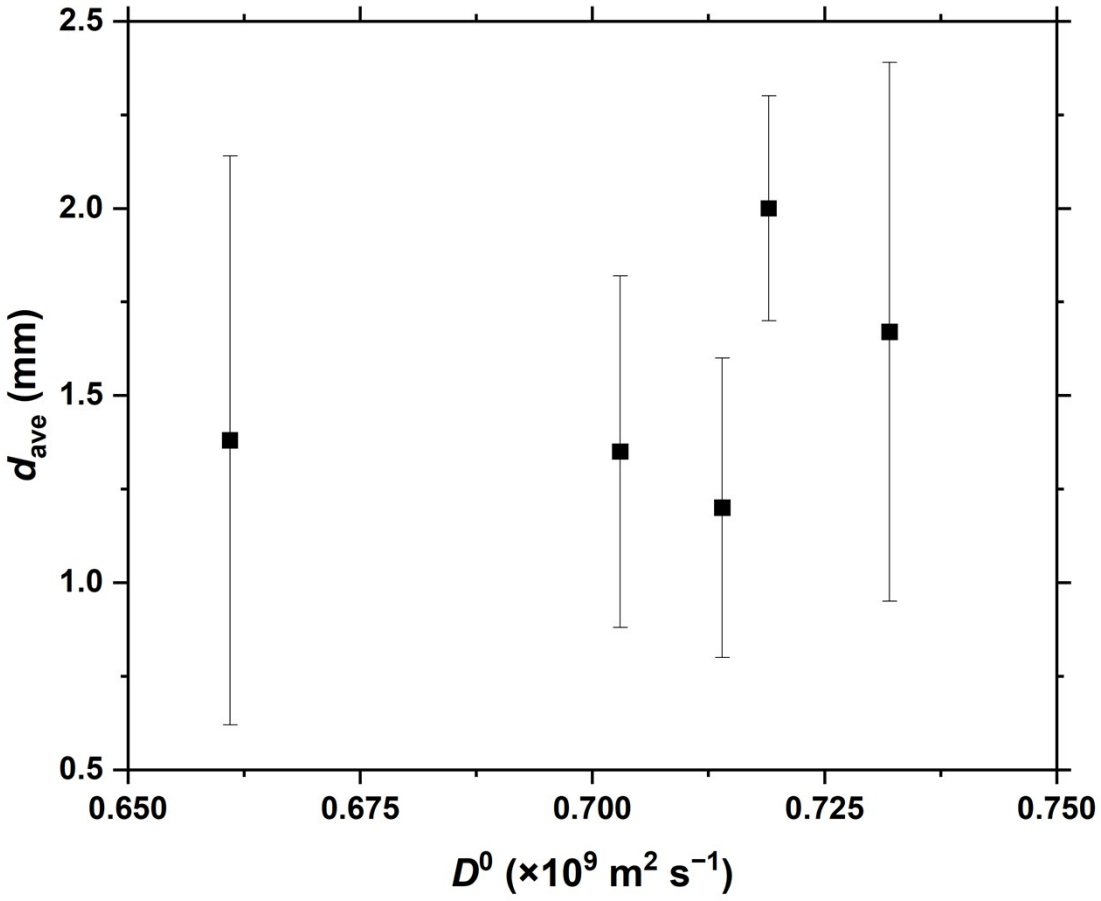

Fig. S2 D^0-dependence of d_{ave} for the Fe, Co, Ni, Cu, and Zn anode RTR systems.

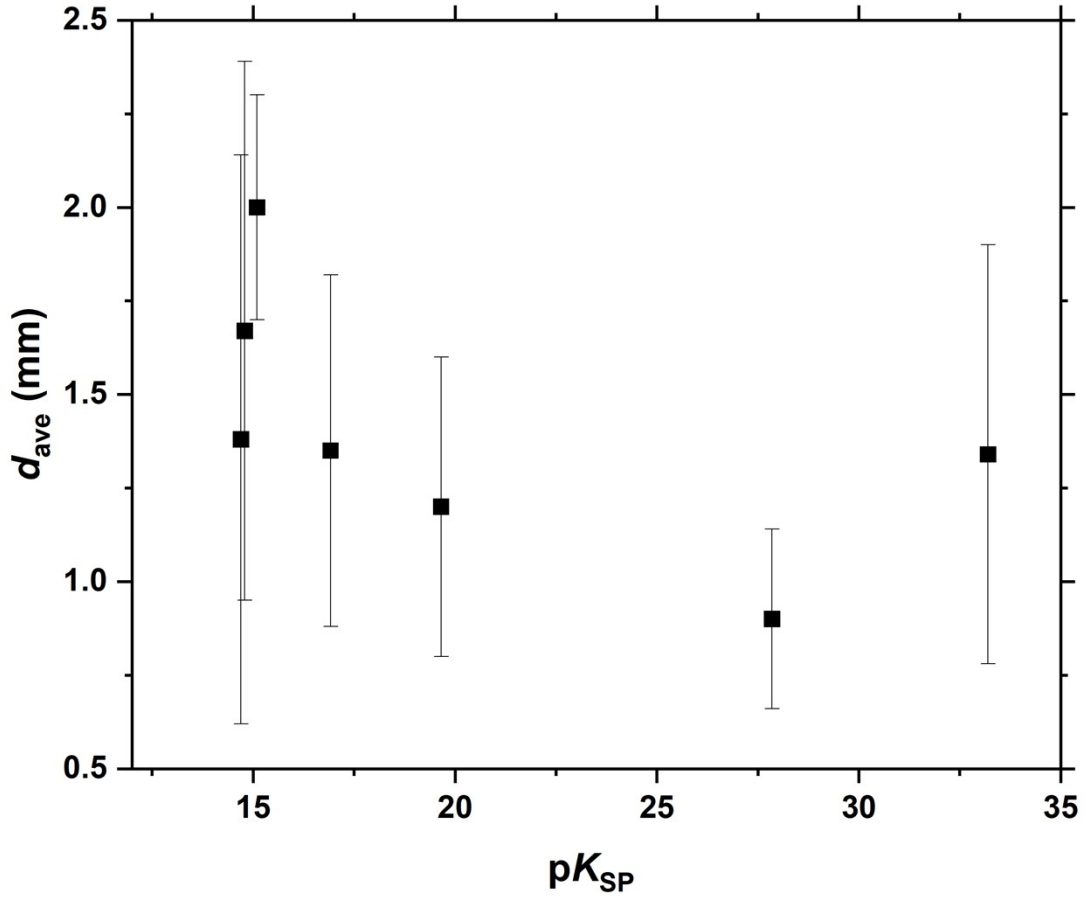

Fig. S3 pK_{sp}-dependence of d_{ave} for the Fe, Co, Ni, Cu, Zn, In, and Sn anode RTR systems

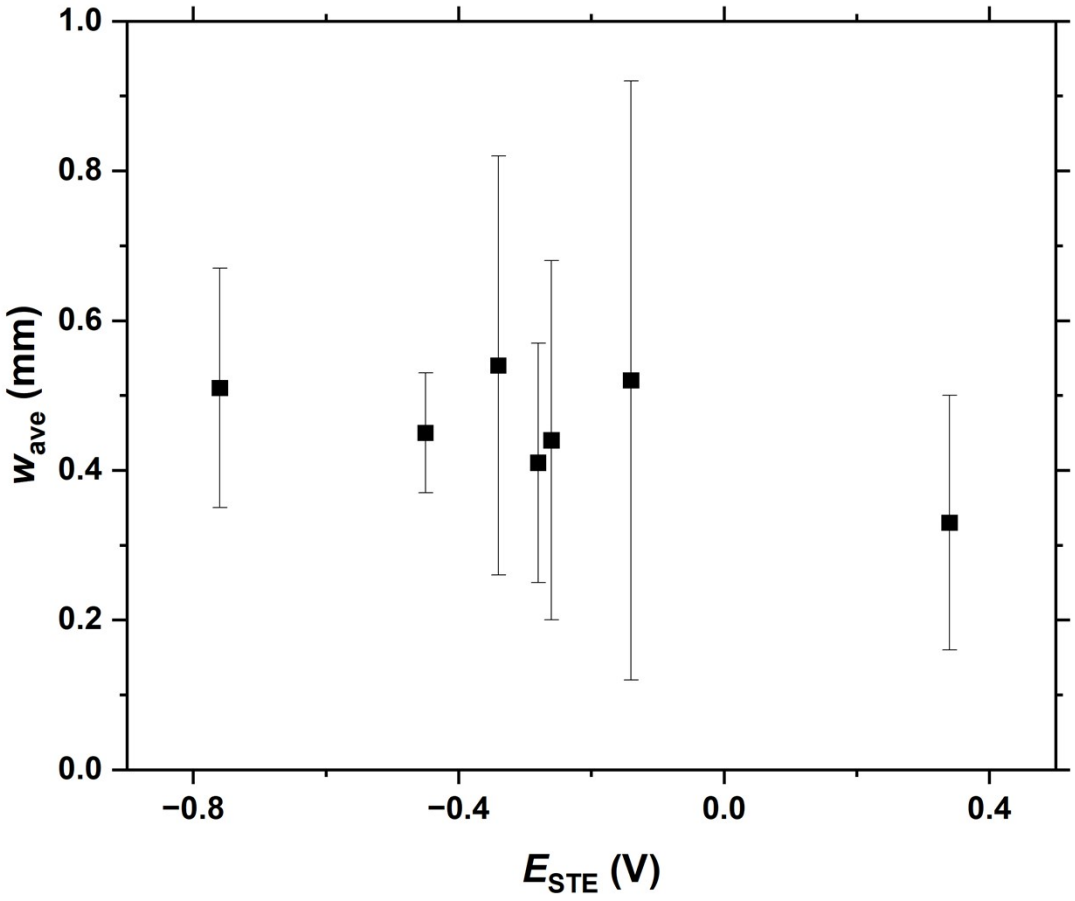

Fig. S4 E_{STE}-dependence of w_{ave} for the Fe, Co, Ni, Cu, Zn, In, and Sn anode RTR systems.

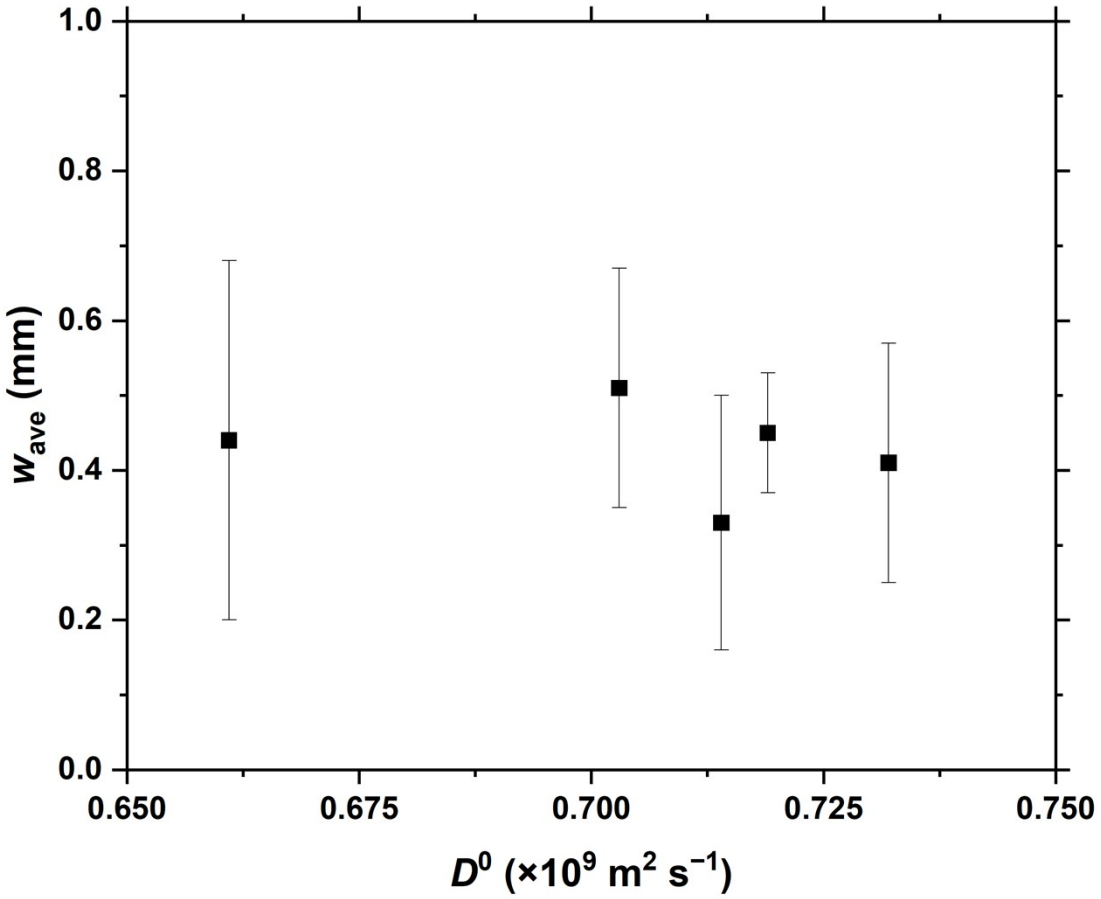

Fig. S5 D^0-dependence of w_{ave} for the Fe, Co, Ni, Cu, and Zn anode RTR systems.

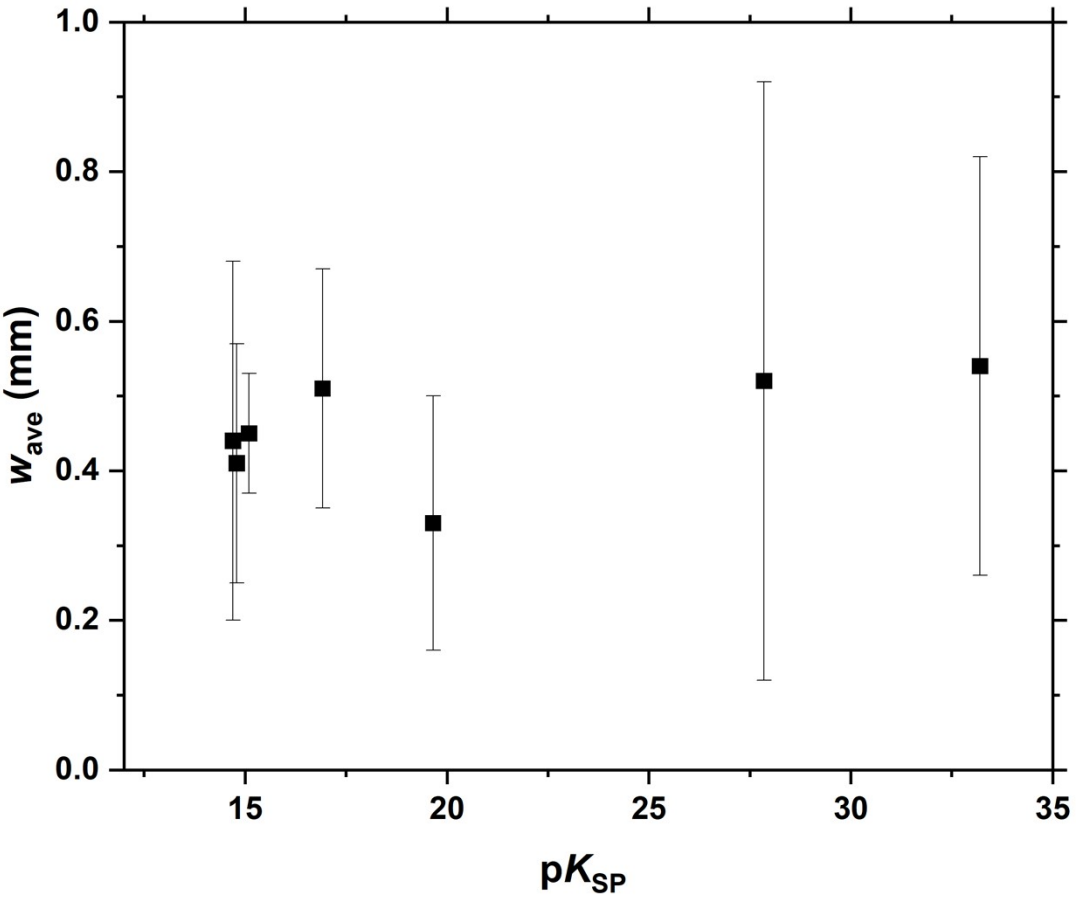

Fig. S6 pK_{sp}-dependence of w_{ave} for the Fe, Co, Ni, Cu, Zn, In, and Sn anode RTR systems.

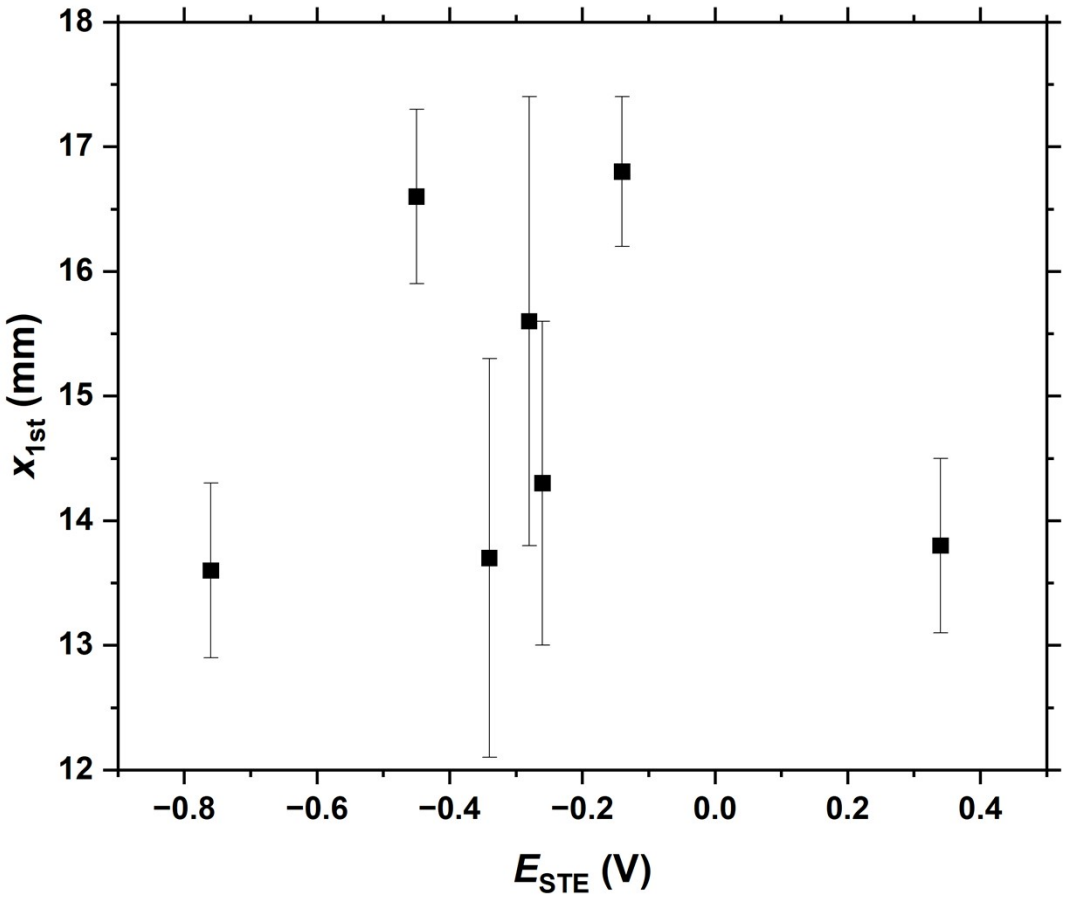

Fig. S7 E_{STE}-dependence of x_{1st} for the Fe, Co, Ni, Cu, Zn, In, and Sn anode RTR systems.

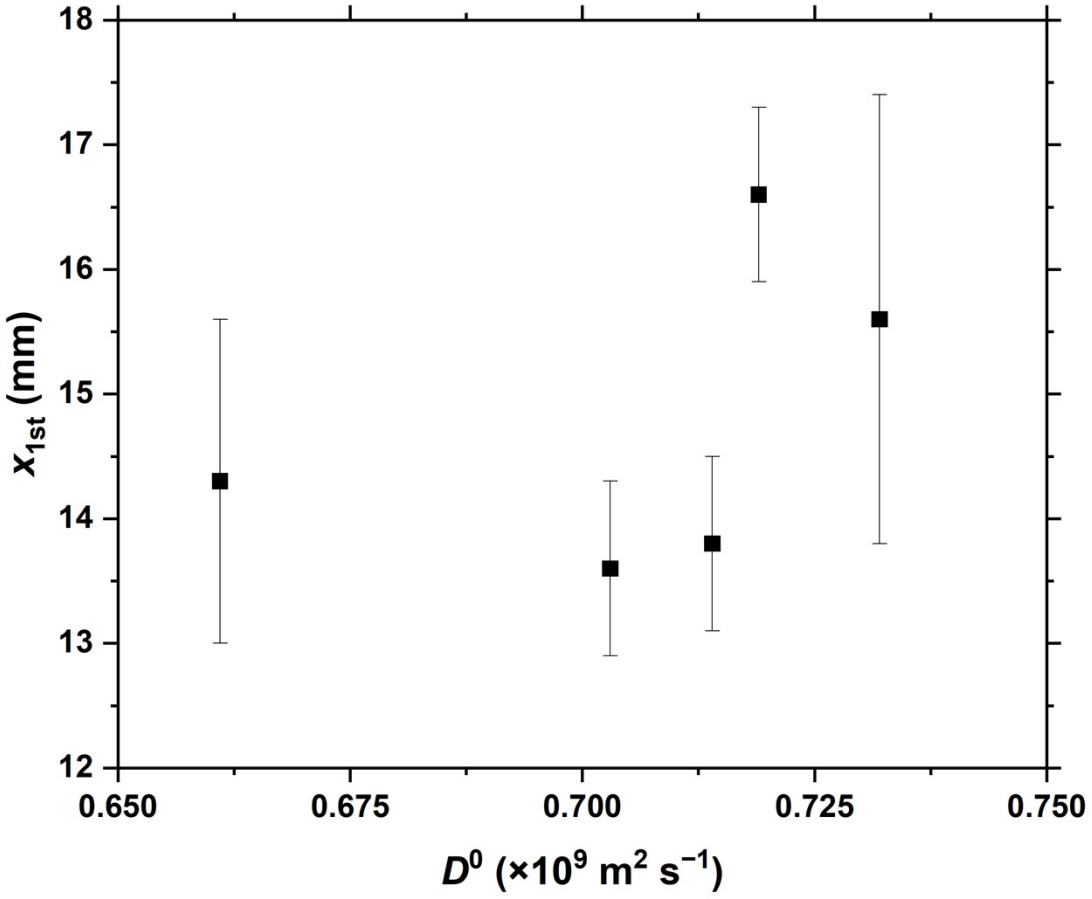

Fig. S8 D^0-dependence of x_{1st} for the Fe, Co, Ni, Cu, and Zn anode RTR systems.

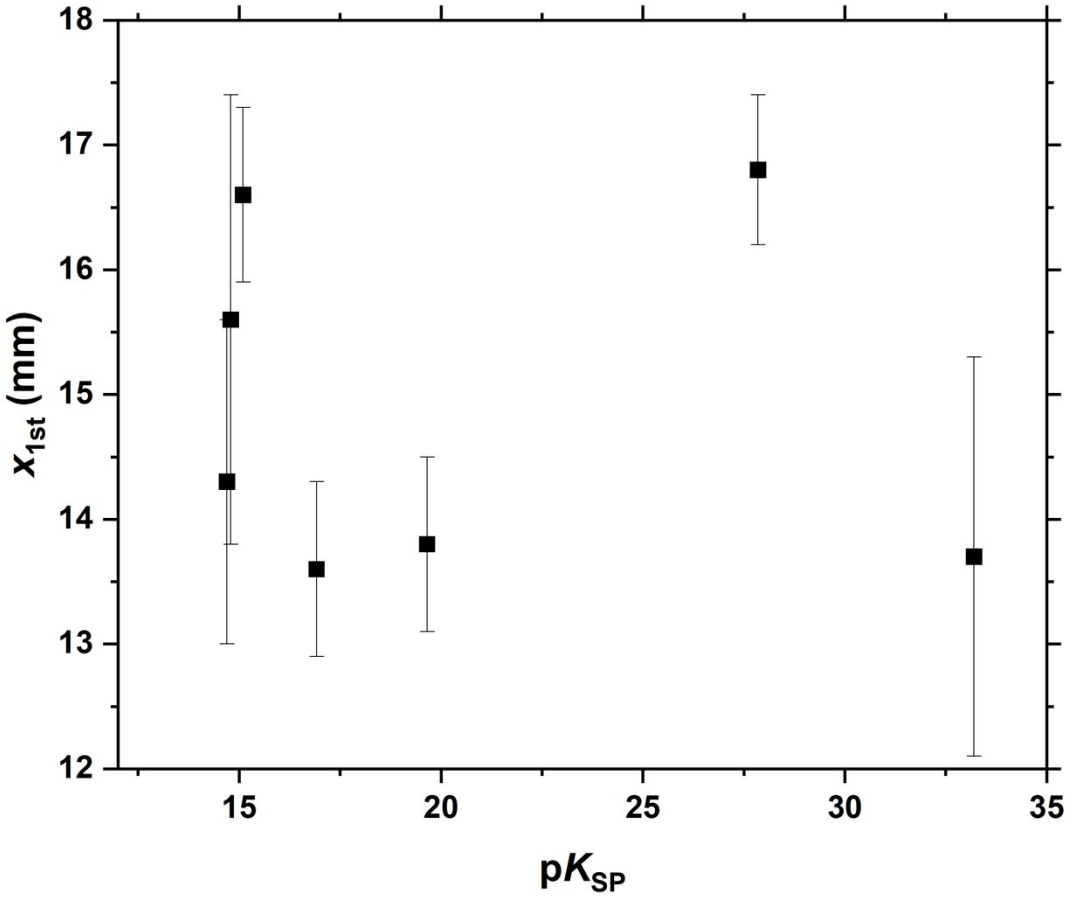

Fig. S9 pK_{sp}-dependence of x_{1st} for the Fe, Co, Ni, Cu, Zn, In, and Sn anode RTR systems.

Table S1. Banding parameters for the periodic bands shown in Fig. 3 (except Mo cathode system).

Cathode	d_{ave} (mm)[a]	w_{ave} (mm)[b]	x_{1st}(mm)[c]
Ti	0.65 ± 0.16	0.33 ± 0.10	12.6 ± 1.1
Ni	0.67 ± 0.20	0.32 ± 0.13	12.9 ± 0.7
Cu	1.20 ± 0.40	0.33 ± 0.17	13.8 ± 0.7
Ag	0.96 ± 0.32	0.30 ± 0.08	13.7 ± 0.7
W	0.69 ± 0.15	0.25 ± 0.11	13.5 ± 1.2

[a] d_{ave}: Average interband distance.

[b] w_{ave}: Average band width.

[c] x_{1st}: Average distance between the anode surface and the first precipitation band to emerge.

Table S2. Banding parameters for the periodic bands shown in Fig. 5.

L (mm)[a]	d_{ave} (mm)[b]	w_{ave} (mm)[c]	x_{1st}(mm)[d]
40	0.70 ± 0.29	0.31 ± 0.12	9.5 ± 0.5
50	1.20 ± 0.40	0.33 ± 0.17	13.8 ± 0.7
60	1.11 ± 0.44	0.32 ± 0.10	15.5 ± 0.9

[a]L: Length of gel column.

[b]d_{ave}: Average interband distance.

[c]w_{ave}: Average band width.

[d]x_{1st}: Average distance between the anode surface and the first precipitation band to emerge.

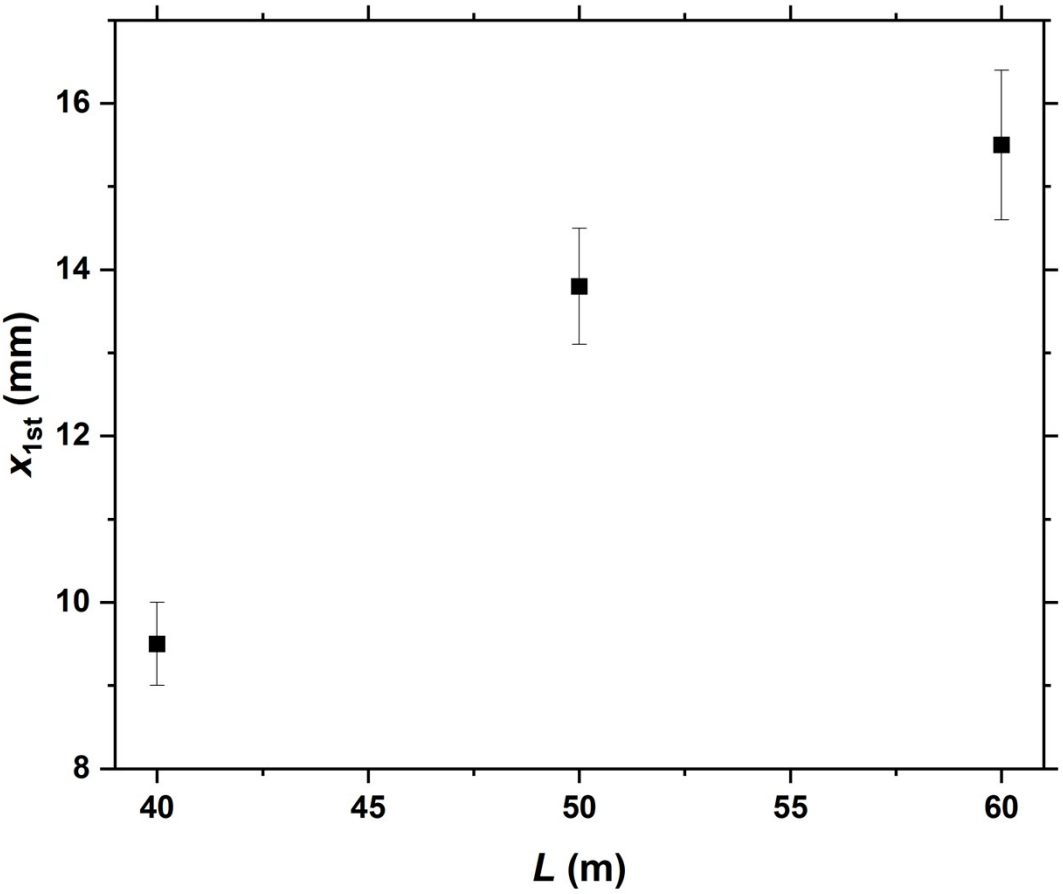

Fig. S10 L-dependence of x_{1st} for the Cu anode RTR system.

Table S3. Banding parameters for the periodic bands shown in Fig. 6.

Φ (mm)[a]	d_{ave} (mm)[b]	w_{ave} (mm)[c]	x_{1st}(mm)[d]
2	0.57 ± 0.30	0.17 ± 0.06	12.4 ± 0.5
4	1.20 ± 0.40	0.33 ± 0.17	13.8 ± 0.7
6	1.19 ± 0.39	0.33 ± 0.17	13.8 ± 0.7

[a]L: Diameter of gel column.

[b]d_{ave}: Average interband distance.

[c]w_{ave}: Average band width.

[d]x_{1st}: Average distance between the anode surface and the first precipitation band to emerge.

Table S4. Banding parameters for the periodic bands shown in Fig. 7.

C_{se} (mM)[a]	d_{ave} (mm)[b]	w_{ave} (mm)[c]	x_{1st}(mm)[d]
5	1.46 ± 0.37	0.36 ± 0.10	14.2 ± 0.7
10	1.20 ± 0.40	0.33 ± 0.17	13.8 ± 0.7
20	1.18 ± 0.30	0.40 ± 0.17	12.6 ± 0.7
30	1.01 ± 0.34	0.48 ± 0.26	12.3 ± 0.8
40	–	–	11.6 ± 0.8

[a]C_{se}: $NaNO_3$ concentration.

[b]d_{ave}: Average interband distance.

[c]w_{ave}: Average band width.

[d]x_{1st}: Average distance between the anode surface and the first precipitation band to emerge.

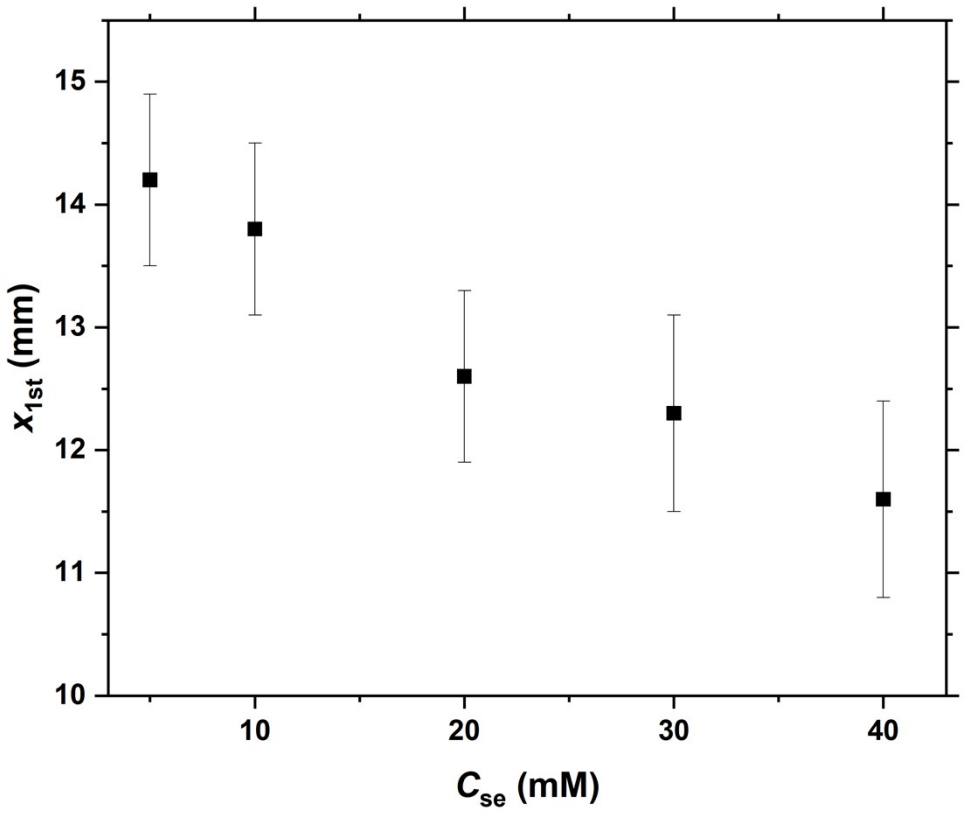

Fig. S11 C_{se}-dependence of x_{1st} for the Cu anode RTR system.

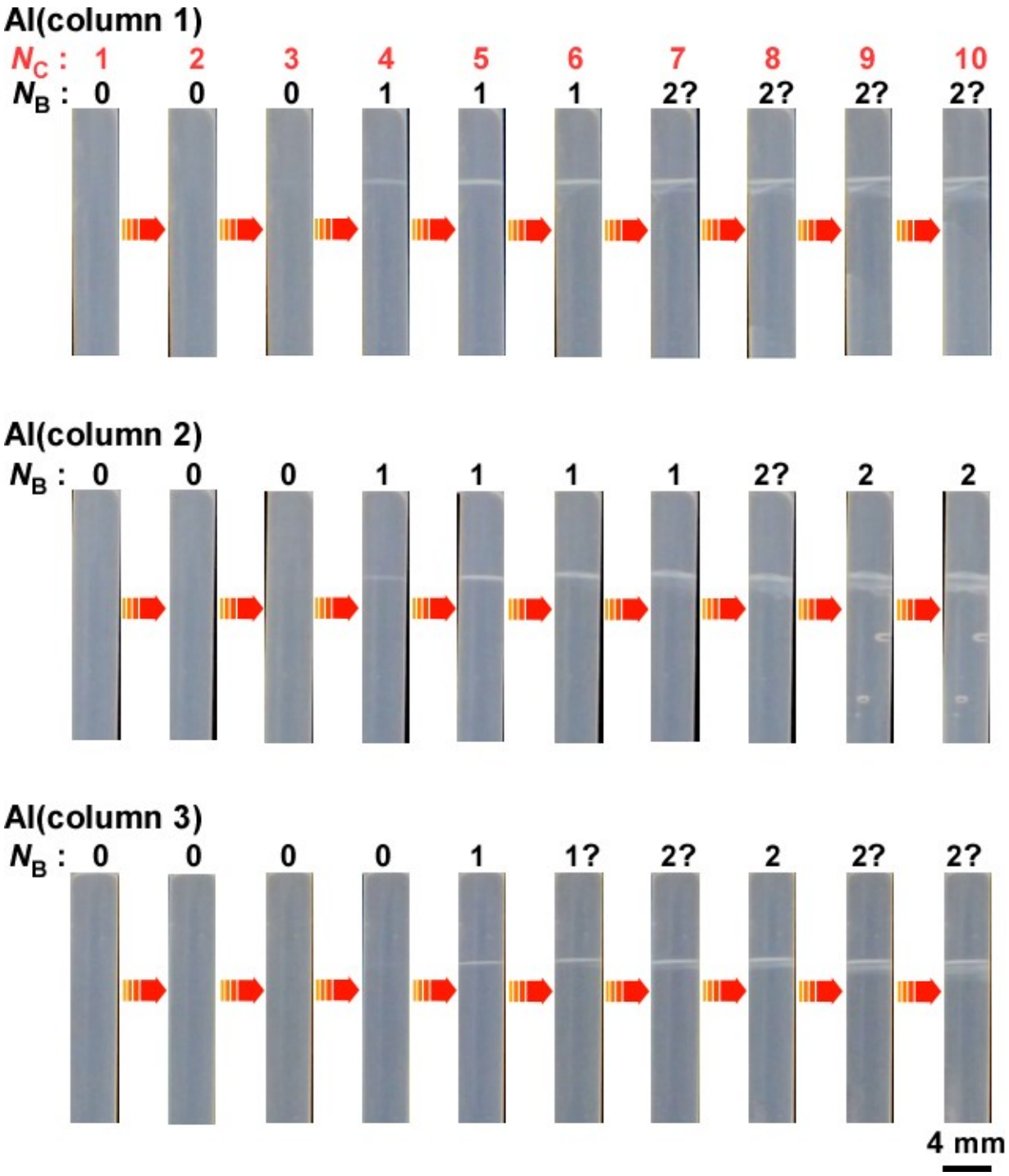

Fig. S12 Spatiotemporal evolution of periodic bands formed in three gel columns (L = 50 mm, ϕ = 4 mm, C_{se} = 10 mM) using an Al anode and Cu cathode at 298 K under the following voltage conditions: E_H = 3 V, E_L = 1 V, T_H = 1 h, and T_L = 2 h. The numbers of periodic bands (N_B) observed in the gel column during each cycle are shown. The cycle numbers (N_C) in which the images were captured are indicated at the top of the image. Some bubbles are visible in the lower part of column 2 for N_C = 9 and 10.

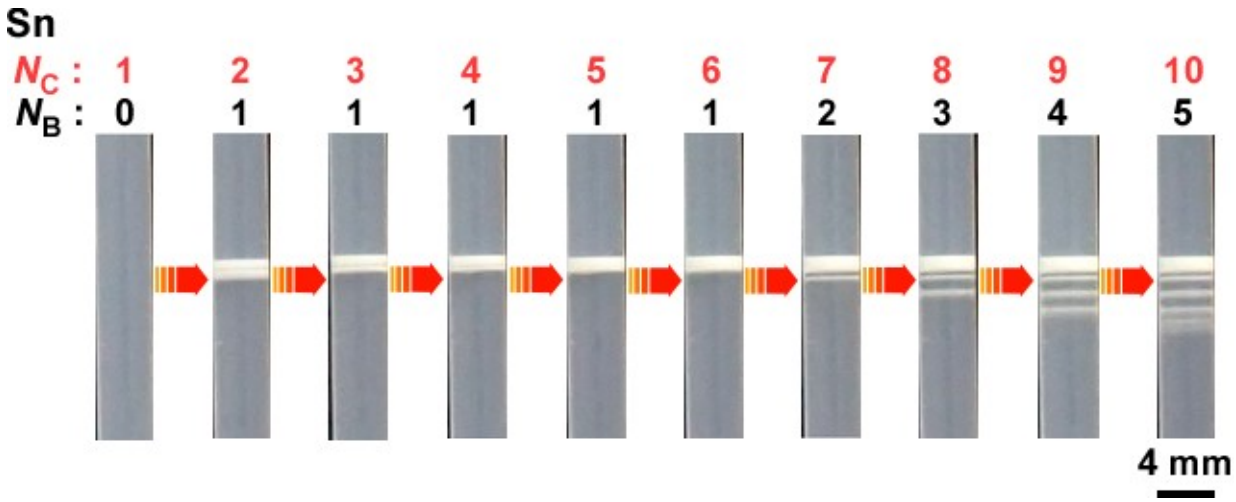

Fig. S13 Spatiotemporal evolution of typical periodic bands formed in gel column (L = 50 mm, ϕ = 4 mm, C_{se} = 10 mM) using a Sn anode and Cu cathode at 298 K under the following voltage conditions: E_H = 3 V, E_L = 1 V, T_H = 1 h, and T_L = 2 h. The cycle numbers (N_C) in which the images were captured and the numbers of periodic bands (N_B) observed in the gel column during each cycle are indicated at the top of the image.

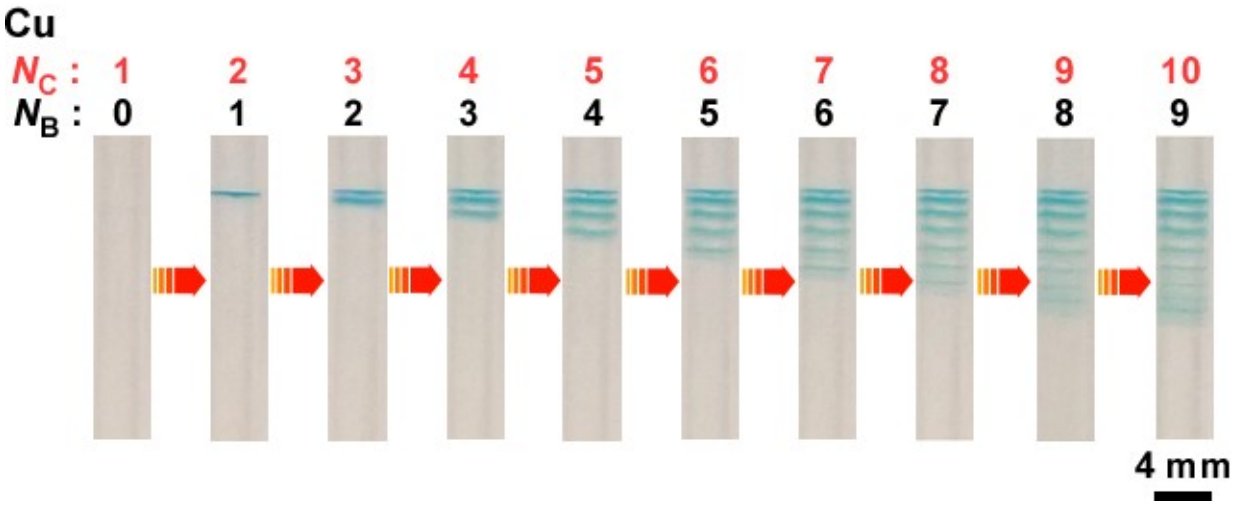

Fig. S14 Spatiotemporal evolution of typical periodic bands formed in gel column (L = 50 mm, ϕ = 4 mm, C_{se} = 10 mM) using a Cu anode and Cu cathode at 298 K under the following voltage conditions: E_H = 3 V, E_L = 1 V, T_H = 1 h, and T_L = 2 h. The cycle numbers (N_C) in which the images were captured and the numbers of periodic bands (N_B) observed in the gel column during each cycle are indicated at the top of the image.

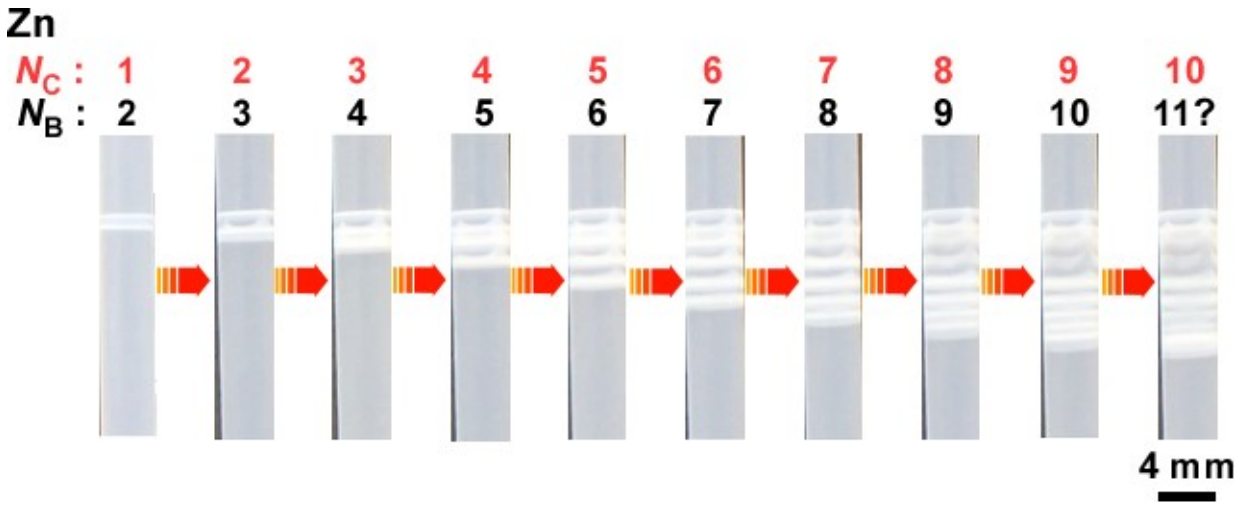

Fig. S15 Spatiotemporal evolution of typical periodic bands formed in gel column (L = 50 mm, ϕ = 4 mm, C_{se} = 10 mM) using a Zn anode and Cu cathode at 298 K under the following voltage conditions: E_H = 3 V, E_L = 1 V, T_H = 1 h, and T_L = 2 h. The cycle numbers (N_C) in which the images were captured and the numbers of periodic bands (N_B) observed in the gel column during each cycle are indicated at the top of the image.

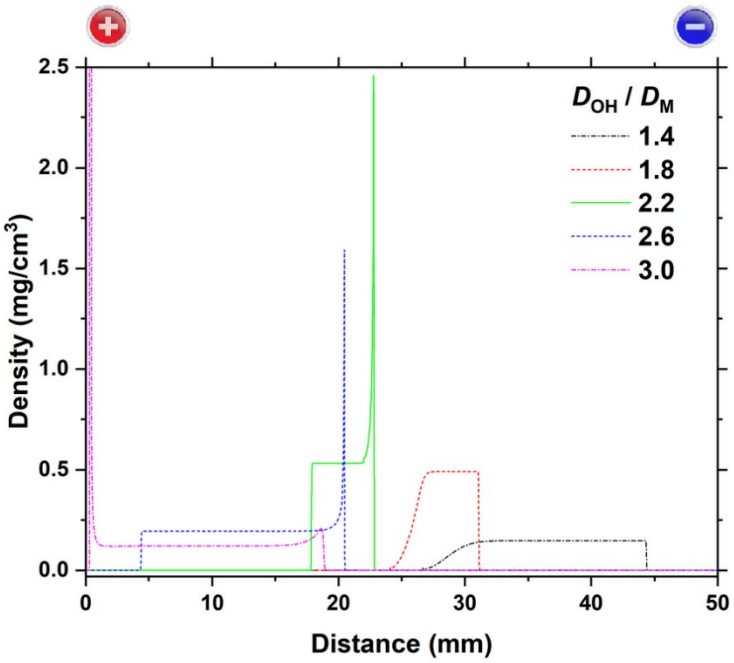

Fig. S16 Examples of precipitate density distributions calculated under constant voltage (3 V) application (t = 24 h, f_i = 1.0). The calculations were conducted for the same D_{OH}/D_M ratios as used in Fig. 11. The sides of the anode (+) and cathode (−), which exist at distances of 0 and 50 mm, respectively, are indicated at the top of the image. These distributions are essentially continuous rather than discrete or periodic, although some have a sharp peak at the ends.

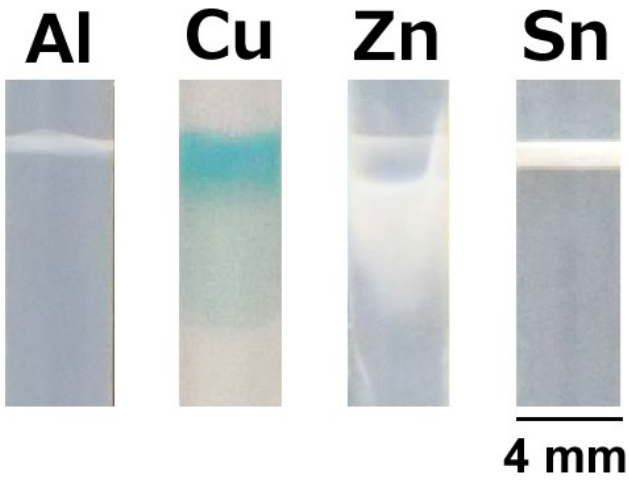

Fig. S17 Examples of precipitate patterns of $M(OH)_n$ (M = Al, Cu, Zn, and Sn; the elements shown in Fig. 8) in gel columns (L = 50 mm, ϕ = 4 mm C_{se} = 10 mM) using M anodes through RTR processes at 298 K under constant voltage (3 V) application (t = 20 h). Each system had a Cu cathode. An essentially single and continuous precipitation band was commonly generated, rather than periodic banding, although the Zn anode system showed considerably inhomogeneous banding.