

## SUPPORTING INFORMATION

### Growth of Porous Anodic Alumina on Low-Index Surfaces of Al Single Crystals

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## Calculation of activation barrier differences and oxidation rate ratio for anodic oxidation of low-index aluminum faces

Calculation of activation barriers height differences for anodic oxidation of low-index aluminum faces and reverse calculation of the oxidation rate ratio was performed directly using following equation (see main text for details):

$$\frac{j_{hk0}}{j_{111}} = \frac{n_{hk0} \nu_{hk0}}{n_{111} \nu_{111}} \cdot \exp[-(W_{hk0} - W_{111}) / kT] \quad (1)$$

where  $n_{hkl}$  is the aluminum atomic density on the  $(hkl)$  facet;  $\nu_{hkl}$  is the vibrational frequency of a surface metal atom on the  $(hkl)$  facet;  $W_{hkl}$  is the activation energy for the  $(hkl)$  facet;  $k$  is Boltzmann constant, and  $T$  is absolute temperature.

We failed to find either experimental or theoretical values of activation energies for aluminum atom release from metal surface to the oxide layer. Therefore, to reveal reaction limiting stage we used several estimates to compare experimentally derived values to various characteristic energy barriers known for aluminum faces, including facet energies,<sup>S1</sup> vacancy formation energies,<sup>S2,S3</sup> work functions,<sup>S4</sup> and anodic pitting potentials.<sup>S5</sup> One can see that all the pathways indicate significant overestimation of the oxidation rates on Al(100) and Al(110) faces, however revealing the same tendency of  $j_{Al(110)} > j_{Al(100)} > j_{Al(111)}$ . Stepped vacancy formation energies and pitting potentials give the closest to experimental results values.

*Table S1.* External parameters, activation barriers and resulting oxidation rates ratios for anodic oxidation of low-index aluminum faces. Calculated oxidation rate ratios are given relative to the Al(111) substrate.

	(100)	(110)	(111)		
Atomic density ( $n_{hkl}$ ), atoms/m <sup>2</sup>	$1.22 \cdot 10^{19}$	$8.62 \cdot 10^{18}$	$1.41 \cdot 10^{19}$		
Vibration frequency ( $\nu_{hkl}$ ), Hz <sup>S6</sup>	$9.69 \cdot 10^{12}$	$8.65 \cdot 10^{12}$	$9.69 \cdot 10^{12}$		
	Barrier height, eV/atom (eV)			Oxidation rate ratio	
	(100)	(110)	(111)	$j_{100}/j_{111}$	$j_{110}/j_{111}$
Experiment (40 V in 0.3 M oxalic acid)	$E_A + 0.014^*$	$E_A (\sim 0.5)^*$	$E_A + 0.020^*$	1.13	1.25
Facet energy <sup>S1</sup>	0.435... 0.690	0.674... 1.010	0.275... 0.532	10...100 <sup>*</sup>	$1.4 \cdot 10^5 \dots$ $1.6 \cdot 10^{7*}$
Vacancy formation <sup>S2</sup>	0.35	0.12	0.55	$4.2 \cdot 10^{3*}$	$4.6 \cdot 10^{7*}$
Vacancy/step formation <sup>S3</sup>	0.142	$0.12^{S2}$	0.215	$19.2^*$	$30.9^*$
Work function <sup>S4**</sup>	4.20	4.06	4.26	$12.8^*$	$4.9 \cdot 10^{3*}$
Pitting potential, V vs. OCP <sup>S5**</sup>	-0.652	-0.612	-0.699	$6.4^*$	$22.0^*$

\* values extracted from eq. 1

\*\* single electron transport reaction per atom was accounted as limiting stage

To estimate an absolute value of the oxidation activation barriers we analyzed both current density and oxidation rates ratio changes in the experiments performed for different substrate faces in the same anodization conditions. Earlier stages of anodic film growth are known to demonstrate much higher current densities due to increased temperature at the Al/Al<sub>2</sub>O<sub>3</sub> interface (especially in case of hard anodization regimes). An assessment of initial temperature increase of ~ 50 °C (for hard anodization regimes) with ~ 30-fold current density (reaction rate) decrease during experiments gives an estimate of the activation barrier in the order of  $0.5 \pm 0.2$  eV, which stay rather close to the values reported earlier for anodic oxidation of aluminum.<sup>S7,S8</sup> Employing the value in eqn.1 results in the reduction of oxidation rates ratio to ~ 1.05-1.10 for different faces fitting well to experimental results and supporting the difference in energy barrier heights in the order of several meV for different aluminum faces.

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