Supporting Information for

A stochastic route to simulate the growth of porous anodic alumina

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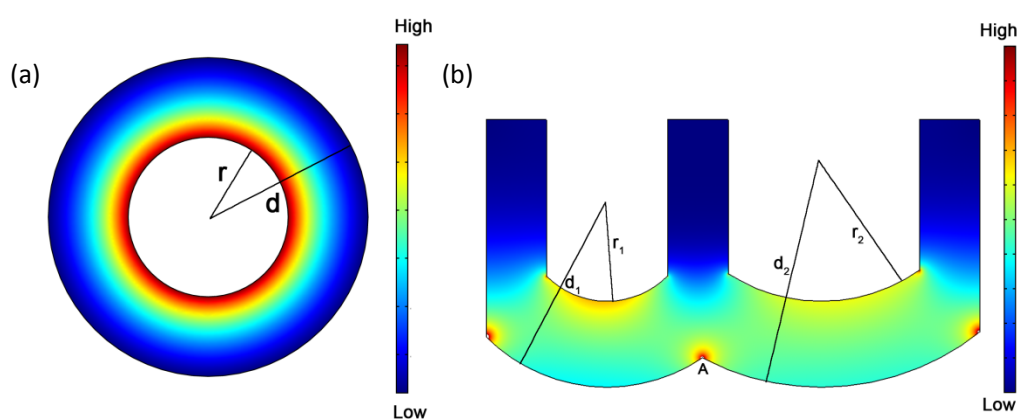
1. Uniformize of PAA

Figure S1. Electric field strength distribution of (a) an imagined alumina ring, outer space of which is aluminum, and inner is electrolyte. (b) cross-section of PAA with different pore size. The bottom space represents aluminum sheet and the top represents electrolyte. A steady voltage is set on aluminum, and the electrolyte is set to 0 V. The electric field strength of pore-edge at larger pore is lower than smaller pore. The electric field distribution is calculated by Comsol 3.5a. This is a schematic figure and not matched with the scale of real PPA.

As the potential Φ is distributed according to Laplace's equation, that is:

$$\Delta\phi=0 \tag{SI 1-1}$$

Considered in polar coordinates, Φ shows independence with polar angle, and the boundary conditions write

$$\begin{cases} \phi(r+d)=U \\ \phi(r)=0 \end{cases} \tag{SI 1-2}$$

The solution of Eq SI 1-1, 2 is

$$\phi(\rho)=\frac{\ln\rho-\ln r}{\ln(r+d)-\ln r}U \tag{SI 2}$$

as a result,

$$E(\rho) = -\nabla\phi(\rho) = -\frac{U}{\ln(r+d)-\ln r}\cdot\frac{1}{\rho} \tag{SI 3}$$

In Figure S1(b), the electron field of both pores at I2 is approximately figured out with Eq SI 3. That is,

$$\frac{E_1}{E_2} = \frac{r_2\left(\ln(r_2+d_2)-\ln r_2\right)}{r_1\left(\ln(r_1+d_1)-\ln r_1\right)} = \frac{d_2-\dfrac{d_2^2}{r_2}+\dfrac{d_2^3}{r_2^2}-\cdots}{d_1-\dfrac{d_1^2}{r_1}+\dfrac{d_1^3}{r_1^2}-\cdots} \tag{SI 4}$$

If $d_1=d_2$ and $r_2>r_1$, we have $E_1>E_2$, therefore, point A tends to react with narrow pore because of a higher potential. For this reason, the pore size becomes uniform with oxidation ongoing.

2. pseudocode and flow diagram of simulation

The main programme and comments are listed below:


```
Initialize;        %initialize the system
for cycle=1:y-21      %x and y are the width and length of the simulation box.
    rand=randomsort(x);      %set a random sort of start position.
    time=1;
    while time<=x
        dis=MAX;
        [begx,begy,ran]=thunder(a,rand(time),1);
                                for multi=1:multifactor %run every randomwalk
                                several times to reduce the occasionality.
        [endx,endy,ran]=thunder(b,…
    begx+ran+sizex*((begx==1&&ran==-1)-(begx==sizex&&ran==1)),begy+1);
    while a(endx+ran+sizex*((endx==1&&ran==-1)-(endx==sizex&&ran==1)),endy+1)
        [begx,begy,ran]=thunder(a,…
    endx+ran+sizex*((endx==1&&ran==-1)-(endx==sizex&&ran==1)),endy+1);
        [endx,endy,ran]=thunder(b…
    ,begx+ran+sizex*((begx==1&&ran==-1)-(begx==sizex&&ran==1)),begy+1);
            end %set the begin and end point of reaction, function 'thunder' returns
            endpoint from startpoint with randomwalk.
    DIS=dist(begx,endx,begy,endy);  %calculate the distance between begin and end
points.
    DIS_mod=DIS-curvature(b,endx,endy);          %modify the distance
        if DIS_mod<dis
            dis=DIS_mod;
```

```matlab
                bx=begx;by=begy;
                ex=endx;ey=endy;
            end      %select the minimum distance.
        end


prob(b(ex+mod(ey,2)*2-1+sizex*((ex+mod(ey,2)*2==1)...
-(ex+mod(ey,2)*2==sizex+2)),ey+1)+b(ex,ey+1)+1)>=random('unif',0,1)

        eva=dis-(1/(4-evaluate(b,endx,endy,num,4)/13))*sigma;    %evaulate function

        prob1=alpha1*exp(beta1/eva);
        prob2=alpha2*exp(beta2/eva)*exp(-kappa*eva);
        prob2=prob2/(prob1+prob2);        %set the probability with both procedures.

            if random('unif',0,1)>prob2
                a(bx,by)=0;b(bx,by)=1;
                b(ex,ey)=0;c(ex,ey)=1;          %matrix a, b and c
            else
                a(bx,by)=0;b(bx,by)=1;
                b(ex,ey)=1;c(ex,ey)=0;
                            end %according to the different type of procedure, the
            component of every block changes.
            time=time+1;
        end
        b=reconstruct(b);
        c=reconstruct(c);
        a=1-c-b;        %reconstruct every block to singular point.

        csvwrite(strcat(int2str(cycle),'b.csv'),b);        %output the result every cycle.
        csvwrite(strcat(int2str(cycle),'c.csv'),c);
end
```
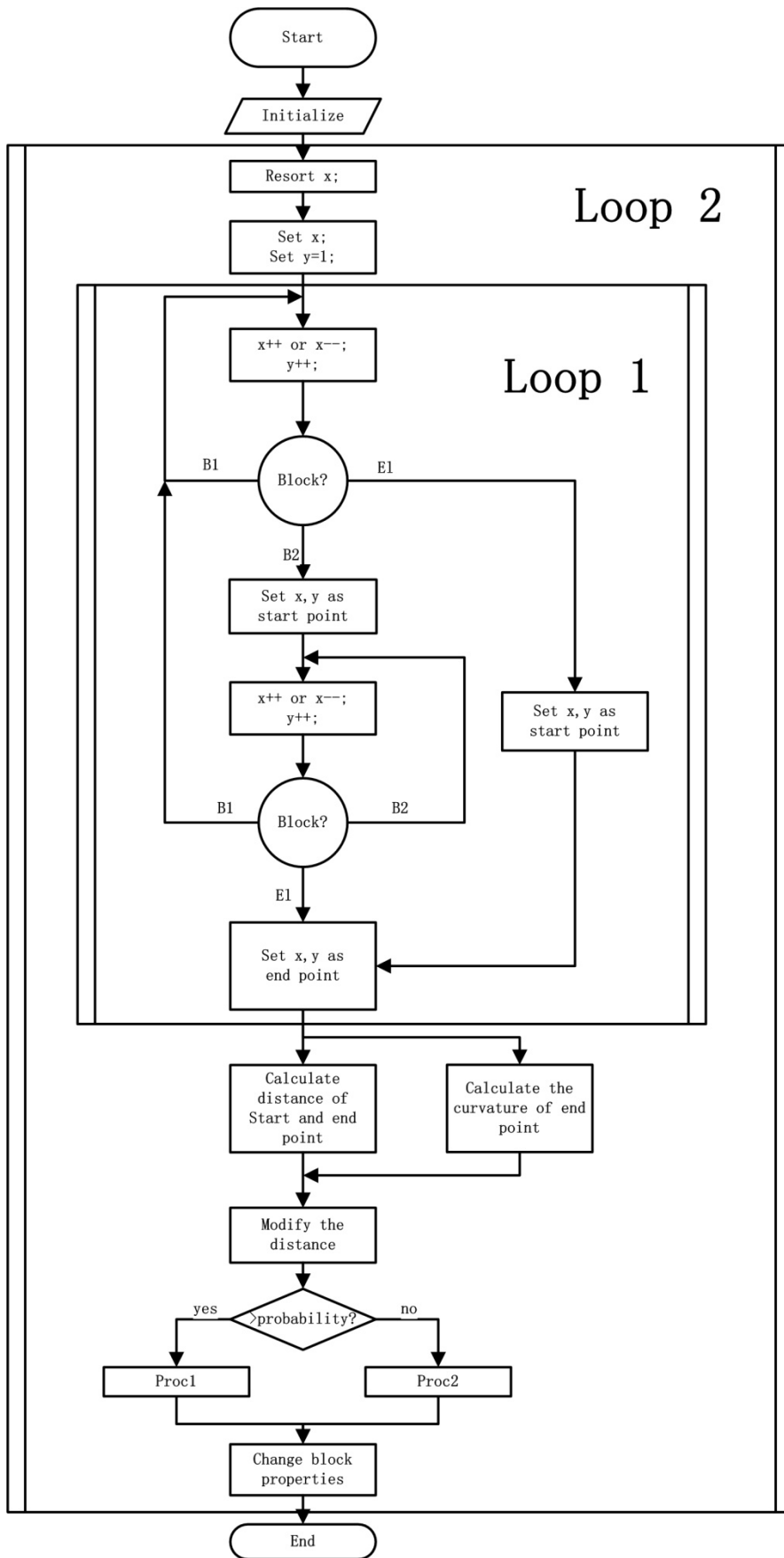
Figure S2. Flow diagram of simulation.

3. Matching of experiment and simulation

In simulation, we set a single step described above as unit time t_0, unit length l_0. Thus, the number of Al^{3+} in a sphere with diameter equal to l_0 can be figured as

$$n_{Al} = \frac{1}{3}\frac{\eta N_A I t_0}{Fa} \tag{SI 5}$$

where, N_A is Avogadro's number, a is the ratio of area with real system and simulation which equals to $A_0/x_{max}l_0^2$, where A_0=3.14 cm^2 is the cross area of our system, x_{max}=200 is the width of PAA film in simulation, I is the current, F is Faraday constant and η is the current efficiency.

In order to calculate l_0, a simulation of amorphous Al_2O_3 is run with MD referred to Adiga et al.[1] Briefly, Al and O atoms in a ratio 2:3 are placed in an orthorhombic supercell of the hexagonal α-alumina lattice. We cut the lattice into a cube with a certain length. Then, the system is heated and equilibrated, cooled and equilibrated for some time to simulate the quenching of alumina. We then take a random sample of 1 nm^3 in quenched amorphous alumina for 10 times to count the average ion density. Here we gain an average ion number 116 ± 6 per nm^3.

Therefore, l_0 is calculated as follows in a unit of nanometer.

$$l_0^3 = \frac{6}{\pi}\cdot\frac{1}{3}\cdot\frac{\eta N_A I t_0}{F\rho a} \tag{SI 6-1}$$

i.e.

$$l_0 = 5.453e4\,\eta I t_0 \tag{SI 6-2}$$

where ρ is the average atom number of aluminum per cubic nanometer, which is 116×0.4=46.4 /nm^3.

The current efficiency η can be estimated experimentally. Then η is

$$\eta = \frac{A_0 r_p t}{\dfrac{N_A I t}{3F\rho}} = \frac{3F\rho A_0 r_p}{N_A I} \tag{SI 7}$$

where the growth rate of PAA film is r_p. From experimental results (see table S1), we can simply calculate the current efficiency η.

Table S1. The current efficiency of different voltage with a 4-hour-oxidation.

| Voltage | Charge | growth rate | efficiency | l_0/t_0 |
V	C	nm/s		nm/s
30	134.5	0.799	59.9%	160
40	249.9	1.76	71.2%	352
50	399.6	3.31	83.5%	662
60	596.6	4.36	73.8%	872

70	729.7	6.17	85.4%	1234

With the data in Table 2, we are able to figure out l_0 and t_0 separately by the simulation above (Figure S3). As voltage is a hidden variable and not directly involved in simulation, we describe the voltage by changing l_0 and t_0.
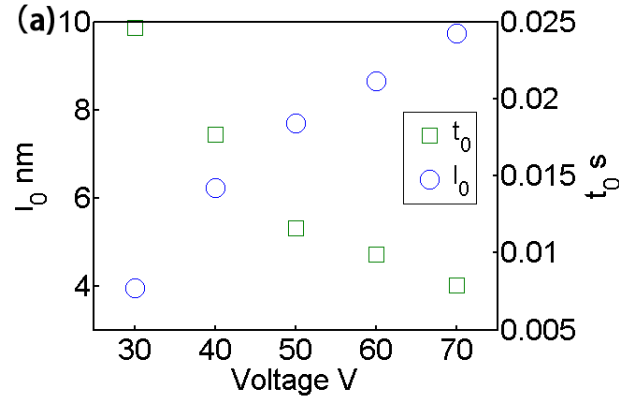

Figure S3. Unit length (l_0) and time (t_0) with different voltages. With the increase of voltage, l_0 increases and t_0 reduces accordingly.

4. Calculation of weighting factor λ with experimental data

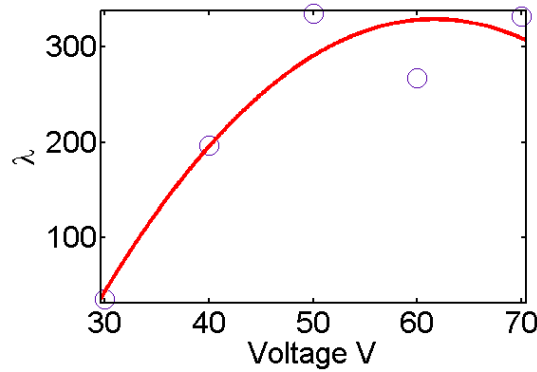**Figure S4.** λ derived from experimental data for different voltages. Red line is the quadratic fit of these data.

According to our simulations with variable λ, the average diameter of unit area (d_{ua}) and diameter of pore (d_p) can be figured out. With the experimental data (Table 1), we can figure out the weighting factor λ following the method below. First, electric field strength is figured out at the end of pore (where ρ equals to r), then d and r are treated as dependent and independent variable respectively, and λ is the gradient of the function of d and $-1/r$ derivated from Eq SI-3 at a certain $r=r_0$.

That is:

$$\lambda = r^2 \left(\left(1 + \frac{U}{rE} \right) \exp\left(-\frac{U}{rE} \right) - 1 \right) \tag{SI 8}$$

5. Furcation criterion of PAA film with simulation

The furcation criterion is figured out by the following methods: simulations with different weighting factor are taken out while other parameters keep the same. The conditions of 300 cycles are selected for investigation. First, pore size is calculated with the same method as Figure 6. For a certain column, pore numbers are marked by counting the conversion of a continuous B2 region to an El region with the width equal to the pore size. Compared with the pore numbers to the direction of oxidation, all the increasement of pore numbers are added because furcation causes the increase of pore numbers. Besides, the major branch can be counted as a reference.

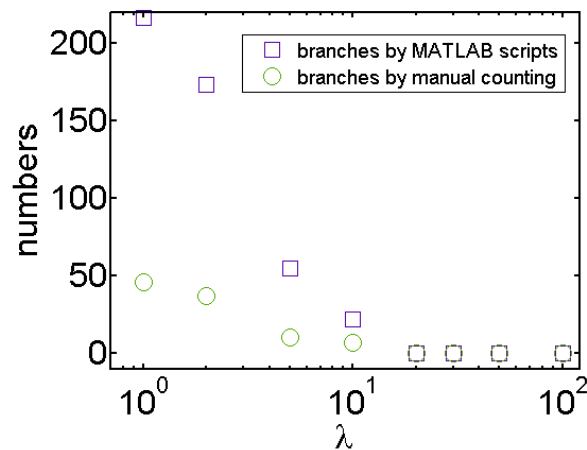Based on the following counting, we consider the PAA films with λ less than 20 as branched, while others as straight.

Figure S5. branching numbers with different weighting factor λ. Square and circle markers represent the counting by MATLAB scripts and manual respectively. When λ is more than 10, no branches are counted by both methods.

References:

1. Adiga SP, Zapol P, Curtiss LA. Atomistic simulations of amorphous alumina surfaces. *Phys. Rev. B* **74**, 064204 (2006).