Supplementary Information

Electrolytic Reduction of Titanium Dioxide in Molten Li_2O/LiCl

Meng Shi[1], Bin Liu[2], Shelly Li[3], Haiyan Zhao[1]*
[1]University of Idaho, 995 MK Simpson. Idaho Falls, 83401, ID USA
[2] Kansas State University, Manhattan, 66506, KS USA
[3]Idaho National Laboratory, Idaho Falls, 83401, ID USA
*Corresponding author. Tel.:+01 2085338123. E-mail: haiyanz@uidaho.edu (Haiyan Zhao)

Table of Contents

1. Rietveld refinement of the soaked and reduced products

The Rietveld refinement was carried out to quantify the phases in the samples after TiO_2 soaking test and for TiO_2 electrolytic reductions at various cathodic potentials (-0.2 V, -0.3 V and -0.4 V vs. Li/Li^+) using 80%, 130% and 150% of theoretical charge. Multiple phases including TiO_2 (01-084-1284), Li_2TiO_3 (01-080-7163), $LiTiO_2$ (01-074-2257) and $Li_{0.54}Ti_{2.86}O_6$ are used for the refinement. The background was fitted manually. The lattice parameters and scale factors of each species were refined, based on which the quantitative compositions (in wt.%) of the samples were obtained. The precision of the fitting in terms of the R values and the χ^2 are all within acceptable range. The fitting results and phase parameters are summarized in Table S1.

Table S1 Rietveld refinement results for the soaked and reduced products

Samples *			Soaked Sample	80% –0.2 V	80% –0.3 V	80% –0.4 V	130% –0.3 V	150% –0.3 V
Products composition (w.t. %)	TiO_2		60.8	14.54	1.69	4.05	0.00	0.00
	Li_2TiO_3		38.0	35.66	28.27	26.22	13.36	0.00
	$LiTiO_2$		---	49.80	70.04	69.73	86.64	100.00
	$Li_{0.54}Ti_{2.86}O_6$		1.2	---	---	---	---	---
R factors	R_{wp} (%)		15.98	6.93	6.06	6.99	6.33	6.42
	R_p (%)		11.23	4.67	4.16	4.77	4.56	4.52
	R_e (%)		5.57	5.73	5.51	5.51	5.58	5.47
	S		2.8653	1.2054	1.0955	1.2644	1.1328	1.1721
	χ^2		8.2101	1.453	1.2002	1.5986	1.2832	1.3737
	Maximum shift e.s.d.		0.339	0.682	0.359	0.075	0.366	0.002
Phases	Parameters							
TiO_2 Rutile, syn (01-084-1284) Space group: 136 : P42/mnm	a (Å)		4.544644	4.58666	4.58666	4.58666	---	---
	b (Å)		4.544644	4.58666	4.58666	4.58666	---	---
	c (Å)		2.927009	2.95407	2.95407	2.95407	---	---
	α (Degree)		90	90	90	90	---	---
	β (Degree)		90	90	90	90	---	---
	γ (Degree)		90	90	90	90	---	---
	V ($Å^3$)		60.452834	62.146099	62.146099	62.146099	---	---
	Scale factor		68(2)	16.3(9)	3.2(14)	5.7(15)	---	---
	Gaussian peak width parameters ($°^2$)	U	0.148(14)	0.16(2)	0.19(5)	0.09(4)	---	---
		V	–0.149(4)	–0.16(3)	–0.26(8)	–0.157(11)	---	---
		W	0.001(4)	0.011(7)	0.06(2)	0.051(4)	---	---
$LiTiO_2$ Lithium titanium(III) oxide (01-074-2257) Space group: 225 : Fm-3m	a (Å)		---	4.1372(4)	4.1457(5)	4.1355(2)	4.1400(5)	4.14000
	b (Å)		---	4.1372(4)	4.1457(5)	4.1355(2)	4.1400(5)	4.14000
	c (Å)		---	4.1372(4)	4.1457(5)	4.1355(2)	4.1400(5)	4.14000
	α (Degree)		---	90	90	90	90	90
	β (Degree)		---	90	90	90	90	90
	γ (Degree)		---	90	90	90	90	90

	V (Å^3)		---	70.813(11)	71.254(15)	70.729(7)	70.957(16)	70.957937
	Scale factor		---	32.8(15)	62.6(17)	54.8(17)	66.9(19)	62.7(17)
	Gaussian peak width parameters (°^{2})	U	---	0.27(3)	0.24(6)	0.204(10)	0.20(4)	1.098(12)
		V	---	–0.16(3)	–0.26(8)	–0.157(11)	–0.17(4)	–1.00(15)
		W	---	0.011(7)	0.06(2)	0.051(4)	0.053(11)	0.248(2)
Li_2TiO_3 Dilithium titanate (IV) (01-080-7163) Space group: 15 : C12/c1,unique-b,cell-1	a (Å)		5.017(3)	5.0604(16)	5.053(3)	5.0588(8)	5.035(6)	---
	b (Å)		8.717(5)	8.777(5)	8.782(6)	8.7354(13)	8.790(2)	---
	c (Å)		9.608(6)	9.760(4)	9.714(6)	9.7254(17)	9.767(4)	---
	α (Degree)		90	90	90	90	90	---
	β (Degree)		99.74(5)	100.12(3)	99.45(7)	99.824(14)	100.22(2)	---
	γ (Degree)		90	90	90	90	90	---
	V (Å^3)		414.1(4)	426.7(3)	425.2(5)	423.22(12)	427.8(2)	---
	Scale factor		40.3 (19)	9.0(7)	12.4(8)	9.2(9)	7.0(6)	---
	Gaussian peak width parameters (°^{2})	U	0.00(14)	0.17(3)	0.6(2)	0.092(11)	0.6(2)	---
		V	0.24(4)	–0.16(3)	–0.26(8)	–0.157(11)	–0.6(2)	---
		W	0.00(3)	0.011(7)	0.06(2)	0.051(11)	0.08(3)	---
$Li_{0.54}Ti_{2.86}O_6$ Lithium titanium oxide	a (Å)		N/A	---	---	---	---	---
	b (Å)		N/A	---	---	---	---	---
	c (Å)		N/A	---	---	---	---	---
	α (Degree)		N/A	---	---	---	---	---
	β (Degree)		N/A	---	---	---	---	---
	γ (Degree)		N/A	---	---	---	---	---
	V (Å^3)		N/A	---	---	---	---	---
	Scale factor		0.99(8)	---	---	---	---	---
	Gaussian peak width parameters (°^{2})	U	1.6(13)	---	---	---	---	---
		V	–1(4)	---	---	---	---	---
		W	0.82(16)	---	---	---	---	---

* Samples named with % and V were achieved by reaching a certain percentage (%) of theoretical charge at a cathodic potential (V) vs. Ni/NiO reference electrode.

2. Density Functional Theory (DFT) simulations

DFT simulations were used for the thermodynamics calculation including crystal structure and free energy calculations, which support the derivation of the TiO_2 eletrolytic reduction mechanism.

2.1 Density Functional Theory

DFT calculations for the crystalline bulks were performed using the Vienna Ab Initio Simulation Package (VASP). [1] The total energies and structural relaxations were carried out using the projector augmented wave (PAW) method to treat core electrons.[2] The energy cutoff up to 520 eV was used for the plane wave basis set. The Perdew-Burke-Ernzerhof (PBE) functional was employed to account for the electron exchange-correlation effects. [3] Spin polarizations were considered in all calculations. A Monkhorst–Pack scheme was used to generate the k-point mesh for the Brillouin zone sampling.

2.2 Crystal models

The most stable phase for each involved bulk crystal (i.e., TiO, TiO_2, Ti, Li_2TiO_3, Li_2O, and $LiTiO_2$) were used. The unit cell structures are illustrated in Figure S1. PBE + U calculations were performed on all oxide and perovskite crystals containing the Ti species, and U-J is set to be 2.0 eV, which has been shown to produce more accurate reaction energies for the PBE+U methods. [4] The optimized bulk lattice structures based on periodic DFT calculations using the described modeling method were tabulated in Table S2.

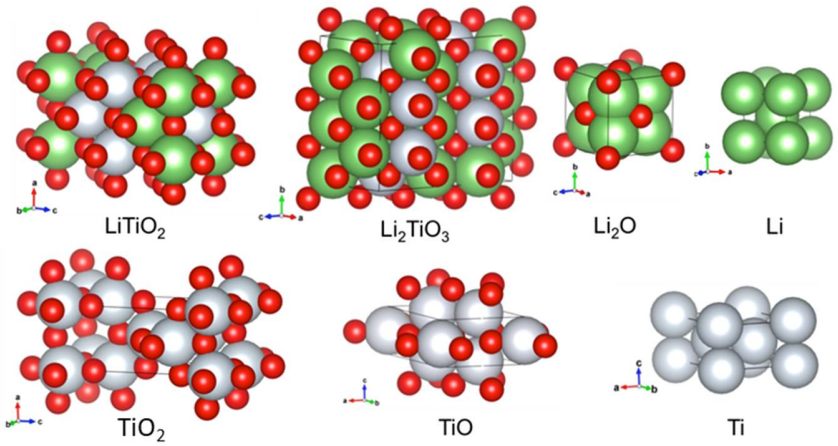

Figure S1. Optimized bulk crystal structures for the Li system, TiO_2, TiO, and Ti. Ti, Li, and O are in grey, green, and red, respectively. Black lines indicate the boundaries of the unit cell. Axis labels along the a, b, c directions are also shown.

Table S2. Optimized bulk lattice parameters.

Crystals	Crystal lattice	
	Space group	Lattice parameters
$LiTiO_2$	$4/mmm$	a = b = 4.08 Å, c = 8.56 Å; α = β = γ = 90°
Li_2TiO_3	$2/m$	a = 5.11 Å, b = 8.88 Å, c = 9.83 Å; α = 90°, β = 100.24°, γ = 90°
TiO	$\bar{6}m2$	a = b = 5.06 Å, c = 2.92 Å; α = β = 90°, γ = 120°
TiO_2	$4/mmm$	a = b = 3.84 Å, c = 9.74 Å; α = β = γ = 90°
Li_2O	$m\bar{3}m$	a = b = c = 4.63 Å; α = β = γ = 90°
Ti	$6/mmm$	a = b = 4.58 Å, c = 2.83 Å; α = β = 90°, γ = 120°
Li	$m\bar{3}m$	a = b = c = 3.43 Å; α = β = γ = 90°

2.3 Free energy calculations

A quasiharmonic approach would be adopted to estimate the thermodynamics of solids at high temperatures. The Helmholtz free energy, $F(V,T)$, a function of both crystal volume (V) and temperature (T), could be expressed by Equation S1,

$$F(T,V) = E(V) + F_{vib}(V,T) + F_{el}(V,T), \quad \text{(S1)}$$

where $E(V)$ is the total energy. $F_{vib}(V,T)$ and $F_{el}(V,T)$ represent the vibrational and thermal electronic contributions to the free energy, respectively.

$E(V)$ of a given crystal can be described by the equation of state (EOS), and its values at different volumes were obtained directly from periodic DFT calculations. Here, the 4th-order Birch-Murnaghan (BM4) EOS was used. Specifically, $E(V)$ is expressed as:

$$E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2}. \quad \text{(S2)}$$

The EOS expressions for all materials considered for free energy calculations are listed in Table S3. Then, the bulk modulus ($B(V)$) and pressure (P), both in GPa, can be represented by Equations S3 and S4, respectively.

$$B(V) = V\frac{\partial^2 E}{\partial V^2}, \quad \text{(S3)}$$

$$P = -\frac{\partial E}{\partial V}. \tag{S4}$$

Values of $B(V)$ at the equilibrium volume (V_0) determined from respective BM4 EOS are also listed in Table S3. The vibrational free energy contribution, $F_{vib}(T)$, can be rigorously obtained from explicit phonon calculations. In this study, the calculation of $F_{vib}(T)$ at the equilibrium volume (V_0) follows the formulation of a simplified Debye model, as expressed in Equation S5,

$$F_{vib}(T) = \frac{9}{8}k_B\Theta_D + k_BT\left\{3ln\left[1 - exp\left(-\frac{\Theta_D}{T}\right)\right] - D\left(\frac{\Theta_D}{T}\right)\right\} \tag{S5}$$

where Θ_D is the Debye temperature; $\mathrm{D}(\Theta_D/T)$ is the Debye function, expressed by Equation S6,

$$D(x) = \frac{3}{x^3}\int_0^x \frac{t^3}{\exp(t)-1}dt. \tag{S6}$$

The Debye temperature was approximated by the Debye-Wang model [5], as in Equation S7,

$$\Theta_D = sAV^{1/6}\left\{\frac{1}{M}\left[B(V) - \frac{2(\lambda+1)}{3}P\right]\right\}^{1/2}, \tag{S7}$$

where $s = 0.617$, $A = 231.04$, and $\lambda = -0.5$. M is the molecular weight in gram/mole. In this work, we assume that the effect related to crystal thermal expansion can be neglected. The values for B and P were taken at V_0, resulting in $P(V_0) = 0$. Then, the Debye temperature can be expressed as $\Theta_D = sAV_0^{1/6}(B(V_0)/M)^{1/2}$.

The electronic free energy contribution $F_{el}(T)$ at V_0 is represented by Equation S8

$$F_{el}(T) = E_{el}(T) + TS_{el}(T) \tag{S8}$$

where $E_{el}(T)$ and $S_{el}(T)$ are the internal energy and entropy due to electronic excitation, and are given by Equations S9 and S10:

$$E_{el}(T) = \int n(\varepsilon)f\varepsilon d\varepsilon - \int^{\varepsilon_f} n(\varepsilon)\varepsilon d\varepsilon, \tag{S9}$$

$$\text{and } S_{el}(T) = -k_B\int n(\varepsilon)[flnf + (1-f)ln(1-f)]d\varepsilon, \tag{S10}$$

where $n(\varepsilon)$ represents the electronic density of states (DOS), and can be obtained from DFT calculations, $f(\varepsilon, T)$ is the Fermi distribution function, as shown in Equation S11,

$$f(\varepsilon, T) = \frac{1}{exp\left(\frac{\varepsilon-\mu}{k_BT}\right)+1}, \tag{S11}$$

where k_B is the Boltzmann's constant, ε_f is the Fermi energy, and μ is the electronic chemical potential, which ensures that the Fermi function produces the total number of electrons at T. Values of μ corresponding to each material can be found in Table S3.

Table S3. Equation of state (Equation S2), equilibrium volumes (V_0) determined from corresponding BM4 EOS, bulk moduli, and electronic potentials for the materials modeled from DFT.

Crystal	BM4 EOS	V_0 (Å^3)	$B(V_0)$ (GPa)	μ (eV)
$LiTiO_2$	$a = -571.9, b = 41551.2$ $c = -1.25 \times 10^6, d = 1.24 \times 10^7$	143.8	139.7	7.07
Li_2TiO_3	$a = -79.3, b = -23671$ $c = 249893, d = 1.68 \times 10^7$	440.9	107.8	2.55
TiO	$a = 177.5, b = -9384.75$ $c = 126016, d = -540527$	65	215.3	8.35
TiO_2	$a = 35.8, b = -6282$ $c = 35014.2, d = 935552$	143.7	180.6	1.88
Li_2O	$a = -1.42, b = -2395.5$ $c = 25495.8, d = 2929.43$	99.4	80.5	1.386
Ti	$a = 26.4, b = -1503.21$ $c = 12977.2, d = -23850.9$	51.4	113	5.9
Li	$a = 1.65, b = -147.2$ $c = 1191, d = -2524.4$	40.7	13.8	0.56

References

1. Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558–561, doi:10.1103/PhysRevB.47.558.
2. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775, doi:10.1103/PhysRevB.59.1758.
3. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868, doi:10.1103/PhysRevLett.77.3865.
4. Hu, Z.; Metiu, H. Choice of U for DFT+U Calculations for Titanium Oxides. *J. Phys. Chem. C* **2011**, *115*, 5841–5845, doi:10.1021/jp111350u.
5. Wang, Y.; Ahuja, R.; Johansson, B. Mean-Field Potential Approach to the Quasiharmonic Theory of Solids. *Int. J. Quantum Chem.* **2004**, *96*, 501–506, doi:10.1002/qua.10769.