Supporting Information to the manuscript entitled

Energy Modeling of Electrochemical Anodization Process of Titanium Dioxide Nanotubes

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The supporting information includes the data used in the analysis and detailed calculations.

Experiment setup: 0.25mm titanium with 99.97% purity, electrolyte is glycerol (99.8%) with NH_4F (98%) concentration in a range 0.1-0.7 wt%

Table S1 Enthalpy of formation and absolute entropy of substances used in the analysis of the chemical reaction processes

Substance	Phase *	Molecular weight (kg/kmol)	h_f° kJ/mol	S° J/mol*K
$TiCl_4$	Titan tetrachloride (g)	189.678	-763.16	354.84
H_2O	Water (g)	18.0153	-241.83	188.84
TiO_2	Rutile Titan oxide (s)	79.866	-938.72	50.62
TiO_2	Anatase Titan oxide (s)	79.866	-938.72	49.82
Ti	Titanium (s)	47.867	13.65	30.72
HCl	Hydrogen chloride (g)	36.4606	-92.31	186.90
O_2	Oxygen(g)	31.9988	0	205.02
Cl_2	Chlorine(g)	70.9054	0	223.08
CH_4	Methane(g)	16.0425	-74.87	186.25
C	Carbon (graphite) (s)	12.0107	0	5.686
H_2	Hydrogen(g)	2.01588	0	130.68
CO	Carbon monoxide(g)	28.0101	-110.53	197.66
CO_2	Carbon dioxide(g)	44.0095	-393.52	213.79
F^-	Fluorine anion	18.9989	79.39	158.78
H^+	Hydrogen cation	1.00739	1555	108.95
TiF_6	Titanium fluoride	104.8637	-66.94	237.31

*(g, gas; l, liquid; s, solid), (NIST CSTL Standard Reference Data Program, Chemistry, T=25C, P= 1 bar)

1.Energy Analysis for Formation of Oxide Layer

The total overall entropy change for the overall process in kJ/mol*K:

$$\Delta S_{Reaction} = \sum_{Products} \gamma_i S_i - \sum_{Reactants} \gamma_i S_i$$

Where $S_i = S_i^{\circ} - R\ln\frac{P_i}{P_0}$

$$\Delta S_{Reaction} = \sum_{Products} \gamma_i S_i - \sum_{Reactants} \gamma_i S_i = -96.42\ \mathrm{J/mol \cdot K}$$

$$Q = \Delta H^{\circ}_{f\,Reaction} = \sum_{Products} \gamma_i H^{\circ}_{fi} - \sum_{Reactants} \gamma_i H^{\circ}_{fi} = -468.71\ kJ/mol$$

$$Q_0 = -Q = 468.71\ kJ/mol$$

$$\Delta S_{Surrounding} = \frac{Q_0}{T_0} = 1570\ J/mol \cdot K$$

$$\Delta S_{Total} = \Delta S_{Reaction} + \Delta S_{Surrounding} = 1473.58 \frac{J}{mol \cdot K}$$

The reversible work associated with the process is:

$$w_{rev} = (H_R - T_0 S_R) - (H_P - T_0 S_P) = -Q - T_0(-\Delta S_R) = 439.98 kJ/mol$$

For Ti itself, it is 439.98kJ·mol^{-1}/79.867g·mol^{-1}=5.51kJ/g.

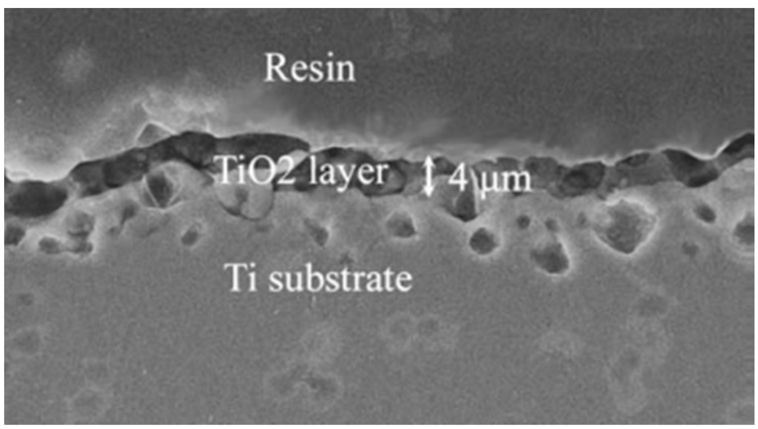

Figure S1 Cross sectional image of TiO2/Ti thick film electrode.

During the lab experiments, with 2 hours the anodization process generates 4µm TiO_2 layer (illustrated in Figure S1~~Figure 1~~), the volume is 2×1.27cm× 2.54cm×4 µm=0.0025cm^3, the density is 3.82g/cm3, and the total mass is 0.01528g. The energy consumption in formation process of the oxide layer is calculated as follows:

$$E = 5.51 kJ/g \times 0.01528 g = 84.19 J$$

2. Energy Analysis for Chemical Diffusion Process

$$TiO_{2(s)} + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O$$

The total overall entropy change for the overall process is:

$$\Delta S_{Reaction} = \sum_{Products} \gamma_i S_i - \sum_{Reactants} \gamma_i S_i = 246.44 + 384.42 - 50.62 - 978.16 - 466.27$$

$$= -864.19\ J/mol \cdot K$$

$$Q = \Delta H^{\circ}_{f\,Reaction} = \sum_{Products} \gamma_i H^{\circ}_{fi} - \sum_{Reactants} \gamma_i H^{\circ}_{fi} = -5831.88\ kJ/mol$$

$$Q_0 = -Q = 5831.88\ kJ/mol$$

$$\Delta S_{Surrounding} = \frac{Q_0}{T_0} = 19570\ J/mol \cdot K$$

$$\Delta S_{Total} = \Delta S_{Reaction} + \Delta S_{Surrounding} = 18705.81 \frac{J}{mol \cdot K}$$

The reversible work associated with the process is:

$$W_{rev} = (H_R - T_0 S_R) - (H_P - T_0 S_P) = -Q - T_0(-\Delta S_R) = 11406.21 kJ/mol$$

For Ti itself, it is 439.98kJ/mol / 79.867g/mol=142.82kJ/g.

During the lab experiments, the total mass is 0.01528g as obtained above. The energy in chemical diffusion process is calculated as follows:

$$E = 142.82 kJ/g \times 0.01528 g = 2.18 kJ$$

3. Energy Analysis of Physical Diffusion Process

Based on the experimental data, the TiO2 nanotube diameter is 35nm, wall thickness is 9nm and length is 1100nm. So the porosity of nanotube is calculated as:

$$p = 1 - \text{volume fraction} = 1 - \frac{V_{TiO2}}{V_{Total}} = \frac{d_i^2}{d_0^2} = 43.6\%$$

The anodic current density at 30V is calculated as:

$$I = \frac{43.6\% \times 4 \times 96485\text{Cmol}^{-1} \times 10^{-5}\text{cm}^2\text{s}^{-1} \times 2.5 \times 10^{-5}\text{mol cm}^{-3}}{1100\text{nm} + 43.6\% \times 10300\text{nm}} = 75\text{ mA} \cdot \text{cm}^{-2}$$

The titanium sheet size is 1cm by 5cm, so the area is calculated as:

$$A = 1\text{cm} \times 5\text{cm} = 5\text{cm}^2$$

The energy input into the diffusion process during 2 hours is calculated as:

$$E_{\text{diffusion}} = \Delta V \cdot I \cdot A \cdot t = 30\text{V} \times 75\text{mAcm}^{-2} \times 5\text{cm}^2 \times 2\text{h} = 0.0225\text{kWh} = 81\text{kJ}$$

4. Energy Analysis for Calcination Process

In this closed calcination system volume is constant, so we can calculate the pressure by classic ideal gas law:

$$PV = nRT$$

$$\frac{P}{P_0} = \frac{T}{T_0} = \frac{723}{273} = 2.648$$

Where heat capacity

$$c_p = \frac{1.068\text{kJ}}{\text{kg} \cdot \text{K}} \times \frac{28.97\text{g}}{\text{mol}} = 30.94\text{J/mol} \cdot \text{K}$$

The minimum physical exergy required to create the conditions necessary to crystallize TiO_2 is calculated in the following:

$$b_{ph} = c_p(T - T_0) - c_p T_0 \ln\frac{T}{T_0} + T_0 R \ln\frac{P}{P_0} = 7.907\text{kJ/mol}$$

$T_0\dot{S}_{gen} = 0$, and the minimum work of crystallization process is obtained as follows:

$$W_{min} = b_{ph} \cdot m = \frac{7.907\text{kJ}}{\text{mol}} \times 17.78\text{cm} \times 12.7\text{cm} \times 25.4\text{cm} \times \frac{0.524\text{mol}}{\text{L}} = 23.76\text{kJ}$$

5. LCI data for raw material upstream process:

The LCI data for upstream process includes cradle to gate data for raw materials: ethylene glycol, deionized water, ammonia, hydrogen fluoride, ammonium fluoride, titanium dioxide () and pure titanium foil.

Table S2 Energy requirement of 1kg ethylene glycol from ethane and oxygen via EO process.

Inputs	Amount (MJ, net calorific value, German)
Crude oil	20.2
Hard coal	1.33
Lignite	1.66
Natural gas	11.4
Oil sand (10% bitumen)	0.000387
Oil sand (100% bitumen)	0.000338
Peat	0.00133
Pit methane	0.024
Primary energy from geothermics	0.00172
Primary energy from hydro power	0.194
Primary energy from solar energy	0.518
Primary energy from wind power	0.394
Secondary fuel	0.00488
Secondary fuel renewable	0.000466
Uranium natural	1.64
Total	37.36912

(PE International GaBi 6 Professional Database)

Table S3 Energy requirement of 1kg deionized water from ion exchange process.

Inputs	Amount (MJ, net calorific value, German)
Crude oil	0.015
Hard coal	0.0128
Lignite	0.0131
Natural gas	0.0204
Oil sand (10% bitumen)	0.00000257
Oil sand (100% bitumen)	0.00000224
Peat	0.00000306
Pit methane	0.000216
Primary energy from geothermics	0.00000332
Primary energy from hydro power	0.00133
Primary energy from solar energy	0.00417
Primary energy from wind power	0.00307
Secondary fuel	0.000114

Secondary fuel renewable	0.0000109
Uranium natural	0.0123
Total	0.082522

(PE International GaBi 6 Professional Database)

Table S4 Energy requirement of 1kg ammonia from Haber-Bosch process.

Inputs	Amount (MJ, net calorific value, German)
Crude oil	0.274
Hard coal	0.959
Lignite	1.26
Natural gas	33.4
Oil sand (10% bitumen)	0.000175
Oil sand (100% bitumen)	0.000152
Peat	0.000169
Pit methane	0.0172
Primary energy from geothermics	0.000161
Primary energy from hydro power	0.127
Primary energy from solar energy	0.393
Primary energy from wind power	0.296
Secondary fuel	0.00471
Secondary fuel renewable	0.000448
Uranium natural	1.17
Total	37.90202

(PE International GaBi 6 Professional Database)

Table S5 Energy requirement of 1kg hydrogen fluoride from conversion of dried fluorspar.

Inputs	Amount (MJ, net calorific value, German)
Crude oil	24
Hard coal	4.45
Lignite	1.44
Natural gas	8.7
Oil sand (10% bitumen)	0.000215
Oil sand (100% bitumen)	0.000188
Peat	0.00026
Pit methane	0.078
Primary energy from geothermics	0.000304
Primary energy from hydro power	0.175
Primary energy from solar energy	0.456
Primary energy from wind power	0.337
Secondary fuel	0.004
Secondary fuel renewable	0.000381
Uranium natural	1.51

Total	41.15135

(PE International GaBi 6 Professional Database)

The energy consumption of producing 1 kg of titanium foil by FCC Cambridge process is 20kWh.[1] Based on the mass flow of electrochemical anodization process, the total energy consumption of raw materials extraction and production (Ti foil, ethylene glycol, deionized water, and ammonia fluoride) required in experiment is approximately 3577.766kJ (234.147MJ/g)

Table S6 Energy consumption for raw material extraction and process

Material	Mass	Energy consumption (kJ)
Pure Ti foil	371.99mg	26.783
Ethylene glycol	94.6g	3535.119
Ammonia fluoride	0.4g	6.966
Deionized water	5g	8.898
Total	100.37199g	3577.766

References

1. Chen, G. Z.; Fray, D. J.; Farthing, T. W., Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. *Nature* **2000,** *407*, (6802), 361-364.