

# Supporting Information

for

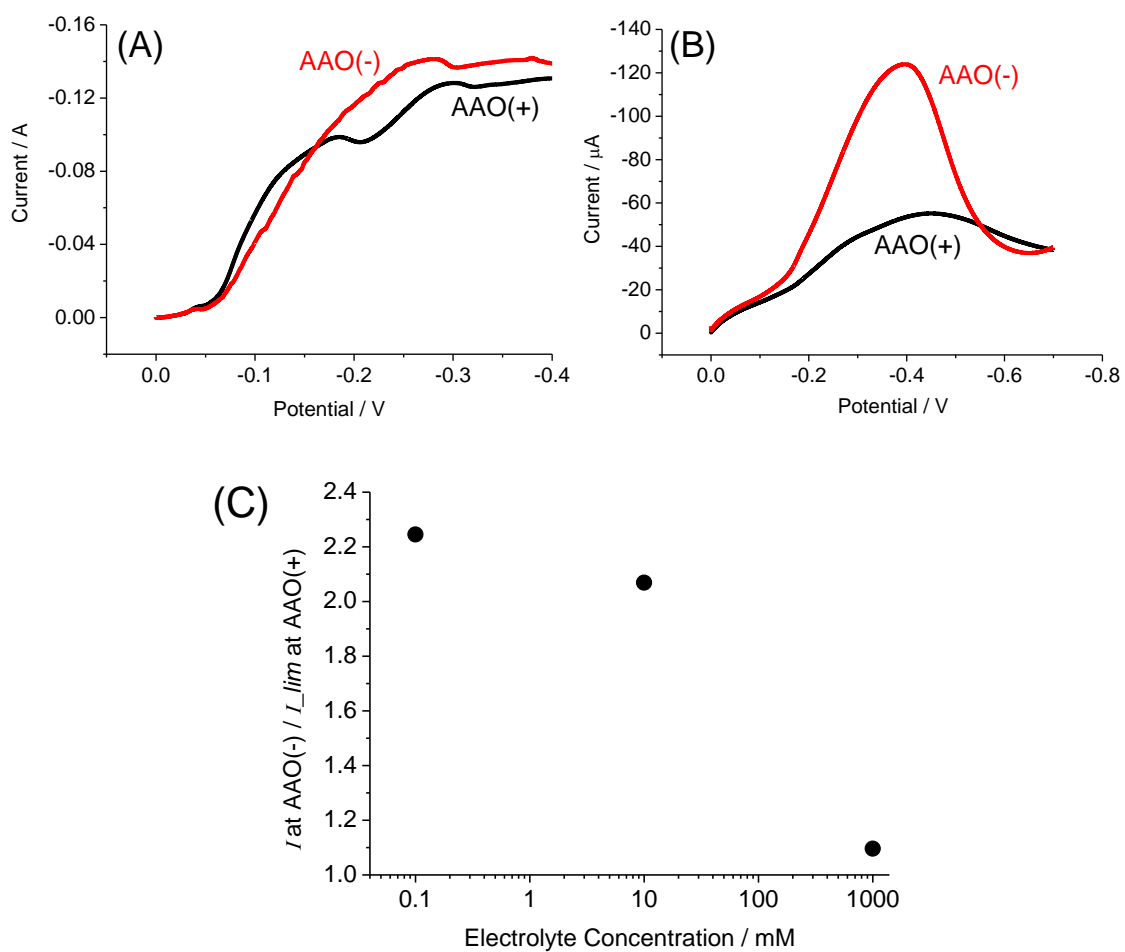
## Over-limiting Current and Control of Dendritic Growth by Surface Conduction in Nanopores

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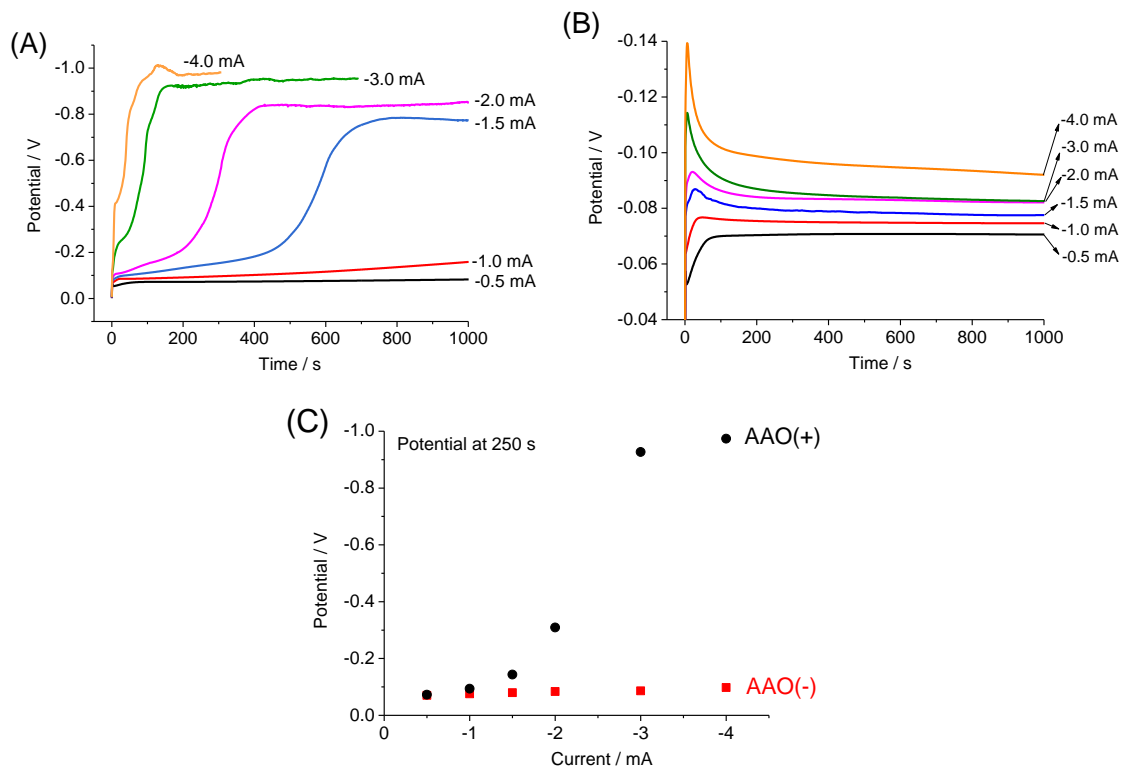
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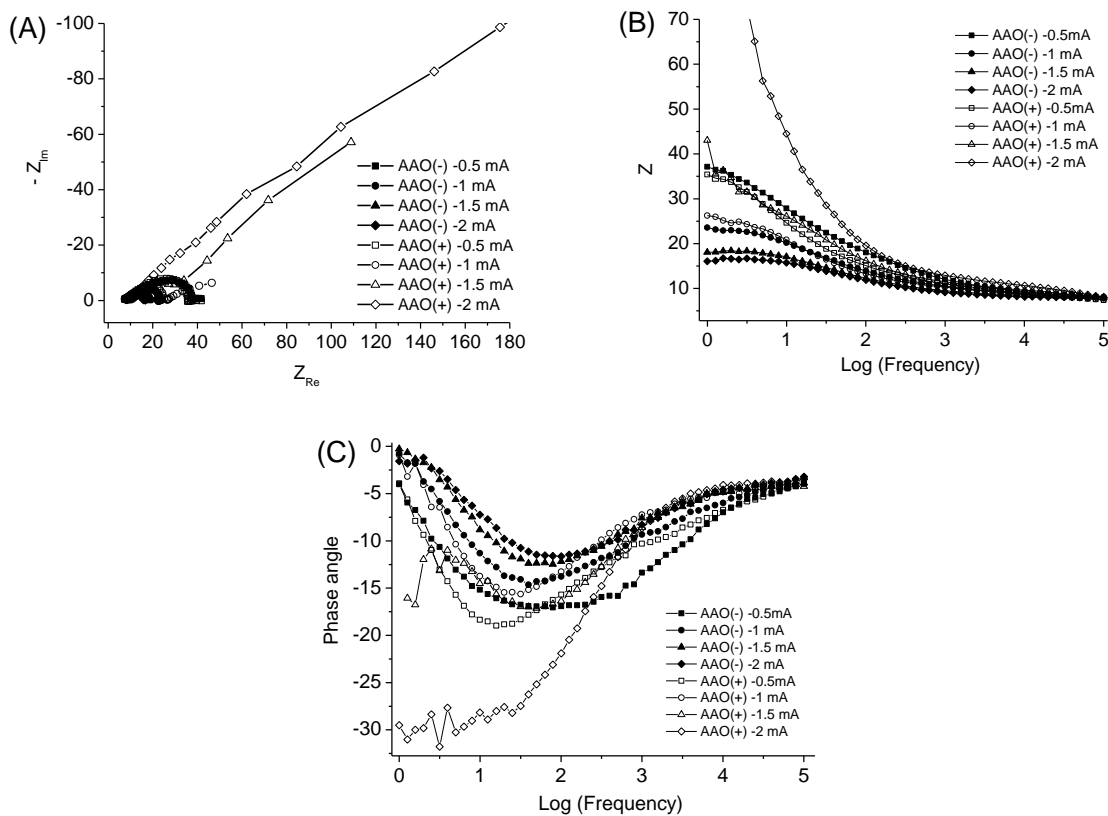
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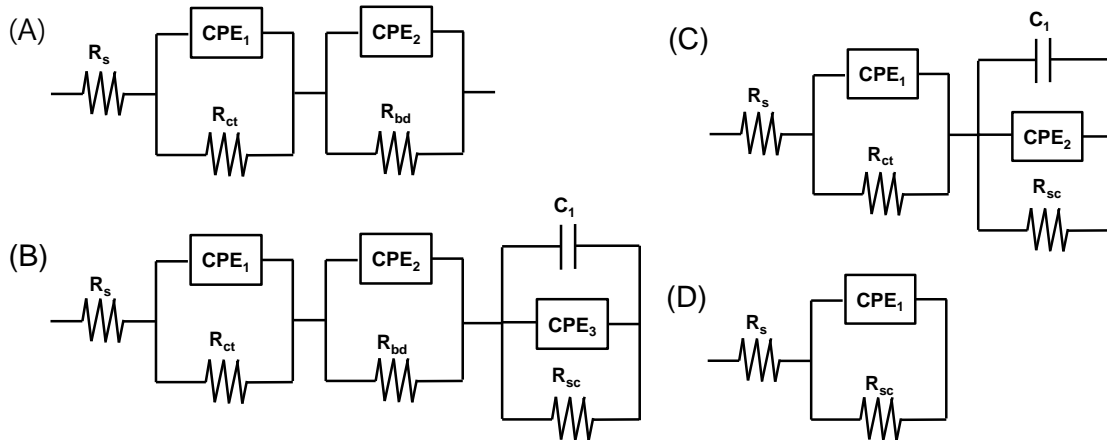
**Figure S1.** The effect of electrolyte concentration on SC-driven OLC. I-V curves of AAO(+) and AAO(-) membranes in (A) 1 M CuSO<sub>4</sub> and (B) 0.1 mM CuSO<sub>4</sub> at a scan rate of 1 mV/s. (C) A plot of current ratio of AAO(-) to AAO(+) as a function of electrolyte concentration.



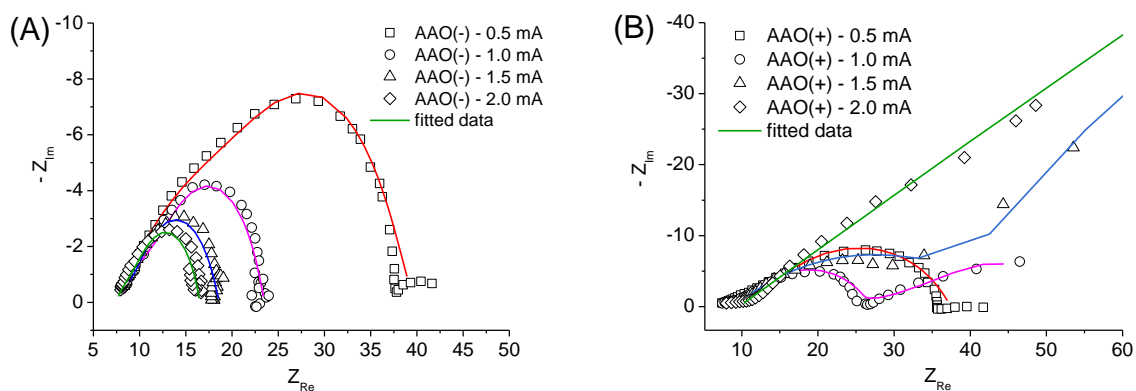
**Figure S2.** V-t curves of (A) AAO(+) and (B) AAO(-) in 10 mM CuSO<sub>4</sub> with different applied currents. (C) A comparison of potential at 250 s as a function of surface charge and applied currents.



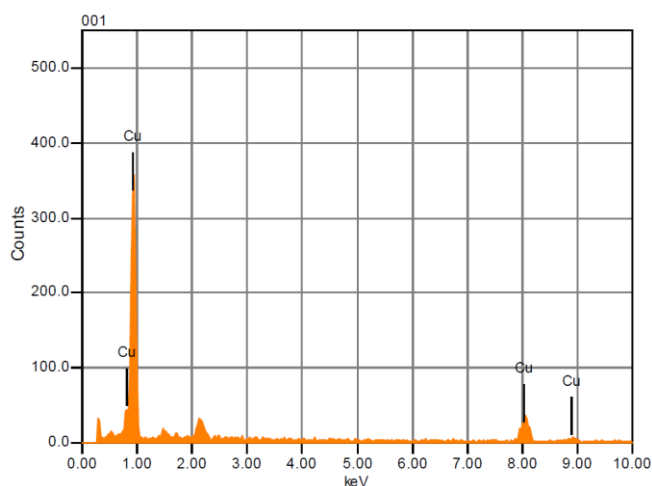
**Figure S3.** Full-scale Nyquist plots (A) and Bode plots (B and C) of AAO(+) and AAO(-) with different direct currents in 10 mM CuSO<sub>4</sub>. (B) Bode plots of total impedance, and (C) Bode plots of phase angle.



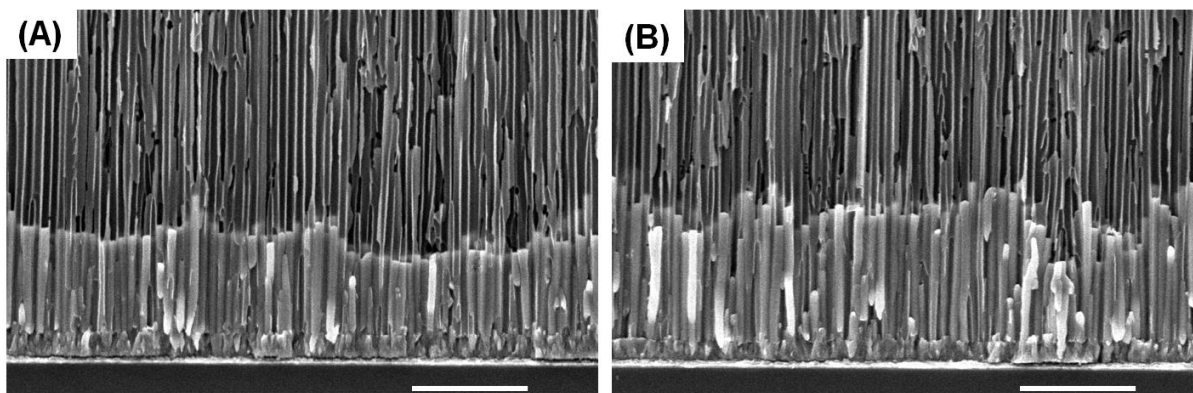
**Figure S4.** Four kinds of equivalent circuit models for (A) AAO(-) at all currents and AAO(+) at -0.5 mA, (B) AAO(+) at -1.0 mA, (C) AAO(+) at -1.5 mA and (D) AAO(+) at -2 mA.



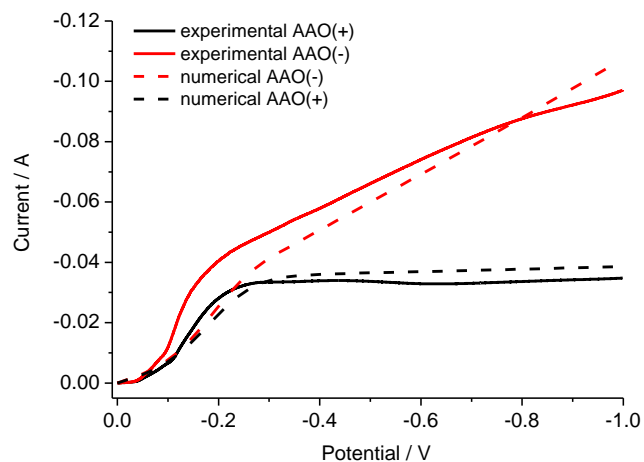
**Figure S5.** Nyquist plots of (A) AAO(-) and (B) AAO(+) with fitted data. The dotted and solid lines are experimental data and fitted data, respectively.



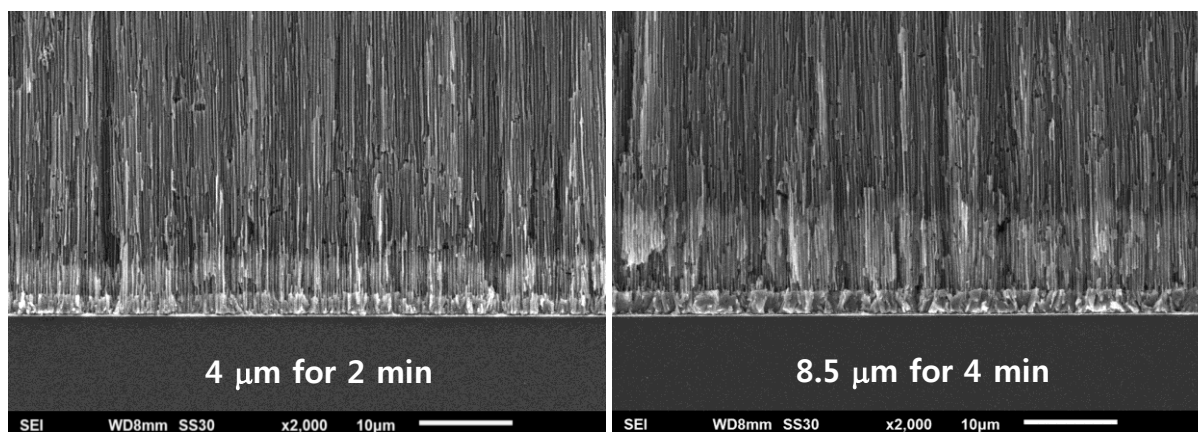
**Figure S6.** EDS data of Cu nanowire arrays.



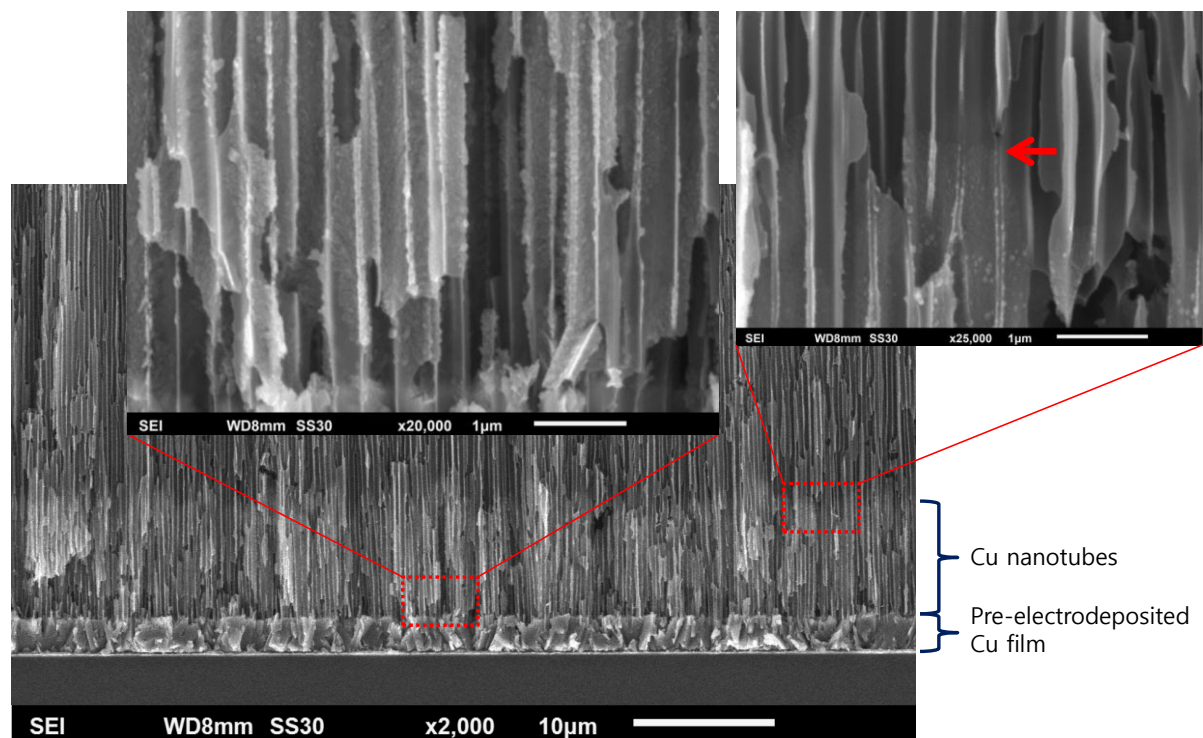
**Figure S7.** SEM images of Cu nanowires electrodeposited from (A) AAO(+) and (B) AAO(-) in 1 M  $\text{CuSO}_4$ . The scale bars are 5  $\mu\text{m}$ .



**Figure S8.** Current data for AAO(+) and AAO(-) membrane in 100 mM  $\text{CuSO}_4$ /100 mM  $\text{H}_3\text{BO}_3$  at a scan rate of 10 mV/s.



**Figure S9.** Cross-sectional SEM images of nanotubes generated in AAO(-) membrane. -1.8 V was applied for 2 and 4 min in 100 mM  $\text{CuSO}_4$  /100 mM  $\text{H}_3\text{BO}_3$  solution at room temperature. The nanotubes are very uniform and growth rate is about 2  $\mu\text{m}$  per min.



**Figure S10.** Cross-sectional SEM images of nanotubes generated in AAO(-) membrane. -1.8 V was applied for 4 min in 100 mM  $\text{CuSO}_4$  /100 mM  $\text{H}_3\text{BO}_3$  solution at room temperature. The red arrow indicates the tip of nanotubes along the walls of AAO membrane.

# Theoretical Analysis

## 1 Assumptions

To predict the overlimiting current (OLC) due to surface conduction (SC), we model the system as a 1D leaky membrane [1, 2, 3, 4]. We consider a charged nanoporous medium with a porosity  $\epsilon_p$ , an internal pore surface area/volume ratio  $a_p$  and a pore surface charge/area ratio  $\sigma_s$ . We define the effective pore size  $h_p$  as

$$h_p \equiv \frac{\epsilon_p}{a_p}. \quad (1)$$

As in [5], denoting the molecular (free solution) and macroscopic diffusivities of species  $i$  as  $D_i^m$  and  $D_i$  respectively and  $\tau$  as the tortuosity of the charged nanoporous medium, we define

$$D_i \equiv \frac{D_i^m}{\tau}. \quad (2)$$

Macroscopic electroneutrality implies that

$$\rho_s \equiv \frac{\sigma_s}{h_p} = \frac{a_p \sigma_s}{\epsilon_p} = - \sum_i z_i e c_i. \quad (3)$$

where  $c_i$  is the concentration of species  $i$  and  $\rho_s$  is the volume-averaged background charge density. We make the following assumptions:

1. Dilute solution theory is applicable.
2. Binary symmetric  $z:z$  electrolyte ( $z = 2$ ) with generally unequal  $D_{\pm}$ .
3. No fluid flow.
4. No homogeneous reactions.
5.  $\tau$ ,  $\epsilon_p$ ,  $h_p$ ,  $a_p$  and  $\sigma_s$  are uniform and constant.
6. Anodic aluminum oxide (AAO) membranes have parallel straight cylindrical pores with a constant pore radius  $r_p$ . Thus,  $h_p = \frac{r_p}{2}$  and  $\tau = 1$ .
7. Butler-Volmer reaction kinetics for copper electrodeposition at the cathode and for copper electrodis-solution at the anode.
8. Anions are inert.

## 2 Transport

The governing equations are given by the Nernst-Planck equations coupled with the macroscopic electroneutrality equation:

$$\epsilon_p \frac{\partial c_{\pm}}{\partial t} + \frac{\partial F_{\pm}}{\partial x} = 0, \quad (4)$$

$$F_{\pm} = -\epsilon_p D_{\pm} \left( \frac{\partial c_{\pm}}{\partial x} \pm \frac{z e c_{\pm}}{k_B T} \frac{\partial \phi}{\partial x} \right), \quad (5)$$



$$D_{\pm} \equiv \frac{D_{\pm}^m}{\tau}, \quad (6)$$

$$\rho_s = ze(c_- - c_+). \quad (7)$$

The current density  $J$  is given by

$$J = ze(F_+ - F_-). \quad (8)$$

The charge conservation equation is given by

$$\frac{\partial J}{\partial x} = 0. \quad (9)$$

Denoting the positions of the anode and cathode interfaces as  $x_m^a$  and  $x_m^c$  respectively and the Faradaic current densities at the anode and the cathode as  $J_F^a$  and  $J_F^c$  respectively, the current  $I$  is given by

$$I = J_F^c(x = x_m^c)A_{\text{active}}^c = -J_F^a(x = x_m^a)A_{\text{active}}^a \quad (10)$$

where  $A_{\text{active}}^{a,c}$  is the total active surface area of the anode or cathode and  $A^{a,c}$  is the total surface area of the anode or cathode (i.e., including both the electrolyte and matrix phases). We note that the superscripts a and c denote the anode and the cathode respectively. For AAO membranes with parallel straight cylindrical pores with a constant pore radius  $r_p$ ,  $\frac{A_{\text{active}}^{a,c}}{A^{a,c}} = \epsilon_p$ .

### 3 Reaction kinetics

Assuming that Butler-Volmer reaction kinetics apply, the Faradaic current density  $J_F$  [6, 7] can be written as

$$J_F = ne \left\{ k_c \hat{c}_O \exp\left(-\frac{\alpha ne \Delta \phi}{k_B T}\right) - k_a \hat{c}_R \exp\left[\frac{(1-\alpha) ne \Delta \phi}{k_B T}\right] \right\} \quad (11)$$

where  $n$  is the number of electrons transferred per charge transfer reaction,  $k_c$  and  $k_a$  are the cathodic and anodic rate constants respectively,  $\hat{c}_O$  and  $\hat{c}_R$  are respectively the dimensionless concentrations of the oxidized and reduced species nondimensionalized by their standard concentrations,  $\Delta \phi \equiv \phi_e - \phi$  where  $\phi_e$  and  $\phi$  are the electric potentials of the electrode and electrolyte respectively, and  $0 \leq \alpha \leq 1$  is the charge transfer coefficient. The reaction mechanism for copper electrodeposition and electrodisolution [7, 8] can be written as



where (aq) indicates aqueous and (ads) indicates adsorbed on the electrode surface. We assume that Butler-Volmer reaction kinetics applies to both elementary charge transfer reactions and that the first step (denoted with the subscript 1) is the slow step or rate-determining step while the second step (denoted with the subscript 2) is the fast step that is at equilibrium. We define the overpotential  $\eta$  as

$$\eta \equiv \Delta \phi - \Delta \phi^{\text{eq}} \quad (14)$$

where  $\Delta \phi^{\text{eq}}$  is the Nernst equation (at equilibrium, which is denoted by the eq superscript) that is given by

$$\Delta \phi^{\text{eq}} = \frac{k_B T}{2e} \ln \left( \frac{k_{c,1} k_{c,2} c_{\text{Cu}^{2+}}}{k_{a,1} k_{a,2}} \right) \quad (15)$$

where we note that the factor of 2 in the denominator accounts for the overall transfer of 2 electrons. At standard conditions (denoted by the  $\Theta$  superscript),  $c_{\text{Cu}^{2+}} = 1$  and

$$E^{\Theta} \equiv \Delta \phi^{\text{eq},\Theta} = \frac{k_B T}{2e} \ln \left( \frac{k_{c,1} k_{c,2}}{k_{a,1} k_{a,2}} \right) \quad (16)$$

where  $E^\ominus = 0.34 \text{ V}$  is the standard electrode potential of  $\text{Cu}^{2+}$  ions. Therefore,

$$\Delta\phi^{\text{eq}} = E^\ominus + \frac{k_{\text{B}}T}{2e} \ln c_{\text{Cu}^{2+}}. \quad (17)$$

Using the definition of the overpotential  $\eta$ , we express  $J_{\text{F}}$  as

$$J_{\text{F}} = J_0 \left\{ \exp\left(-\frac{\alpha_1 e \eta}{k_{\text{B}}T}\right) - \exp\left[\frac{(2 - \alpha_1) e \eta}{k_{\text{B}}T}\right] \right\} \quad (18)$$

where

$$J_0 = 2e(k_{\text{c},1}c_{\text{Cu}^{2+}})^{1 - \frac{\alpha_1}{2}} \left(\frac{k_{\text{a},1}k_{\text{a},2}}{k_{\text{c},2}}\right)^{\frac{\alpha_1}{2}}. \quad (19)$$

Suppose that we know the value of  $J_0$  at a given reference concentration  $c_{\text{Cu}^{2+}}^{\text{ref}}$  and we denote this value of  $J_0$  as  $J_0^{\text{ref}}$ . Then,

$$J_{\text{F}} = J_0 \left\{ \exp\left(-\frac{\alpha_1 e \eta}{k_{\text{B}}T}\right) - \exp\left[\frac{(2 - \alpha_1) e \eta}{k_{\text{B}}T}\right] \right\} \quad (20)$$

where

$$J_0 = J_0^{\text{ref}} \left(\frac{c_{\text{Cu}^{2+}}}{c_{\text{Cu}^{2+}}^{\text{ref}}}\right)^{1 - \frac{\alpha_1}{2}}. \quad (21)$$

We note that  $J_0^{\text{ref}}$  is denoted by  $I_0$  and  $\alpha_1$  is denoted by  $\alpha$  in the main text.

## 4 Initial conditions and boundary conditions

### 4.1 Initial conditions

$$c_-(t=0) = c_0, \quad (22)$$

$$x_{\text{m}}^{\text{a}}(t=0) = 0, \quad (23)$$

$$x_{\text{m}}^{\text{c}}(t=0) = L. \quad (24)$$

### 4.2 Boundary conditions

We define  $\hat{n}$  as the unit normal that points outwards from the electrolyte. At  $x = x_{\text{m}}^{\text{a,c}}$ , because the anions are inert and the cations are electroactive,

$$\hat{n} \cdot F_-(x = x_{\text{m}}^{\text{a,c}}) = 0, \quad (25)$$

$$A^{\text{a,c}} \hat{n} \cdot F_+(x = x_{\text{m}}^{\text{a,c}}) = \frac{J_{\text{F}}^{\text{a,c}}}{ze} A_{\text{active}}^{\text{a,c}}. \quad (26)$$

Mass conservation of copper metal at the anode and cathode interfaces implies that

$$v_{\text{n}}^{\text{a,c}} = -\Omega_{\text{Cu}} \hat{n} \cdot F_+(x = x_{\text{m}}^{\text{a,c}}) \quad (27)$$

where  $\Omega_{\text{Cu}} = \frac{M_{\text{Cu}}}{\rho_{\text{Cu}}}$  is the atomic volume of copper metal,  $M_{\text{Cu}}$  is the atomic mass of copper metal,  $\rho_{\text{Cu}}$  is the mass density of copper metal and  $v_{\text{n}}^{\text{a,c}}$  is the normal velocity of the anode/cathode interface. We denote the electric potentials of the anode and cathode as  $\phi_{\text{e}}^{\text{a}}$  and  $\phi_{\text{e}}^{\text{c}}$  respectively. We ground the anode at all times and impose a linearly varying (in time) electric potential at the cathode for linear sweep voltammetry:

$$\phi_{\text{e}}^{\text{a}} = 0, \quad (28)$$

$$\phi_{\text{e}}^{\text{c}} = \beta t, \quad \beta < 0, \quad (29)$$

where  $\beta$  is the sweep rate.

## 5 Limiting current

To derive an expression for the limiting current  $I_{\text{lim}}$  given by Equation 1 in the main text, we consider a 1D system at steady state with  $\rho_s = 0$  and ignore Faradaic reactions at both the anode and the cathode. The boundary conditions for the system are

$$F_-(x=0) = F_-(x=L) = 0 \quad (30)$$

where we assume that the anions are inert and cannot leave the system. That the anions cannot leave the system also implies that the number of anions in the system is conserved:

$$\epsilon_p A \int_0^L c_- dx = \epsilon_p A \int_0^L c_0 dx \Rightarrow \int_0^L c_- dx = c_0 L \quad (31)$$

where  $c_-(t=0) = c_0$ . The limiting current density  $J_{\text{lim}}$  is determined by setting  $c_-(x=L) = 0$ . Therefore,

$$J_{\text{lim}} = \frac{4ze\epsilon_p D_+ c_0}{L} = \frac{4ze\epsilon_p D_+^m c_0}{\tau L}, \quad (32)$$

$$I_{\text{lim}} = J_{\text{lim}} A = \frac{4ze\epsilon_p D_+ c_0 A}{L} = \frac{4ze\epsilon_p D_+^m c_0 A}{\tau L}, \quad (33)$$

where we note that  $D_+^m$  is denoted by  $D_0$  in the main text.

## 6 Steady-state current-voltage relations and overlimiting conductances

### 6.1 Reservoir boundary condition at anode

To derive an expression for the overlimiting conductance  $\sigma_{\text{OLC}}$  given by Equation 2 in the main text, we consider a 1D system at steady state and ignore Faradaic reactions at both the anode and the cathode. The boundary conditions are given by

$$c_-(x=0) = c_0, \quad (34)$$

$$\phi(x=0) = \phi_0, \quad (35)$$

$$F_-(x=L) = 0, \quad (36)$$

$$\phi(x=L) = \phi_0 - V, \quad (37)$$

where  $\phi(x=L) - \phi(x=0) = -V$  is the potential difference across the electrolyte and we note that  $V \geq 0$ . Solving for the steady-state current-voltage relation, we obtain

$$I = I_{\text{lim}}^{\text{reservoir}} \left[ 1 - \exp\left(-\frac{zeV}{k_B T}\right) \right] - \sigma_{\text{OLC}} V \quad (38)$$

where we define

$$I_{\text{lim}}^{\text{reservoir}} \equiv \lim_{V \rightarrow \infty} I(\sigma_s = 0) = \frac{1}{2} I_{\text{lim}} = \frac{2ze\epsilon_p D_+^m c_0 A}{\tau L} \quad (39)$$

and

$$\sigma_{\text{OLC}} \equiv \frac{zeD_+^m A a_p \sigma_s}{\tau L k_B T} = \frac{zeD_+^m A \epsilon_p \sigma_s}{\tau L k_B T h_p}, \quad \sigma_s < 0 \quad (40)$$

and we note that  $D_+^m$  is denoted by  $D_0$  in the main text.

## 6.2 Zero anion flux boundary condition at anode

To derive an expression for the overlimiting conductance  $\sigma_{\text{OLC}}$  given by Equation 2 in the main text, we consider a 1D system at steady state and ignore Faradaic reactions at both the anode and the cathode. The boundary conditions are given by

$$F_-(x=0) = 0, \quad (41)$$

$$\phi(x=0) = \phi_0, \quad (42)$$

$$F_-(x=L) = 0, \quad (43)$$

$$\phi(x=L) = \phi_0 - V, \quad (44)$$

where  $\phi(x=L) - \phi(x=0) = -V$  is the potential difference across the electrolyte and we note that  $V \geq 0$ . In addition, there is an integral constraint that describes the conservation of the number of anions:

$$\int_0^L c_- dx = c_0 L. \quad (45)$$

We define

$$\tilde{\rho}_s \equiv \frac{\rho_s}{ze c_0}, \quad (46)$$

$$\tilde{V} \equiv \frac{zeV}{k_B T}. \quad (47)$$

Solving for the steady-state current-voltage relation, we obtain

$$I = I_{\text{lim}} \frac{(\tilde{\rho}_s + 2) [1 - \exp(-\tilde{V})] + \sqrt{\left\{ (\tilde{\rho}_s + 2) [1 - \exp(-\tilde{V})] \right\}^2 - 4 [1 - \exp(-2\tilde{V})] \tilde{\rho}_s \tilde{V}}}{4 [1 - \exp(-2\tilde{V})]} [1 - \exp(-\tilde{V})] - \sigma_{\text{OLC}} V \quad (48)$$

where we define

$$\sigma_{\text{OLC}} \equiv \frac{ze D_+^m A a_p \sigma_s}{\tau L k_B T} = \frac{ze D_+^m A \epsilon_p \sigma_s}{\tau L k_B T h_p}, \quad \sigma_s < 0 \quad (49)$$

and we note that  $D_+^m$  is denoted by  $D_0$  in the main text. In the limit  $V \rightarrow \infty$ ,

$$\lim_{V \rightarrow \infty} I \approx -\sigma_{\text{OLC}} V. \quad (50)$$

Therefore, by assuming that all the applied potential is equal to the potential difference across the electrolyte for high applied potentials, computing the gradient of the linear region of the experimental current-voltage relation gives an estimate of  $\sigma_{\text{OLC}}$ .

## References

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