Reversible oxygen scavenging at room temperature using electrochemically reduced titanium oxide nanotubes

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1. Reduction Chemistry

Acidic Reductions:
The reductions in acidic solution were carried out in both nitric acid and hydrochloric acid, with pH 3. On the titanium dioxide (nanotube) cathode, the dominant reducing reaction is likely to be:

Cathode:
\[ 2\text{H}^+ + \text{TiO}_2(s) + 2e^- \rightarrow \text{TiO}_2(s) + \text{H}_2\text{O}(l) \]  
(R1)

Anode:
\[ \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2(g) + 2e^- + 2\text{H}^+ \]  
(R2)

Here, protons present in the acidic solution combine with electrons and elemental oxygen from the titania electrode to form water.

There are however other side-reactions that can occur on the electrode. In particular, the reduction of protons to hydrogen gas is competitive in acidic solutions:

Cathode:
\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \]  
(R3)

Anode:
\[ \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2(g) + 2e^- + 2\text{H}^+ \]  
(R4)

This side reaction competes with the water-forming reaction and thus limits the current efficiency when reduction occurs in acidic conditions. During reduction, vigorous bubbling is observed on both electrodes, which supports the hypothesis that most of the reactions occurring are gas-forming side reactions. Hence, acidic solutions appear to be ill-suited for the selective reduction of titania.

Basic Reductions:
The reductions in basic solution were carried out in aqueous solutions of potassium hydroxide with a pH of 13. With a much lower concentration of protons in the solution, the most dominant reduction reaction is likely to be:

Cathode:
\[ \text{TiO}_2(s) + 2e^- \rightarrow \text{TiO}_2(s) + \text{O}_2^{2-}(aq) \]  
(R5)

Anode:
\[ 2\text{O}_2^{2-}(aq) \rightarrow \text{O}_2(g) + 4e^- \]  
(R6)

The oxide ion is extremely basic and very easily protonated. It is thus unlikely it exists in aqueous solution, no matter what the pH. Assuming the limited availability of protons in solution, there is likely another reaction with hydroxide ions:

Cathode:
\[ \text{TiO}_2(s) + 2e^- + \text{H}^+ \rightarrow \text{TiO}_2(s) + \text{OH}^-(aq) \]  
(R7)

Anode:
\[ 2\text{OH}^-(aq) \rightarrow \text{O}_2(g) + 2\text{H}^+ + 2e^- \]  
(R8)

Here, a proton is pulled close to the negatively charged electrode where it can react with reduced oxygen anions. The drastically lower concentration of free protons in the basic solution should significantly reduce the rate of the two proton reaction that produces hydrogen gas on the titania cathode. This greater
selectivity towards the desired oxide reduction may explain the improved oxygen scavenging performance of nanotubes when they are prepared in basic solutions instead of acidic solutions.

In the main text, we show that all methods of reduction lead to superficially black samples; this color change suggests that oxygen vacancies have been generated in the titania nanotubes. However, we found that only samples reduced in basic solutions are capable of measurable oxygen scavenging.

Although we do not have definitive proof as to why the basic reduction produces a superior oxygen scavenger, we will share three hypotheses that may account for poor oxygen scavenging for samples reduced in acidic conditions. Firstly, we propose that the relatively high selectivity towards the hydrogen producing reaction in acidic solutions may result in a lower number of oxygen vacancies merely because the vacancy producing reactions compete against hydrogen production via proton reduction. This hypothesis is supported by the currents recorded during the reduction step that have profiles as shown in Figure S1 for the two cases (acidic vs. basic). The reduction current measured in the acidic solution is much higher than that measured in the basic case (for identical nanotube samples) and does not decay appreciably over time. The higher current and lack of decay is consistent with the hydrogen-producing side reaction being responsible for most of the measured current.

A related factor that potentially contributes to the efficacy of basic reduction and selectivity that favors (or enables) oxygen extraction only at high pH is the fact that the absolute Fermi-energy of metal oxides (and hence the ability of the metal oxide to chemically or electrochemically reduce) shift more negative as pH increase as described by the Pourbaix diagram of the relevant metal oxide.²

In addition to the supposition that selectivity under acidic conditions may lead to the reduction of protons to form H₂, there is pre-existing evidence that protons may also intercalate into the negatively charged electrode from an acidic solution.³ These protons can be reduced to interstitial atomic hydrogen, or form

![Figure S1. The current profiles throughout the reduction step for both electrochemical reduction environments.](image)
intercalated OH- or trapped water\textsuperscript{3-6}. Hence, whereas electrochemical reduction in proton poor conditions may lead to the formation of O\textsuperscript{2-} species that leave the lattice (and form O\textsubscript{2} at the counter electrode) electrochemical reduction in proton rich conditions may predominantly result in an H\textsubscript{2} generation side reaction (essentially the dominant reaction is water splitting electrolysis - at sufficiently high voltages, bubbles indeed are visible at both electrodes). In addition to the water-splitting side reaction that may dominate at acidic conditions, the reduction of TiO\textsubscript{2} to TiO\textsubscript{2-x} is less likely to proceed by oxo-species like O\textsuperscript{2-} leaving lattice (as is desirable for our oxo-sponge application). Instead, in proton rich (acidic) conditions the reduction of TiO\textsubscript{2} to TiO\textsubscript{2-x} may well proceed by the interstitial formation of trapped OH- and H\textsubscript{2}O.\textsuperscript{3-6} The latter possibility implies that the water forming reaction (R1) listed above occurs but not on the surface; instead, it occurs within the lattice. In this latter scenario the sample will indeed show the characteristic blackening that result from vacancy formation. However, instead of the reduced sample consuming a net amount of atmospheric oxygen when exposed to air, it may simply consume the intercalated water and hydroxyls in the reverse of reaction (R1) when there is no applied voltage.

A third factor that may contribute to the efficacy (in producing a powerful O\textsubscript{2} spunge) of basic over acidic reduction is the possibility that a film intercalated with protons and/or with a fully protonated surface simply lacks the surface free electron density required\textsuperscript{7-10} to rapidly adsorb and decompose gaseous species like O\textsubscript{2}. The fact that external dopants, intercalated species, or adsorbed species can in general inhibit or shut-down the sequence of O\textsubscript{2} adsorption, dissociation and uptake in metal oxides like TiO\textsubscript{2} has been demonstrated experimentally\textsuperscript{1,11}. More specifically, DFT calculations suggest that the ‘intercalated OH’ or lattice ‘Ti-OH’ species that may form upon hydrogen doping produce predominantly localized electrons\textsuperscript{6} – a prediction that if correct would explain the relative lack of O\textsubscript{2} adsorption and

**Figure S2. Results of XRD analysis on one sample annealed as described in methods**
decomposition in a hydrogen doped sample.

In summary, the existing electrochemical data suggests that the discovery of reduction conditions that succeed in extracting a significant fraction of oxygen from the lattice and nanotube array is the key to achieving a reactive material that has a high uptake rate and capacity. The main discovery here, therefore, may be that by using very basic aqueous conditions with intermediate voltages (3 V optimal), oxygen may be extracted from the nanotube array and produce molecular oxygen (bubbles) at the positively charge platinum anode (counter-electrode).

As described in the main text, we also attempted to produce oxygen scavenging nanotube arrays using chemical reducing agents as opposed to electrochemical reduction. In all cases, poor reduction was achieved, as evidenced by less sample discoloration than with the electrochemical approach and no measurable scavenging capacity. We hypothesize that the reducing agent has inferior contact with the interior nanotube surface and virtually no reduction within the nanotube walls as a result of limited thermal diffusion of oxygen vacancies at room temperature (see main text).

2. X-Ray Diffraction and effect of annealing

The reduction treatments investigated in the main text include purely chemical reduction and electrochemical reduction in both basic and acidic electrolytes. These reduction methods can be applied either on the nanotube samples as fabricated (amorphous TiO$_2$) or after an additional annealing step (this step converts the amorphous nanotubes into polycrystalline anatase nanotubes). The annealing conditions

![Graph](image)

**Figure S3.** A comparison of the oxygen uptake profile of otherwise identical non-annealed/amorphous (5 samples) and annealed/anatase (red squares) nanotube arrays. To help distinguish the two sets, the annealed sample data has been fitted. As is the case for all samples measured in this work, equation (6.5) provides an excellent fit of the data (red line). Observe that the early uptake rate of the amorphous samples are somewhat higher than those for anatase, but the long range asymptotic limit (capacity) of the anatase sample is somewhat higher than for amorphous samples.
that yield polycrystalline anatase nanotubes are well established\textsuperscript{12-23}. Shown in Figure S2 is an X-ray diffraction pattern of an annealed nanotube film, revealing expected anatase peaks as well as titanium metal peaks from the foil substrate that supports the array (recall that the nanotube array is grown from a titanium foil and thus is imbedded in a titanium foil substrate).

It was found (see Figures 3 and S3) that the specific rates of oxygen uptake in the annealed samples is somewhat lower than those of the amorphous samples after both samples have been subjected to identical basic reduction treatments. On the other hand, Table S1 and Figure 4 show that even though polycrystalline (annealed) samples in our trials display slower uptake rates they do have slightly higher specific capacities (after > 2h) than the amorphous samples.

<table>
<thead>
<tr>
<th>Annealed</th>
<th>Reduction</th>
<th>Maximum Observed Rate</th>
<th>Maximum Specific Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>425°C for 1 hour</td>
<td>Basic</td>
<td>0.74 mmol O\textsubscript{2}/g-min</td>
<td>3.3 mmol O\textsubscript{2}/g</td>
</tr>
<tr>
<td>No</td>
<td>Basic</td>
<td>14.5 mmol O\textsubscript{2}/g-min</td>
<td>2.2 mmol O\textsubscript{2}/g</td>
</tr>
</tbody>
</table>

Table S1.

Enhanced uptake rates for amorphous (unannealed) over polycrystalline (annealed) samples are consistent with recent studies of HfO\textsubscript{2}\textsuperscript{24} and titanate\textsuperscript{25,26} and older work on aluminum oxide\textsuperscript{27}. Our results support the hypothesis that oxygen self-diffusion (at high temperature) appears to be significantly enhanced by the presence of various defects in crystal structure. Defects that enhance diffusion have sometimes been called “fast-paths (for oxygen diffusion)”\textsuperscript{26} and are attributed to grain boundaries in polycrystalline samples\textsuperscript{26}.

Additionally, the adhesion of the amorphous samples to the metallic foil substrate is inferior to that of the annealed samples. As a result, the amorphous samples are prone to flaking when cycled through reduction and oxidation as in figure 4, while the annealed samples have better long term mechanical stability and are thus able to maintain oxygen absorption capacity over multiple uptake and regeneration cycles.

3. Effect of titanium purity on O\textsubscript{2} uptake

Prior work suggest that the presence of trace impurities in TiO\textsubscript{2} may measurably affect properties relevant to this work such as diffusion rates\textsuperscript{28-30}, oxygen dissociation chemistry\textsuperscript{7}, and resistivity\textsuperscript{6}. We performed the following experiment to test whether the presence of trace impurities (such as Fe) in the titanium foil (from which the TiO\textsubscript{2} nanotube arrays were synthesized) plays a role in the remarkably high oxygen uptake:

1. Three different sources of titanium foil with different certified purities were obtained (see table S2).
2. Nanotube arrays were prepared from every starting material using identical anodization conditions (60 V in 0.05 M NH\textsubscript{4}F in ethylene glycol with 2 vol% water at 15 °C for 16 h).
3. All three sample sets was electrochemically reduced using the pH 13 conditions as described in methods.
4. The oxygen uptake for every sample was measured at room temperature in standard air.

<table>
<thead>
<tr>
<th>Supplier/Specification</th>
<th>AMS 4902/CP Grade 2</th>
<th>STREM/Pure Ti</th>
<th>Sigma-Aldrich/Pure Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified purity</td>
<td>&gt; 98.9 %</td>
<td>&gt; 99.7 %</td>
<td>&gt; 99.99 %</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt; 0.3 %</td>
<td>300 ppm</td>
<td>Trace metals ≤ 150 ppm</td>
</tr>
<tr>
<td>O</td>
<td>&lt; 0.25 %</td>
<td>0.04 %</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>&lt; 0.08 %</td>
<td>0.01 %</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>&lt; 0.03 %</td>
<td>0.008 %</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>&lt; 0.03 %</td>
<td>0.0026 %</td>
<td></td>
</tr>
<tr>
<td>Any individual residual</td>
<td>&lt; 0.1 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total residuals</td>
<td>&lt; 0.4 %</td>
<td></td>
<td>Trace metals ≤ 150 ppm</td>
</tr>
<tr>
<td>Source</td>
<td>Certified specification</td>
<td>Certificate of analysis</td>
<td>Specification test passed</td>
</tr>
</tbody>
</table>

Table S2.

The measured specific oxygen uptake by nanotube arrays, labelled by the purity of its starting material, (pre-cursor/substrate Ti-foil) is shown in figure S4. We conclude that effect on oxygen uptake performance of nanotube arrays by trace impurities in the titanium foil (from which the nanotube arrays were synthesized) is smaller than the measurement noise. In particular, the data suggests that it is unlikely that Fe levels have a significant role in rapid oxygen uptake because the 99.7 % sample has at least twice as much Fe as the 99.99 % and there is no measurable impact on oxygen uptake rate or capacity.

Figure S4. A comparison of the oxygen uptake by identically fabricated and reduced nanotube arrays. The only difference between the samples is the purity specification of the titanium foil used as the starting material from which the anodic nanotube arrays were fabricated.
4. Nanotube length, specific surface area and performance

Different anodization or growth times were used when fabricating nanotube arrays. For the sample labeled “Nanotube 90 µm” the anodization time was 91 h and for the sample labeled “Nanotube 114 µm” the anodization time was 47 hours. SEM analysis revealed that the longer growth time resulted in shorter nanotubes, specifically 90 µm (± 4 µm) for the 91 h growth vs. 114 µm (± 5 µm) for the 47 h growth. However the fact that the longer growth time resulted in shorter nanotubes may appear counter-intuitive, since generally longer growth time leads to longer nanotubes. The latter trend (longer growth time results in longer tubes) is indeed invariably true for short (< 10 h) growth times. However, the nanotube growth rate is fastest right at the onset of anodization and then it monotonically and gradually decreases with time. Concurrently, there is a nanotube dissolution reaction that dissolves the nanotubes relatively slowly (compared to the initial growth rate). The dissolution reaction rate stays relatively constant for a given fixed temperature, electrolyte composition and voltage (these are carefully maintained in our experimental reactor).13,15-20,22,31-34 Hence, the growth rate at large times eventually diminishes to the point that the dissolution rate dominates, and the net effect is that nanotube arrays may become shorter with time. From our results to date it appears that nanotube arrays up to ~ 100 µm have comparable specific (per mass) oxygen uptake capacity. However, nanotubes with lengths exceeding ~ 100 µm tend to have slower uptakes and lower total specific capacities. It is not clear why this is the case, but we speculate that when the nanotube arrays get longer than a critical length the reduction step may not be as uniform and complete as it is with shorter nanotube arrays.

The average nanotube diameters and wall thicknesses for all samples in this study were identical to within statistical noise. This similarity in outer diameter and wall thickness is to be expected since the primary synthesis parameters controlling the diameter and wall thickness of anodic nanotubes are voltage, electrolyte composition and temperature.13,15-20,22,31-34 These parameters were kept constant for all the nanotube arrays used in this study.

We report in Figure 3C the highest specific rate measured for any given reduction treatment. The nanotube array fabrication conditions, annealing treatments (if any), and reduction treatments used for every sample set reported in Figure 3C are summarized in Table S3.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Anodization time (h)</th>
<th>Annealing</th>
<th>Reduction (see methods for description)</th>
<th>Max specific O₂ uptake rate (mmol O₂/g-min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic 1</td>
<td>91</td>
<td>No</td>
<td>Basic</td>
<td>14.59 (±0.10)</td>
</tr>
<tr>
<td>Basic 2</td>
<td>47</td>
<td>No</td>
<td>Basic</td>
<td>7.14 (±0.14)</td>
</tr>
<tr>
<td>Annealed</td>
<td>5</td>
<td>425°C for 1 hour</td>
<td>Basic</td>
<td>0.68 (±0.12)</td>
</tr>
<tr>
<td>Acidic</td>
<td>2</td>
<td>No</td>
<td>Acidic</td>
<td>0.07 (±0.06)</td>
</tr>
<tr>
<td>Chemical</td>
<td>2</td>
<td>No</td>
<td>Chemical</td>
<td>0.00 (±0.05)</td>
</tr>
</tbody>
</table>

Table S3. A summary of the fabrication conditions and treatments of all samples reported in Figure 3C. The anodization voltage, anodization temperature and electrolyte composition for all nanotube samples were identical (see methods).
Typical BET surface area for anodic TiO$_2$ nanotube arrays synthesized at room temperature is ~ 30 m$^2$/g$^{33,35}$. However, here we synthesized the arrays at 15 °C with a reduced anodization temperature that results in thicker walls and better nanotube array adhesion to the Ti substrate since enhanced adhesion is necessary for the reduction step. However, the thicker walls also result in a lower specific surface area (8 m$^2$/g by BET).

5. Estimation of the bulk to surface ratio of oxygen atoms in TiO$_2$ nanotubes

The average wall thickness of the nanotubes in this study was approximately 373 Å with the spacing in oxygen planes (in the relevant 101 direction$^{21,36}$) 3.52 Å$^{37}$. If we assume that only the inner surface is active (since the tubes are tightly packed, see SEM in figure 1) the active surface to bulk ratio for lattice oxygen atoms was ~ 1:106.

6. Comparison of resistivity change and oxygen uptake

Perfect stoichiometric TiO$_2$, with a bandgap of 3.0 to 3.2 eV, would be an insulator at room temperature.$^{3,29,37,38}$ However, thermodynamic equilibrium of both the rutile and anatase phases with air does not result in a perfect stoichiometric material but instead a marginally oxygen deficient material TiO$_{2-x}$.$^{38-42}$ Oxygen deficient TiO$_{2-x}$ is an n-type semiconductor with a free electron density, and hence conductivity, that to a first order roughly scales with or tracks the donor density.$^{3,6,29,37,38,40,43,44}$ In particular, Li et al. found that V$_o$ density (inferred through $^{18}$O absorption) and resistivity both correlate with “the bulk reduction state of the crystal”.$^{43}$ The possible intrinsic donors are titanium interstitials and oxygen vacancies; the nature of the dominant donor may depend on the type and extent of the reduction process.$^{5,37,40,42,43,45}$ For anodic metal oxide in general and for titanium dioxide in particular, several researchers have found that oxygen vacancies dominate.$^{44,46}$ When exposed to air, a reduced TiO$_2$ sample equilibrates with the partial pressure of O$_2$ at the surface. (This process may be fast or very slow, depending on the relevant kinetics and transport.$^{39}$) This equilibration proceed through the adsorption of O$_2$, and subsequent dissociation of O$_2$ and uptake of O$^-$ species (and eventual annihilation of the relevant donor defect), a process that removes free electrons from reduced TiO$_{2-x}$ and increases its resistivity rapidly.$^{7,10,40,45,47,48}$ This is the fundamental physics exploited by low cost yet sensitive resistive TiO$_2$-based O$_2$ sensors.$^{39,49-52}$

Recently Gopal and Haile$^{53}$ demonstrated that, in addition to simply detecting and quantifying the partial pressure of O$_2$, the resistivity transient of reduced metal oxides can be the basis for accurately measuring the bulk oxygen diffusivity in a given metal oxide. These authors call this approach the “electrical conductivity relaxation technique” or ECR. Hence, using the transient resistivity of thin films as a proxy for oxygen uptake is not without precedent.

Before comparing the recovery of resistivity in reduced TiO$_2$ thin films with the oxygen uptake profiles in reduced TiO$_2$ nanotube arrays (Fig. 5) we compared the recovery of resistivity in reduced TiO$_2$ nanotube arrays with the oxygen uptake profiles of the same nanotube arrays (Fig S5). As with the comparisons in Fig 5, it is evident that there is good agreement between the oxygen uptake and resistivity curves. The transients recorded by these two different measurements indeed have almost exactly the same timescales,
suggesting that the change in resistivity is closely related to material changes induced by oxygen adsorption and uptake.

Figure S5. A comparison of the normalized oxygen uptake profiles (normalized by the final values of each data set) of 5 different nanotube array samples with the change in resistance measured during oxygen uptake of an identical nanotube array. All the samples were amorphous nanotubes (non-annealed). Al samples were reduced right before oxygen uptake using the basic reduction procedure (see methods).

However, at the same time, it should be noted that the normalized profiles are not an exact match. There are several reasons why this is perhaps to be expected:

1) Although conductivity is generally proportional to free carrier density, it is also proportional to free electron mobility. The dominant effect of oxygen adsorption and eventual bulk uptake is to reduce the free electron density. However, if bulk oxygen uptake indeed proceeds by removing donor defects \((V_{o})\), then a secondary effect of the oxygen uptake process would be an increase in the mobility of the remaining free electrons (by decreasing impurity scattering). This nontrivial evolution of resistivity with oxygen uptake suggests that the resistivity transient and oxygen uptake transients may not necessarily track each other exactly during the oxygen uptake process—this indeed appears to be the case in figure S5. On the other hand, since the change in resistivity is driven fundamentally by oxygen adsorption and uptake, the overall timescale of the oxygen uptake and resistivity transients are expected to be the same, this is indeed observed in the data of figure S5.

2) While the total oxygen uptake up to a given moment in time is a simple scalar number, the spatial defect distribution in a nanotube or thin film may not be uniform. Hence, the nanotube film and thin films may have spatially dependent electrical conductivity. For instance, defects close to the outer surface may be removed faster than those deeper down. This spatial inhomogeneity may translate into measured ‘bulk sample’ resistivity profiles that evolve in a more complex manner than for the simpler scalar
quantity that is simply the ‘amount of oxygen removed from the air’ - even though these two quantities are related.

3) The evolution of contact resistance (at the two Ti-TiO₂ contacts formed to enable the measurement) may change as the free carrier density and Fermi energy in the metal oxide change. The evolution of contact may cause a further slight deviation between the shape of the oxygen uptake profiles and that of the measured resistivities. (Note that for the thin films we measured the resistivity across the 40 to 100 nm thin films. For the nanotube arrays, we measured the resistivity change along the 100 μm length of the nanotube arrays.)

The close agreement between the overall timescales for completion of the resistivity and the oxygen uptake profiles strongly suggest that both these measurements are related to the same underlying process (oxygen uptake and the resulting electron scavenging and defect annihilation). However, consideration of the physical processes that affect the finer details of the bulk sample resistivity profile caution against over-interpreting the reasons for the differences in the exact shape of the respective transients.

In summary, we suggest that the agreement in overall timescale of the resistivity and oxygen uptake transients in figure 5 indicate that the re-oxidation of thin films and nanotube films consisting of comparable thickness (wall vs film thickness) and crystalline phase proceed at comparable rates. This means that the nanotube re-oxidation rate is similar to that for the thin film re-oxidation.

7. Survey of recently published evidence in support of interstitial oxygen diffusion

The current literature overwhelmingly describes diffusion of the two most prevalent point defect types, namely oxygen vacancies and metal interstitials, as being the dominant defect transport mechanisms in metal oxides generally and TiO₂ specifically. ⁷, ¹⁰, ¹²-¹⁵ There has however in recent years emerged evidence suggesting that the dominant transport mechanism for oxygen uptake into the metal oxide bulk need not necessarily be oxygen vacancy diffusion to the surface ¹⁰, ¹²-¹⁴, but that oxygen transport may also proceed by the direct permeation of oxygen (or a molecular derivative of oxygen, Oₓ⁻) into the bulk. Hollister et al. in particular tracked mobile oxo-species with isotope labelling in experiments that suggest the existence of mobile interstitial oxo-species but do not explain how such mobile oxo-species form or exactly what species it is. ¹⁴ Experiments observing the formation of interstitial oxo-species from adsorbed molecular oxygen was published very recently; Setvin et al. ⁷ induced O₂ decomposition on anatase into oxo-species (O₂²⁻, O²⁻ and interstitial or “bridging (O₂)₀”) with STM at 105 K. The observation of interstitial oxygen in the (O₂)₀ configuration is of particular interest because earlier DFT calculations ⁵⁴ suggests this species to be the energetically most stable configuration of excess O also in the anatase bulk. In the study of Setvin et al. decomposed oxo-species combined with V₀ in the subsurface only if the applied voltage of the STM tip pulled a V₀ sufficiently near the surface. In summary, recent STM work identified DFT predicted chemistry capable of O₂ decomposition into oxo-species on the anatase surface. Isotope tracer studies revealed that oxo-species derived from adsorbed O₂ can penetrate deep into the bulk. ¹⁴, ⁵⁵ However, since there is no STM tip to induce bulk to surface transport under ‘normal’ circumstances this work still leave open the question regarding the transport mechanism for oxygen uptake in materials like anatase.

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8. Thermally reduced suboxides vs. electrochemically reduced nanotubes

The oxygen uptake capacity of the ordered nanostructured electrodes suggests that the combination of a nanotube morphology with low temperature electrochemical treatment enables unprecedented high levels of reduction without (irreversible) phase transition. Both amorphous TiO$_2$ and polycrystalline anatase with unprecedented high levels of bulk vacancies were generated. Oxygen vacancies are more stable in the bulk of anatase than on or near the surface, and hence are mostly confined to the bulk.$^{7,56}$ Bulk defects nonetheless ‘activate’ the surface by donating delocalized electrons that are capable of inducing adsorption and chemistry at the surface.$^{7,8,45,56-58}$

![Graph showing concentration profiles](image)

**Figure S6:** Concentration profiles from Hollister et al.$^1$ that show isotopic oxygen ($^{18}$O) diffusion profiles in rutile TiO$_2$ subsequent to annealing (650°C, 750°C, 800°C) in $^{18}$O$_2$ gas at 10$^5$ Torr. The exponential profile shapes in the deep bulk (linear on the semi-log scale shown) suggest diffusion of a highly mobile intermediate species. [Reprinted with permission from reference 1: Copyright 2013, AIP Publishing LLC.]

The hypothesis that there exists an “exceptionally mobile defect” as proposed by Seebauer and co-workers$^{1,55}$ that can rapidly re-oxidize a reduced sub-oxide as observed in the experiments reported here raise the following question: Why is it possible to create metastable sub-oxide TiO$_{2-x}$ materials by generating $V_0$ at high temperature and then ‘freeze in these defects’ by cooling the material to room temperature? Why are such thermally engineered defects not also rapidly annihilated by this hypothesized “exceptionally mobile defect” as soon as these samples are exposed to room temperature and air?

This question naturally requires further investigation to answer definitively. We can, however, suggest two factors that may be relevant:

1) When a metal oxide such as TiO$_2$ is reduced at high temperatures (with or without a reducing gas present) then, in mildly reducing conditions, the result is a non-stoichiometric oxide solid solution.$^{37,59-61}$ Under conditions more favorable to reduction (higher temperature, lower $P_{O_2}$ or higher $P_R$ where $R$ is a
reducing gas), lattice reorganization occurs and new phases (such as the well-studied Magnéli phases) appear.\textsuperscript{37,59-61} From this point of view, it is possible that the room temperature electrochemical reduction reported here is an efficient means by which produce a meta-stable sub-oxide with a high non-equilibrium $V_o$ concentration. A similar material may not be achievable by high temperature methods because of the structural and thermodynamic reorganization to more stable phases that will inevitably occur at higher temperature and would thus either remove the $V_o$ generated or lock it into more stable sub-oxide phases. Specifically, samples like the 90 \textmu m array in Fig. 2 are TiO$_{2-x}$ with $x \leq 0.2$. That is, the material is a reduced titanium dioxide with approximately 1 in 10 O atoms removed by the basic reduction treatment described in the text. This stoichiometry corresponds to a material with the nominal stoichiometry of the Magnéli phase Ti$_5$O$_9$, a system for which the most stable thermodynamic state at room temperature is a solid solution of rutile + Ti$_2$O$_3$.\textsuperscript{37,59,60} None of the XRD patterns from the reduced samples in this study have shown any detectable traces of Magnéli, suboxide, or rutile phases. The only crystalline phase within the nanotubes seen in the XRD patterns is the anatase peaks in the annealed samples (as in Fig. S2). Hence, the basic electrochemical reduction appears to yield a novel meta-stable material with high oxygen scavenging capability that is not realizable through thermal reduction.

2) In their recent, work Seebauer and co-workers\textsuperscript{1,55} show experimentally that oxygen can be transported into the lattice by an oxo-species with a diffusivity two orders of magnitude larger than that of $V_o$. They proposed that in some systems the much slower $V_o$ diffusion appears to be the dominant transport mechanism with the faster oxo-species diffusion largely absent in spite of its much higher diffusivity. Seebauer and co-workers suggest that the ability of the surface to produce and inject the highly oxo-species depends strongly on the availability of suitable surface sites. They support this hypothesis experimentally by pre-exposing the TiO$_2$ surface to sulfur which adsorbs in small amounts to the TiO$_2$ surface; this sulfur inhibits the surface flux of highly mobile oxo-species injected into the TiO$_2$ bulk when exposed to oxygen. This sulfur pretreatment of the surface does not incorporate any sulfur into the TiO$_2$ bulk, nor does it alter the diffusion rate of any oxo-species that makes it past the surface and migrate into the bulk. Hence, they suggest that the surface is a gateway that can be used to control or “kinetically constrain” the presence or absence of highly mobile oxo-species. In the even more recent paper of Setvin et al., O$_2$ adsorption on the anatase surface is experimentally probed. The dynamics of the incorporation of adsorbed oxygen into the anatase sub-surface described by Setvin et al. is consistent with the hypothesis of the gateway role of the surface. In the absorption dynamics described by Setvin et al., bulk donor defects like $V_o$ donate one or two electrons that become delocalized\textsuperscript{6}. It is these delocalized electrons that render the TiO$_2$ surface capable of adsorbing species like O$_2$. Furthermore, these electrons support the reduction chemistry that produces the oxo-species that in Setvin et al’s framework is funneled to the subsurface. \textit{It therefore appears that anodic TiO$_2$ nanotubes, reduced in basic conditions, present ample surface sites suitable for the adsorption of oxygen. Concurrently, there is an ample supply of delocalized electrons that drive the chemistry required to produce the mobile oxo-species capable of fast lattice diffusion.} On the other hand, reduction in acidic conditions seem to yield a surface that is more protonated, or perhaps also different in some other significant way that inhibits the fast re-uptake of oxygen as observed with basic reduction (analogous to the sulfur treatment of Seebauer and co-workers\textsuperscript{1,55}).
9. Mathematical Models

There are two main hypotheses for oxygen uptake by the annihilation of oxygen vacancies in sub-stoichiometric titanium dioxide. They are: 1) ‘Interstitial’ oxygen or ‘oxo-species’ diffuse inward (not assisted by mobile V_o) from the surface into the bulk with the annihilation reaction (O_i + V_o → no defect) occurring with stationary oxygen vacancies distributed throughout the bulk. 2) Mobile oxygen vacancies diffuse from the bulk to the surface with all annihilation occurring at the surface or the subsurface. Sections 9.1 and 9.2 summarize results of two mathematical models corresponding to these hypothesized pathways.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Model solution</th>
<th>Predicted uptake profile</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Description</strong></td>
<td><strong>Species</strong></td>
<td><strong>Spatiotemporal profile of diffusing species</strong></td>
</tr>
<tr>
<td><strong>Vacancy Diffusion</strong></td>
<td>( C_{V_o}(x,t) )</td>
<td>( \text{erf}(\frac{x}{2\sqrt{D}\tau}) )</td>
</tr>
<tr>
<td><strong>Interstitial Oxygen Diffusion</strong></td>
<td>( C_{O_i}(x,t) )</td>
<td>( e^{-\frac{x}{\sqrt{D}\tau}} \text{ as } t \to \infty )</td>
</tr>
</tbody>
</table>

**Table S4.** The spatial profiles and uptake predicted by models describing the two alternative pathways for oxygen uptake into the bulk of sub-stoichiometric oxides. Existing direct measurements of spatial profiles\(^1,55\) and the measurements of temporal profiles reported here are consistent with inward interstitial oxygen self-diffusion being the dominant pathway. Here, \( C_{V_o}(x,t) \) and \( C_{O_i}(x,t) \) are the concentrations of vacancies and oxo-species, respectively, where \( x \) is distance into the solid, and \( t \) is time. Also, \( D \) is the diffusion coefficient associated with the respective mechanisms, and \( \tau \) is a time scale for oxygen uptake. (The mathematical details of these models are provided in the Supplemental Information.)

9.1 Model 1: Oxygen Migration with Annihilation of Vacancies in Bulk

As explained in the main text, the extremely fast rate of oxygen uptake is not easily reconciled with the expected slow room temperature diffusion of oxygen vacancy (V_o) from the TiO\(_2\) bulk to the surface. An alternative explanation is provided by the mechanism recently promoted and studied by Seebauer et al.\(^1,55\) according to which oxo-species diffuse inward at a rate higher than vacancies diffuse outward. Setvin et al.\(^7\) has confirmed experimentally that there exists a facile route by which O\(_2\) reacts at the reduced TiO\(_2\) surface to produce oxo-species that are readily transferred to the subsurface. The Seebauer et al. experiments confirm that there exists a highly mobile oxo-species, formed during O\(_2\) uptake into TiO\(_2\), with lattice diffusion that is orders of magnitude higher than that of oxygen vacancies. Seebauer and co-workers also find that the spatial profile of isotope-labeled \(^18\)O incorporated into the TiO\(_2\) bulk from the surface is exponential (linear on a log plot) with distance as seen in Figure S6; they concluded, similar to expression (9.9) below that this profile is consistent with the independent (not V_o mediated) inward diffusion of oxo-species.

To explore the hypothesis that oxo-species self-diffusion plays a role in the unexpected rapid uptake of oxygen into the nanotube bulk, we propose the following mathematical model. Let \( C(x,t) \) be the concentration of a diffusing oxo-species at time \( t \) and position \( x \) below the TiO\(_2\) surface. Likewise, let \( Z(x,t) \) be the concentration of remaining oxygen vacancies initially produced by the reduction step at time \( t \) and location \( x \). A simple model that describes the diffusion of \( C \) (with diffusion coefficient \( D \) into
the lattice and mutual annihilation of $C$ and $Z$ through a reaction that is first order in both species (with rate constant $k$) is:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kCZ \quad (9.1a)$$

$$\frac{\partial Z}{\partial t} = -kCZ \quad (9.1b)$$

$$C = A \text{ at } x = 0, \ C \to 0 \text{ as } x \to \infty \forall t \quad (9.1c)$$

$$C = 0, \ Z = B \text{ at } t = 0, \forall x \quad (9.1d)$$

In the above, $A$ is the concentration of oxo-species at $x = 0$ and $B$ is the initial concentration of vacancies throughout the domain; the dimensionless version of this system is given by (A2) in the Appendix. The solution of this model is also provided in the Appendix in the limit of $A/B \to 0$, i.e., for cases where the concentration of vacancies exceeds that of the oxo-species. In our experiments, $B$ is indeed exceptionally large ($\sim 17 \text{ mmol/cm}^3 = 1 \cdot 10^{22} \text{ cm}^{-3}$ see Table S5) and hence $A/B$ is indeed expected to be small. Also note that expression (9.5) is the asymptotic solution that result from an expansion around $\varepsilon = A/B \approx 0$ which in the system A2 effectively means keeping (or approximating) the vacancy density as being at its initial value. This approximation seems to work well for predicting most of the uptake profiles (like Figures 2, 5 & S5) since most of the uptake occurs at early time when the vacancy concentration is large and a relatively small fraction of the uptake occurs at long time when the vacancy density starts getting depleted. We also calculated the asymptotic solution of the system A2 to a first order in $\varepsilon$ (i.e., allowing the bulk vacancies to be consumed) and found that the first order correction to expression (9.5) result only in a small modification to the functional shape of uptake profiles predicted by expression (9.5).

The dependent variables in the Appendix are written as $y_1(x, t)$ and $y_2(x, t)$ to emphasize the generality of the math solution; they are identified with the variables in (9.1) as follows: $C(x, t) \equiv y_1(x, t)$ and $Z(x, t) \equiv y_2(x, t)$. Below, we explore the main features of the solution that provides a mathematical form to compare with experiment.

### 9.1a Uptake of Oxygen with Time

The amount of oxygen that is incorporated in the lattice can be extracted from its diffusive flux, $q$, across the surface at $x = 0$, which is given in accordance with Fick’s law as:

$$q = -D \left. \frac{\partial C}{\partial x} \right|_{x=0} \quad (9.2a)$$

In (9.2a), $D$ is the diffusion coefficient of oxo-species. The total uptake of oxygen into the solid, $U(t)$, can be extracted from the flux, $q$, as:
\[ U(t) = S \int_0^t q(t') dt' \]  

(9.2b)

where \( S \) is the surface area for diffusion at \( x = 0 \). Upon substitution of the dimensional form of the concentration solution (A7) into (9.2a) (again noting that \( C \equiv y_1 \) in the Appendix) we obtain:

\[ q \sim A \sqrt{\frac{D}{\tau}} \left( \frac{1}{\sqrt{\pi}} e^{-\frac{t}{\tau}} + \text{erf} \left( \frac{\sqrt{t/\tau}}{\sqrt{\tau}} \right) \right) \quad \tau = \frac{1}{k_B} \]  

(9.3)

The corresponding uptake, \( U(t) \), may be obtained after substitution of (9.3) into (9.2b) and performing the indicated integration:

\[ U(t) \sim SA \sqrt{D \tau} \left\{ \left( \frac{t}{\tau} + \frac{1}{2} \right) \text{erf} \left( \frac{\sqrt{t/\tau}}{\sqrt{\tau}} \right) + \frac{\sqrt{t/\tau}}{\sqrt{\pi}} e^{-\frac{t}{\tau}} \right\} \]

\[ \sim SA \sqrt{D \tau} \left\{ \frac{1}{2} \text{erf} \left( \frac{\sqrt{t/\tau}}{\sqrt{\tau}} \right) + \frac{\sqrt{t/\tau}}{\sqrt{\pi}} \right\} \quad \text{as} \quad t \to \infty \]  

(9.4)

where we have used the following integrals:

\[ \frac{2}{\sqrt{\pi}} \int_0^t \frac{e^{-t'/\tau}}{\sqrt{t'/\tau}} dt' = 2 \int_0^{\sqrt{t/\tau}} e^{-\theta^2 / \tau} 2\tau \theta dt' = 2 \text{erf} \left( \sqrt{\frac{t}{\tau}} \right) \]

\[ \int_0^t \text{erf} \left( \sqrt{\frac{t'}{\tau}} \right) dt' = \tau \left( \frac{t}{\tau} - \frac{1}{2} \right) \text{erf} \left( \sqrt{\frac{t}{\tau}} \right) + \frac{\sqrt{t/\tau}}{\sqrt{\pi}} e^{-t/\tau} \]

Expression 9.4 motivates the following fitting equation

\[ U(t) = A \text{erf} \left( \sqrt{\frac{t}{\tau}} \right) + Bt \quad \text{for} \quad t \gg \tau \]  

(9.5)

with \( A \) and \( B \) fitting constants. At early time the first term dominate and

\[ U(t) \approx A \text{erf} \left( \sqrt{\frac{t}{\tau}} \right) \]  

(9.6)
where $A$ is a positive constant.

Expression (9.5) with fitting parameters $A$, $B$ and $\tau$, indeed provides a very good fit to every oxygen profile in reduced TiO$_2$ nanotube arrays we have measured to date (examples are Figs. 2, 4, 5, S3 and S4).

### 9.1b Asymptotic Limits of Absorbed Oxygen Profile

The spatial distribution of vacancies in the solid at any time is given by equation (A7). In the long time limit, the dimensional form of the asymptotic solution for $C(x,t)$ is given by equation (A14), which is written in dimensional form as:

$$C(x,t) \sim Ae^{-\frac{x}{\sqrt{D\tau}}} \quad \text{as} \quad t \to \infty \quad \text{for fixed } x,$$

(9.7)

where $\tau$ is a constant defined in equation (9.3). The result (9.7) is an agreement with the Hollister et al. experimental results\(^1\) (see Figure S6). In the Hollister et al. experiments, the initial $V_O$ concentration, denoted here as $B$, is just the native $V_O$ concentration in the pristine rutile film. It is therefore expected to be much smaller than the value corresponding to our experiments. That is, most of the isotope labelled oxygen in the experiment Hollister et al. may well remain interstitial as opposed to incorporated into the lattice by annihilating oxygen vacancies. Note that the oxygen vacancy concentration that is annihilated by injected oxygen, namely $1 - Z(x,t) = 1 - y_2(x,t)$, will through relation (A8) (which gives $y_2(x,t)$ in terms of $C(x,t) = y_1(x,t)$) also have exponential profiles of the form (9.7) in the long time limit. Hence, whether oxygen interstitials remain interstitial or annihilate vacancies, model 1 predicts that at long time tracer species should have exponential spatial profiles within the lattice whenever diffusion occur by the direct interstitial diffusion of these species. Hence, we see that our model (9.1) yields a solution that in the long time limit agrees with the spatial profile measurements of $^{18}$O tracers by Seebauer and co-workers (see Figure S6), in addition to yielding a time dependent result that fits well to our own experiments.

We note that our experiments are with amorphous TiO$_2$ and polycrystalline anatase as opposed to the experiments of Seebauer and co-workers that is with rutile, our work is at room temperature and theirs at $\geq 650$ $^\circ$C, and we have much higher initial defect densities. Hence, the agreement between the long time spatial profile of our non-equilibrium model and their measured spatial profiles may be accidental, or it may be that the long time limit of our non-equilibrium model correctly approaches the ‘closer to equilibrium’ situation Seebauer and co-workers measured and modelled.

### 9.1c Effect of Finite Domain

The result (9.5) above is attractive as it suggests the error function solution form (9.6), that fits our experimental data quite well. However inspection of the full solution (9.5) reveals that at large times the linear term will dominate and will yield an unbounded solution for the oxygen uptake. We examine here key results to see how a finite domain affects these mathematical results.

Upon substitution of the dimensional form of equation (A16) into (9.2a) (again noting that $C \equiv y_1$ in the Appendix)) we obtain:
\[ q \sim \frac{2AD}{L} \sum_{n=0}^{\infty} \frac{1}{1+\alpha_n^2} \left( 1 + \alpha_n^2 e^{-(1+\alpha_n^2)t/\tau} \right) \]  
\text{(9.8a)}

where

\[ \alpha_n = (2n + 1) \frac{\pi}{L} \sqrt{D\tau}, \quad \tau = \frac{1}{k_B} \]  
\text{(9.8b)}

The corresponding uptake, \( U(t) \), is obtained after substitution of (9.8) into (9.2b) and performing the indicated integration:

\[ U(t) \sim \frac{2AD\tau}{L} \left[ \left( \frac{t}{\tau} \right) \sum_{n=0}^{\infty} \frac{1}{(1+\alpha_n^2)} + \sum_{n=0}^{\infty} \frac{\alpha_n^2}{(1+\alpha_n^2)^2} \left( 1 - e^{-(1+\alpha_n^2)t/\tau} \right) \right] \]  
\text{(9.8c)}

The result (9.8c) clearly indicates that the oxygen uptake profile is zero at \( t = 0 \), and is linear at large times, i.e.:

\[ U(t) \sim \frac{2AD\tau}{L} \left[ \left( \frac{t}{\tau} \right) \sum_{n=0}^{\infty} \frac{1}{(1+\alpha_n^2)} - \sum_{n=0}^{\infty} \frac{\alpha_n^2}{(1+\alpha_n^2)^2} \right] \quad \text{as } t \to \infty \]  
\text{(9.8d)}

Since the large time limit of the uptake profile is also linear for an infinite domain (see equation (9.5)), we conclude that unbounded oxygen uptake is not a consequence of the domain length. The result (9.8d), however, is consistent with the intuition that in the limit as \( A/B \to 0 \) (used in the derivation of the above results) the domain continues to absorb oxygen since the number of vacancies far exceeds the amount of oxo-species. Physical intuition suggests the number of vacancies will be depleted with time in a finite domain and the uptake must eventually decrease to zero. The full numerical solution of the governing system (9.1) is required to examine this case, as the \( A/B \to 0 \) limit is incapable describing situations in which there is a large depletion of vacancies. Since most of the fast uptake measured here occurs before the vacancies become depleted, or close to depleted, the asymptotic form (9.5) may well be capable of fitting most of the uptake with the exception of the final few percent which indeed appears to be the case for all the measured uptake profiles presented (Figs. 2, 4, 5, S3 and S4).

### 9.2 Model 2: Vacancy Migration with Annihilation of Vacancies at Surface

We now explore the alternative hypothesis that vacancies migrate to the surface and interact with oxygen there. Let \( Z(x, t) \) be the concentration of oxygen vacancies initially produced by the reduction step at time \( t \) and location \( x \), where \( x \in [0, \infty) \) corresponds to the bulk solid domain. We assume that oxygen vacancies diffuse from the bulk lattice towards the surface where an annihilation reaction occurs between \( Z \) and a constant supply of oxygen (or activated oxo-species). We assume that the surface reaction is diffusion limited, so once vacancies reach the surface they are depleted immediately; as a result, the surface concentration of oxygen vacancies is negligible compared with that in the bulk. A simple model that describes this process is given as follows:
\[
\frac{\partial Z}{\partial t} = D \frac{\partial^2 Z}{\partial x^2} \quad (9.9a)
\]

\[
Z = 0 \text{ at } x = 0, \quad \frac{\partial Z}{\partial x} \rightarrow 0 \text{ as } x \rightarrow \infty \quad \forall t \quad (9.9b)
\]

\[
Z = B \text{ at } t = 0 \quad \forall x \neq 0 \quad (9.9c)
\]

In the above, \(D\) is the oxygen vacancy diffusion constant (at the relevant temperature), and \(B\) is the initial concentration of oxygen vacancies; in our experiments, \(B\) is determined by the electrochemical reduction step. The solution of this system is standard\(^\text{5,30,41,62}\), and an exact analytical solution is easily obtained through a similarity transformation. The solution of this system is:

\[
Z(x, t) = B \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (9.10)
\]

Note that the expression (9.10) provides the concentration of vacancies in the domain, and our interest is in examining the oxygen uptake implied by this expression. This is examined in what follows.

By assumption, the surface reaction is diffusion limited, which accounts for our use of the boundary condition (9.9b) at the surface. In this limit, we expect that the flux of oxygen into the bulk will be equal to the number of vacancies that arrive there via diffusion, i.e.

\[
q = D \left. \frac{\partial Z}{\partial x} \right|_{x=0} \quad (9.11)
\]

In (9.11), note the absence of the minus sign in the flux expression, since the migration of oxygen is opposite to the direction of vacancy diffusion. Upon insertion of (9.10) in (9.11), the flux of oxygen is thus obtained:

\[
q = B \sqrt{\frac{D}{\pi t}} \quad (9.12)
\]

The corresponding uptake, \(U(t)\), may be obtained by substituting (9.12) into (9.2b) to obtain:

\[
U(t) = 2SB \sqrt{\frac{Dt}{\pi}} \quad (9.13)
\]

where again \(S\) is the surface area at \(x=0\). This result shows that the oxygen uptake has a square-root dependence for all times.
9.3 Comparison of Model 1 and Model 2 and Parameter Extraction

Model 1 (diffusion of oxo-species into bulk) predicts an exponential spatial profile of oxygen at large times (see equation (9.7)) consistent with the measurements of Seebauer and co-workers. It can be seen in the main text (Figs 2 & 5) that the solution to the interstitial oxygen self-diffusion model fits the measured time vs. oxygen uptake data well for all reduced nanotube samples measured in this study. The solution to the oxygen vacancy diffusion model does not have the spatial profile to fit the measurements shown in Fig. S6, nor does it have the right temporal profile to fit the uptake vs time data in the main text (see for example attempt in Fig. 2). The value for \( V_o \) diffusion at room temperature is obtained by an extrapolation to room temperature from high temperature Arrhenius expressions measured for \( V_o \) diffusion gives negligibly small values on the order of \( D_{V_o} \approx 1 \cdot 10^{-30} \text{ cm}^2/\text{s} \) or smaller (essentially this is the result for the activation energy for diffusion being on the order of 2.4-2.9 eV). A value recently inferred from EIS measurements of oxygen diffusion within amorphous thin film TiO\(_2\) electrodes (without the ability of unambiguously know the transport mechanism) is 2.6-10\(^{-16}\) cm\(^2\)/s. These latter thin film electrodes were fabricated with anodization of Ti foil similar to the amorphous thin film electrodes in Figs 5 & S5.

Is conventional vacancy diffusion indeed too slow to explain the observed uptake data?

We can estimate how long the oxygen uptake in this study would take if transport proceeded by \( V_o \) diffusion by substituting the Arrhenius extrapolation \( D_{V_o} = 1 \cdot 10^{-30} \text{ cm}^2/\text{s} \) into expression (9.13).

We also will use the following relevant parameter values:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( U - \text{total specific uptake} )</th>
<th>( S - \text{surface area} )</th>
<th>( B - \text{initial vacancy density} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>2.2 mmol/g</td>
<td>8 m(^2)/g</td>
<td>17 mmol/cm(^3) = 1 \cdot 10^{23} \text{ cm}^-3</td>
</tr>
<tr>
<td>Source</td>
<td>Total uptake measured</td>
<td>BET surface area</td>
<td>Based on total uptake</td>
</tr>
</tbody>
</table>

Table S5. Parameters used to estimate the total uptake time assuming \( V_o \) diffusion and using existing literature values in the Arrhenius expression for \( V_o \) diffusion

With the total observed uptake using \( D_{V_o} = 1 \cdot 10^{-30} \text{ cm}^2/\text{s} \) and the parameters in Table S5, it would take 6.7 \cdot 10^{10} years to achieve the uptake observed for the amorphous samples.

On the other hand, if we use the value inferred by Roh et al. for the diffusion of oxygen, namely 2.6 \cdot 10^{-16} cm\(^2\)/s, then expression (9.13) with the parameters in Table S5 yields 136 min for the observed uptake. In doing this, we consciously make two assumptions that cannot be verified: 1) The value 2.6 \cdot 10^{-16} cm\(^2\)/s for oxygen diffusivity measured by Roh et al. indeed refers to \( V_o \) diffusion and 2) diffusion occurs through \( V_o \) diffusion so that it is correct to use expression (9.13). Although actual uptake in the amorphous samples takes only around 25 min, the 136 min result based on the Roh et al value is significantly closer than the Arrhenius values. This unambiguously shows that the only conceivable way that traditional \( V_o \) diffusion could be the dominant transport mechanism that accounts for the uptake observed in our experiments is if there exists a mechanism for enhanced vacancy transport. This would need to exceed
the extrapolation of its known Arrhenius expression established at high temperature, and would need to have a value on the order of $D_{V_0} \approx 10^{-15}$ cm$^2$/s.

Note that an enhanced value for $D_{V_0}$ could explain the discrepancies between the timescale for uptake observed and that predicted for the Arrhenius extrapolation. However, it cannot explain why uptake profiles appear to follow expression (9.5) which is consistent with interstitial oxygen diffusion and bulk vacancy annihilation, as opposed to expression (9.13) which is valid for surface vacancy annihilation.

**Extracted values of $D_{Oi}$**

The good fits of expression (9.5) to all data including both the amorphous and polycrystalline anatase nanotubes allow us to extract estimated values for the effective interstitial oxygen diffusion coefficient from expressions (9.4) & (9.5).

The relevant values are listed in Table S6. The surface area $S$ is as in Table S5 and it is assumed that the concentration of oxo-species in the pile-up zone next to surface, parameter $A$, is pinned at the initial vacancy density $B$ (17 mmol/cm$^3$ for the amorphous samples and 25 mmol/cm$^3$ for the anatase samples). This is an assumption but should give the correct order of magnitude value.

The fitting parameters are defined by expression (9.5).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$A$</th>
<th>$\tau$</th>
<th>$D_{Oi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amorphous</strong></td>
<td>1.7 mmol/g</td>
<td>316 sec</td>
<td>2.0$\times10^{-14}$ cm$^2$/s</td>
</tr>
<tr>
<td><strong>Polycrystalline Anatase</strong></td>
<td>2.6 mmol/g</td>
<td>1 631 sec</td>
<td>4.1$\times10^{-15}$ cm$^2$/s</td>
</tr>
</tbody>
</table>

Table S6. Data fitting parameters and extracted diffusion constant using the fits of expression (9.5) to the measured specific oxygen uptake profiles.
Appendix

Model for Oxygen Migration with Annihilation of Vacancies in Bulk (Model 1)

A-1 Problem Statement and Governing Equations

We consider one-dimensional penetration of an oxo-species of concentration \( y_1 \) into a semi-infinite titanium dioxide solid as a function of time, \( t \), and distance, \( x \), where \( x \in [0, \infty) \). The reduction of the solid effectively leads to an initially uniform concentration of vacancies, \( y_2 \), that react with the oxo-species with a reaction rate first order in both species having rate constant \( k \). The free oxygen undergoes molecular diffusion and obeys Fick’s law with constant diffusion coefficient, \( D \). The concentration of the free oxygen at \( x = 0 \) is given by \( y_1 = A \) for all \( t \) and approaches zero as \( x \to \infty \). Initial conditions at \( t = 0 \) are \( y_1 = 0 \) and \( y_2 = B \) for all \( x > 0 \).

Dimensionless variables are defined as:

\[
\bar{y}_1 = \frac{y_1}{A}, \quad \bar{y}_2 = \frac{y_2}{B}, \quad \bar{t} = tkB, \quad \bar{x} = x\left(\frac{kB}{D}\right)^{1/2} \tag{A1a}
\]

and a single dimensionless parameter arises:

\[
\varepsilon = \frac{A}{B} \tag{A1b}
\]

With these definitions, the following dimensionless boundary value problem arises:

\[
\frac{\partial \bar{y}_1}{\partial \bar{t}} = \frac{\partial^2 \bar{y}_1}{\partial \bar{x}^2} - \bar{y}_1 \bar{y}_2 \tag{A2a}
\]

\[
\frac{\partial \bar{y}_2}{\partial \bar{t}} = -\varepsilon \bar{y}_1 \bar{y}_2 \tag{A2b}
\]

\[
\bar{y}_1 = 1 \text{ at } \bar{x} = 0; \quad \bar{y}_1 \to 0 \text{ as } \bar{x} \to \infty \tag{A2c}
\]

\[
\bar{y}_1 = 0, \quad \bar{y}_2 = 1 \text{ at } \bar{t} = 0 \tag{A2d}
\]

The above system (A2) is well posed to solve for the unknown concentrations \( \bar{y}_1 \) and \( \bar{y}_2 \) as a function of \( \bar{x} \) and \( \bar{t} \).

In our physical configuration, the parameter \( \varepsilon \) is small, and it is natural to look for a solution via asymptotic techniques. We assume the following expansions which are valid as \( \varepsilon \to 0 \):

\[
\bar{y}_1 \sim \bar{y}_{10} + O(\varepsilon) \tag{A3a}
\]

\[
\bar{y}_2 \sim \bar{y}_{20} + \varepsilon \bar{y}_{21} + O(\varepsilon^2) \tag{A3b}
\]
Note that in (A3b), we have elected to expand $\bar{y}_2$ to a higher order than in (A3b), as we will see later on that nontrivial dependences on variables space and time variables occur at $O(\varepsilon)$; nontrivial dependences are evident to lowest order in $\bar{y}_1$ and we will only consider the lowest order in (A3a) as shown.
Substituting (A3) into the system (A2) and rearranging, the lowest order boundary value problem is given as:

$$\frac{\partial \bar{y}_{10}}{\partial \bar{t}} = \frac{\partial^2 \bar{y}_{10}}{\partial \bar{x}^2} - \bar{y}_{10}\bar{y}_{20} \quad (A4a)$$

$$\frac{\partial \bar{y}_{20}}{\partial \bar{t}} = 0 \quad (A4b)$$

$$\bar{y}_{10} = 1 \text{ at } \bar{x} = 0; \quad \bar{y}_{10} \to 0 \text{ as } \bar{x} \to \infty \quad (A4c)$$

$$\bar{y}_{10} = 0, \quad \bar{y}_{20} = 1 \text{ at } \bar{t} = 0 \quad (A4d)$$

The next order problem can be written to solve for $\bar{y}_{21}$ in (A3b) as:

$$\frac{\partial \bar{y}_{21}}{\partial \bar{t}} = -\bar{y}_{10}\bar{y}_{20} \quad (A5a)$$

$$\bar{y}_{21} = 0 \text{ at } \bar{t} = 0 \quad (A5b)$$

It is observed that the $O(\varepsilon)$ correction $\bar{y}_{21}$ is expressed solely in terms of the lowest order solutions $\bar{y}_{10}$ and $\bar{y}_{20}$.

**A-2 Asymptotic Solution**

We now solve the lowest order system (A4). After integrating (A4b) and applying the appropriate boundary condition in (A4d), we obtain:

$$\bar{y}_{20} = 1 \quad (A6a)$$

The result (A6a) is substituted into (A4a) which yields a linear equation to solve for $\bar{y}_{10}$, which is well posed to find a solution with boundary and initial conditions found in (A4c) and (A4d). The resulting equation is solved using by taking the Laplace transform in time, solving the resulting spatial differential equation in $\bar{x}$, and inverting the transform using standard techniques. The result is given as:

$$\bar{y}_{10} = \frac{1}{2}e^{-\bar{x}}\left[1 + \text{erf}\left(\sqrt{\bar{t}} - \frac{\bar{x}}{2\sqrt{\bar{t}}}\right) + e^{2\bar{x}}\text{erfc}\left(\sqrt{\bar{t}} + \frac{\bar{x}}{2\sqrt{\bar{t}}}\right)\right] \quad (A6b)$$

where $\text{erf}$ and $\text{erfc}$ are the error function and complementary error functions, respectively. The final piece of our desired solution is obtained by substituting (A6) into (A5) and integrating, to obtain:
\[ \bar{y}_{21} = - \int_{0}^{\bar{t}} \bar{y}_{10} (\bar{x}, T) dT \]  

(A6c)

In (A6c), T is a dummy variable that replaces the time dependence in (A6c) in the integrand. The final solution, then, is obtained by substituting (A6) into the original expansion (A3) to obtain:

\[ \bar{y}_1 (\bar{x}, \bar{t}) \sim \frac{1}{2} e^{-\bar{x}} \left[ 1 + \text{erf} \left( \sqrt{\bar{t}} - \frac{\bar{x}}{2\sqrt{\bar{t}}} \right) + e^{2\bar{x}} \text{erfc} \left( \sqrt{\bar{t}} + \frac{\bar{x}}{2\sqrt{\bar{t}}} \right) \right] + O(\epsilon) \text{ as } \epsilon \to 0 \]  

(A7)

\[ \bar{y}_2 \sim 1 - \epsilon \int_{0}^{\bar{t}} \bar{y}_1 (\bar{x}, T) dT + O(\epsilon^2) \text{ as } \epsilon \to 0 \]  

(A8)

This completes the desired asymptotic solution of the problem.

**A-3 Asymptotic Solution for Long Times and Large Penetration Depths**

We now consider limiting cases of the result (A7). To do so, we make use of the following standard asymptotic limits (Abramowitz and Stegun\textsuperscript{65}) for error function and complementary error functions:

\[ \text{erf}(p) \sim 1 - \frac{1}{p\sqrt{\pi}} e^{-p^2} \text{ as } p \to \infty \]  

(A9a)

\[ \text{erf}(p) \sim -1 - \frac{1}{p\sqrt{\pi}} e^{-p^2} \text{ as } p \to -\infty \]  

(A9b)

\[ \text{erfc}(p) \sim \frac{1}{p\sqrt{\pi}} e^{-p^2} \text{ as } p \to \infty \]  

(A9c)

We first consider the limit where \( \bar{x} \to \infty \) holding \( \bar{t} \) fixed, which corresponds to \( \bar{x} \gg \bar{t} \). In this limit, the error function and complementary error functions in (A7) are written according to (A9b) and (A9c) as:

\[ \text{erf} \left( \sqrt{\bar{t}} - \frac{\bar{x}}{2\sqrt{\bar{t}}} \right) \sim \text{erf} \left( \sqrt{\bar{t}} \right) \sim 1 - \frac{2}{\sqrt{\pi}} \frac{\sqrt{\bar{t}}}{\bar{x}} e^{-\bar{x}^2/(4\bar{t})} \]  

(A10a)

\[ \text{erfc} \left( \sqrt{\bar{t}} + \frac{\bar{x}}{2\sqrt{\bar{t}}} \right) \sim \text{erfc} \left( \frac{\bar{x}}{2\sqrt{\bar{t}}} \right) \sim \frac{2}{\sqrt{\pi}} \frac{\sqrt{\bar{t}}}{\bar{x}} e^{-\bar{x}^2/(4\bar{t})} \]  

(A10b)

Substituting these results into (A7) and rearranging, we obtain:

\[ \bar{y}_1 (\bar{x}, \bar{t}) \sim \frac{\sqrt{\bar{t}}}{\bar{x}\sqrt{\pi}} e^{-\bar{x}^2/(4\bar{t})} + O(\epsilon) \text{ as } \epsilon \to 0 \text{ and } \bar{x} \gg \bar{t} . \]  

(A11)

The second limit we wish to consider corresponds to \( \bar{t} \to \infty \) holding \( \bar{x} \) fixed, which corresponds to \( \bar{t} \gg \bar{x} \). In this limit, the error function and complementary error functions in (A7) are written according to (A9a) and (A9c) as:

\[ \text{erf} \left( \sqrt{\bar{t}} - \frac{\bar{x}}{2\sqrt{\bar{t}}} \right) \sim \text{erf} \left( \sqrt{\bar{t}} \right) \sim 1 - \frac{1}{\sqrt{\pi \bar{t}}} e^{-\bar{t}} \]  

(A12a)
erfc\left(\sqrt{t} + \frac{x}{2\sqrt{t}}\right) \sim \text{erfc}\left(\sqrt{\bar{t}}\right) \sim \frac{1}{\sqrt{\pi \bar{t}}} e^{-\bar{t}} \tag{A12b}

Substituting these results into (A7) and rearranging, we obtain:

\[ \bar{y}_1(\bar{x}, \bar{t}) \sim e^{-\bar{x}} + e^{-\sqrt{\bar{t}}\pi} \sinh(\bar{x}) + O(\varepsilon) \text{ as } \varepsilon \to 0 \text{ and } \bar{t} \gg \bar{x}. \tag{A13} \]

For very long times (A13) simplifies to

\[ \bar{y}_1(\bar{x}, \bar{t}) \sim e^{-\bar{x}}, \tag{A14} \]

which describes an exponentially decaying oxygen concentration profile in space.

A-4 Effect of Finite Domain

We now consider the effect of finite domain length, \( L \), on the solution to the system (A2). To do so, we replace the boundary condition in (A2c) at infinite distance with the new constraint as:

\[ \frac{\partial \bar{y}_1}{\partial \bar{x}} = 0 \text{ at } \bar{x} = \bar{L}, \text{ where } \bar{L} = L \left(\frac{k_B}{D}\right)^{1/2} \tag{A15} \]

With this adjustment, the system (A2) can be solved following the asymptotic approach in sections A-1 and A-2 above. The solution for \( \bar{y}_1 \) can be obtained via eigenfunction expansion as:

\[ \bar{y}_1(\bar{x}, \bar{t}) \sim 1 - \frac{2}{\bar{L}} \sum_{n=0}^{\infty} \frac{1}{\alpha_n (1 + \alpha_n^2)} \left(1 + \alpha_n^2 e^{-(1+\alpha_n^2)\bar{t}}\right) \sin(\alpha_n \bar{x}) + O(\varepsilon) \text{ as } \varepsilon \to 0 \tag{A16a} \]

where

\[ \alpha_n = \left(2n + 1\right) \frac{\pi}{\bar{L}} \tag{A16b} \]

The solution for \( \bar{y}_2(\bar{x}, \bar{t}) \) may be extracted by substituting equation (A16) into (A8).
References


3 Finklea, H. O. in *Semiconductor electrodes* Ch. 2, 43-145 (Elsevier, 1988).


