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Metal-to-Oxide Molar Volume Ratio: The Overlooked Barrier to Solid-State Electroreduction and a “Green” Bypass through Recyclable NH_4HCO_3**

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As early as 1923 Pilling and Bedworth reported the dependence of metal oxidation behavior on the metal-to-oxide molar volume ratio.[1a] In 1910 and 1940, respectively, Hunter and Kroll succeeded in carbochlorination of TiO_2 (rutile) to $TiCl_4$, and sodio- and magnesiothermic reduction of the chloride to titanium.[1b,c] They did not consider at all the metal-to-oxide molar volume ratio. Unfortunately, even after 60 years of research and industrial development, the Kroll process is still highly energy and carbon intensive (45–55 kWh and >2 kg CO_2 per kg Ti sponge; see Supporting Information).[1d] This makes titanium too costly to use widely, although it has very rich resources, and is ideal for making energy-saving vehicles, durable medical implants, and lightweight and corrosion-resistant off-shore wind turbines.

Alternatives to the Kroll process have long been sought.[2] In particular, the solid-state electroreduction (or electro-deoxidation) of metal oxides to the respective metals or alloys in molten salts has emerged with the merits of, for example, simple and fast operation and low energy consumption and emission.[3] In the past decade, worldwide research on this electrolytic process has shown acceptable energy consumption (e.g., 33 kWh/kg Ti), but the current efficiency is still too low (e.g., 15 %) to achieve a low O content in the produced Ti (≤ 0.3 wt% O).[4a,b] The irony is that, when the method is applied to produce Cr (< 0.2 wt% O), the current efficiency can exceed 75 %.[4c] ZrO_2 was also recently electroreduced to Zr (0.18 wt% O) at 45 % current efficiency, although Zr and Ti have many comparable properties, for example, high solubility for oxygen.[4d] Apparently, an unseen barrier remains in the electroreduction of TiO_2 to Ti. This communication identifies the metal-to-oxide molar volume ratio as an intrinsic barrier to the solid-state reduction of TiO_2 to Ti. More importantly, an effective green bypass is demonstrated through recyclable use of NH_4HCO_3 and two-voltage electrolysis.

Electroreduction of a solid oxide has been confirmed to proceed through the propagation of the metal | oxide | electrolyte three-phase interlines (3PIs), starting from the surface and then entering the oxide precursor.[3a,c,4c,5] According to the 3PI models,[6] the initially formed metal layer on the oxide surface must be sufficiently porous to allow molten salt to access the underlying oxide to form new 3PIs. Thus, the reduction-generated O^{2-} ions can diffuse through the electrolyte in the pores of the metal layer before entering the bulk electrolyte and being discharged at the anode.

Formation of the porous metal layer may be attributed to one or both of two factors. First, removal of oxygen from the solid oxide is expected to leave vacancies, and hence a porous metal. Second, when a porous oxide precursor is used, it may also benefit formation of porous metal during solid-state reduction. The latter is experimentally controllable to a certain degree, but the former could only be true if oxygen removal did not cause a decrease in atom packing density. In other words, the molar volume of the metal, $V_m = M_m/\rho_m$, should be smaller than the equivalent molar volume of its oxide, $V_o = M_o/n\rho_o$, where the subscripts m and o represent the metal and oxide, respectively, V is the molar volume, M the molar mass, ρ the density, and n the number of metal atoms in the oxide formula (e.g. $n = 1$ for TiO_2 and MgO, $n = 2$ for Cr_2O_3 and Ta_2O_5, and $n = 3$ for Fe_3O_4).

Table 1 lists the V_m/V_o ratios for some typical metals. For most metals listed (and many more unlisted), $V_m/V_o < 1$, which accounts for the success in using the electroreduction method to produce these metals. If negligible movement of metal atoms occurs with respect to the oxide precursor geometry, the V_m/V_o ratio, if smaller than unity, is the intrinsic

Table 1: Metal-to-oxide molar volume ratios (see Supporting Information).

M/ MO_x	Ta/ Ta_2O_5	Cr/ Cr_2O_3	Zr/ ZrO_2	Al/ Al_2O_3	Mg/ MgO	Ti/ TiO_2	Ti/ Ti_2O_3	Ti/ TiO
V_m/V_o	0.40	0.50	0.66	0.78	**1.25**	0.63	0.74	0.91

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porosity or maximum porosity achievable in the reduction-generated metal layer on the oxide surface, which differs from the overall porosity of the oxide precursor.

If $V_m/V_o \geq 1$, the metal layer on the oxide surface would be nonporous. There are three possible consequences. Firstly, if O is insoluble in the metal, electroreduction would cease once the oxide is fully covered by the metal layer. This prediction is in agreement with the facts that 1) the V_m/V_o ratio for Mg/MgO is larger than unity, as shown in Table 1, and 2) there have not yet been any reports on successful solid-state reduction of MgO to pure Mg.[7a] Secondly, the V_m/V_o ratio is sufficiently smaller than unity for Ti/TiO$_2$, but very close to unity for Ti/TiO (see Supporting Information). TiO has been identified as the later intermediate phase in the electroreduction of TiO$_2$.[4a,b] Thus, the reduction of TiO to Ti must be kinetically difficult because the intrinsic porosity of the Ti metal layer on TiO is too small, particularly considering the inevitable sintering of the metal at high temperatures. However, unlike Mg, Ti can dissolve O to form solid solutions. The mobility of dissolved O also increases with increasing temperature. Thus, reduction of the remaining TiO can proceed via O diffusion through the metal layer, in agreement with electrodeoxygenation of titanium metal in molten CaCl$_2$.[7b,c] Finally, the V_m/V_o ratio would be of no or little relevance if the metal phase disintegrates from, or grows in such a way as to allow continuous electrolyte access to the oxide base, although these mechanisms are yet to be verified for $V_m/V_o \geq 1$.

Oxygen diffusion through the electroreduction-generated titanium layer may be compared with some solid-state reactions, such as the electrochemistry of hexacyanometalates[7d] in which the product and the reactant form various solid solutions through diffusion. In such cases, even if the product-to-reactant molar volume ratio is close to or greater than unity, its retarding effect is compromised to a certain degree. However, diffusion in a solid is generally much slower than in a liquid.

While it is unlikely to alter the O diffusion rate within the metal layer at a given temperature, the overall rate of O removal from TiO should increase on enlarging the metal/electrolyte interface. This can be assisted by increasing the porosity of the oxide precursor, which is 40–50% for TiO$_2$ pellets prepared by pressing or slip casting. Porosity higher than 75% is achievable by using a fugitive agent, for example, graphite or polymer powder, which can be burnt out from the precursor during sintering in air at elevated temperatures.[8a] This approach, however, increases cost and CO$_2$ emission. CaO (or CaCO$_3$ which is converted to CaO on heating) may be added to the precursor and then dissolve in molten CaCl$_2$ to increase the precursor porosity in situ,[4a,8b] but accumulation of CaO in the molten salt is detrimental to electrolysis.

In this work, the use of NH$_4$HCO$_3$ as a recyclable and cheap fugitive agent was investigated for the preparation of high-porosity TiO$_2$ precursors (pellets), with the aim of bypassing the intrinsic barrier of the V_m/V_o ratio to the electroreduction of TiO$_2$ to Ti. NH$_4$HCO$_3$ decomposes to NH$_3$, CO$_2$, and H$_2$O at temperatures above 86 °C at 1 atm, and can reform from NH$_3$, CO$_2$, and H$_2$O at lower temperatures.[9] For confirmation, TiO$_2$ (1.0 g) and NH$_4$HCO$_3$ (0.5–1.5 g) powders were mixed and die-pressed (20 mm die, 4–8 MPa) into cylindrical pellets, and then placed at the bottom of a long quartz tube (see Supporting Information). The tube was sealed with a rubber balloon, and then heated over an alcohol burner (see Supporting Information). The heating caused expansion of the balloon, indicative of gas production. Crystals were seen on the unheated parts of the internal wall of the tube, and in the balloon after cooling. The weight of the collected crystals reached 97% of that of NH$_4$HCO$_3$ in the pellet, which confirms very high recyclability. The TiO$_2$ pellets recovered from the test tube were then sintered at 900 °C for 2 h to give various porosities (> 50%). For comparison, low-porosity (< 50%) pellets were prepared by sintering die-pressed (8 MPa) TiO$_2$ pellets at high temperatures (900–1300 °C; see Supporting Information).

The sintered TiO$_2$ pellets were electrolyzed in molten CaCl$_2$ under different conditions. Figure 1 a shows the XRD

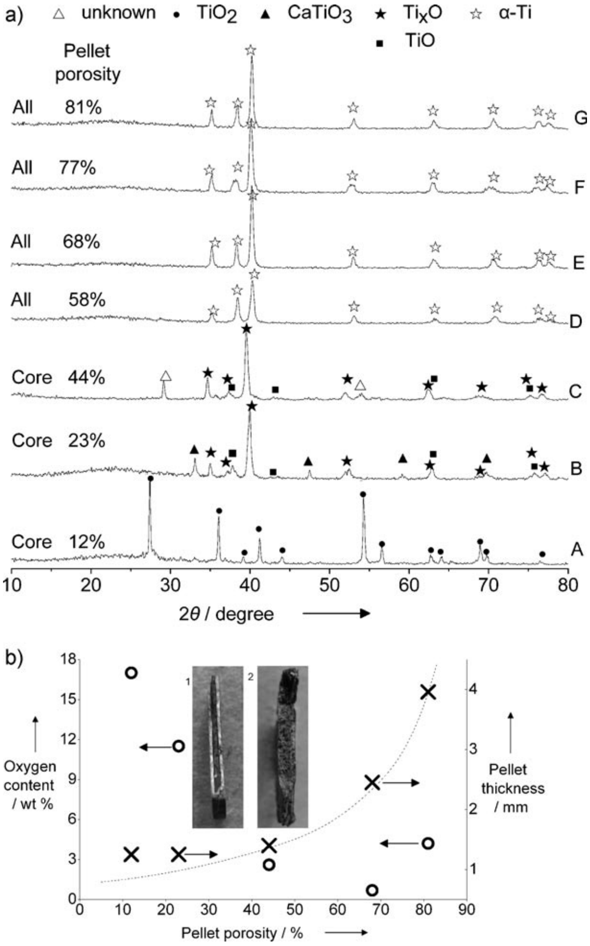

Figure 1. a) XRD patterns of products from electrolysis of 1.0 g TiO$_2$ pellets of indicated porosities in molten CaCl$_2$ at 3.1 V and 850 °C for 3 h. b) Variations of measured (×) and calculated (-----, no radial shrinkage) thickness of the TiO$_2$ pellet, and the measured overall oxygen content (○) in product from electrolysis at 3.2 V for 3 h or 5 h for low-porosity (< 50%) pellets versus pellet porosity. (cf. TiO contains 25.04 wt% O.) Photos in b) show pellets of 1) 23% porosity electrolyzed at 3.2 V for 5 h, which have an unreduced core and a dense surface Ti layer, and 2) 68% porosity electrolyzed at 3.2 V for 3 h (see Supporting Information).

patterns of the products from electrolysis at 3.1 V for 3 h. Incomplete reduction of low-porosity pellets is in line with O diffusion being difficult when fewer pores are present in the pellet. As shown in Figure 1 b, with increasing TiO_2 pellet porosity, the O content in the product decreases to a minimum at a pellet porosity of 68 % (pattern E in Figure 1 a). The slightly higher O content at higher porosities is explainable. When the mass and diameter are fixed, the thickness of the cylindrical pellet increases with increasing porosity, and this is more significant at high porosities, as shown in Figure 1 b. Thus, O diffusion through the pores takes longer, and more O is in the product when the same electrolysis time is applied.[8a] Note that Figure 1 b shows discrepancies at low porosities between the measured and calculated pellet thicknesses. This is due to the radial shrinkage of the low-porosity TiO_2 pellets after sintering at 1100–1300 °C, which was not considered in the calculation.

After 3 h of electrolysis at 3.1 V, the products from the low-porosity pellets (< 50 %) always showed an unreduced core enclosed in a Ti layer (inset of Figure 1 b).[4a,5b] The core varied in composition from TiO_2 (12 % porosity, pattern A in Figure 1 a), through $Ca_\delta TiO_x$ ($x/\delta \geq 2$, 23 % porosity, pattern B), and then to mixed TiO and Ti_xO (B and C). The $Ca_\delta TiO_x$ or perovskite phase, previously identified as a kinetic barrier,[4a] was detected in the sample with 23 % porosity (pattern B). On intensifying the reduction by electrolysis at 3.2 V for 5 h, the product was still mixed TiO and/or Ti_xO (see Supporting Information). The amount of the metallic pseudo-oxide phases Ti_xO ($x \geq 2$)[7c] increases at the expense of TiO when the porosity increases to 44 %, which suggests the reaction $(x-1)\,Ti + TiO \rightarrow Ti_xO$ or $x\,TiO + 2(x-1)\,e \rightarrow Ti_xO + (x-1)\,O^{2-}$. On the contrary, all of these intermediate phases were absent in the high-porosity samples after 3 h of electrolysis. Thus, these findings are strong evidence for the reduction of TiO to Ti being another kinetically slow step, whose influence, however, can be mitigated by increasing the pellet porosity.

In line with previous findings,[4–7] the O content in the final product decreased with both increasing electrolysis time and cell voltage, but to the detriment of current efficiency. Table 2 compares the data from electrolysis of TiO_2 pellets with optimal porosity of 68 %. In addition to kinetics, the efficiency decay is related to direct electron conduction through molten $CaCl_2$.[10] This effect may be reduced to a certain degree by a diaphragm or chemical means (see Supporting Information),[11] but improvement without altering the existing simple cell configuration and process operation would be welcome.

Table 2: Product oxygen content and process efficiency for electrolysis of TiO_2 pellet (68 % porosity, 1.0 g) at 850 °C.

Electrolysis conditions	Oxygen content [wt %]	Current efficiency [%]	Energy consumption [kWh (kg Ti)$^{-1}$]
3.0 V, 3 h	1.45	54.4	12.3
3.2 V, 3 h	0.68[a]	36.3	19.2
3.2 V, 5 h	0.39	28.7	24.9
3.2 V, 3 h + 2.6 V, 3 h	0.19	32.3	21.5

[a] Average of five analyses with maximum error of ± 0.35.

Titanium and its alloys are highly resistive to corrosion due to a 2–4 nm thick and naturally formed dense surface oxide layer, which, however, can be an important origin of O in small Ti particles. After washing in water and drying in air, the O content in the product from electrolysis of TiO_2 pellets of 68 % porosity at 3.2 V for 5 h was determined to be 0.39 wt % by inert-gas fusion oxygen analysis (LECO; see Supporting Information). If this O content were solely from a 3 nm-thick surface TiO_2 layer on Ti spheres, the diameter would be about 2 μm, which agrees broadly with the nodule sizes in the SEM image in Figure 2 a (see Supporting Information). It is thus likely that at the end of electrolysis, the metallized pellet contained very little oxygen, if not zero.[7b,c] Similarity can be found in previous work on Ta_2O_5 and Nb_2O_5 with HRTEM evidence.[3d,e]

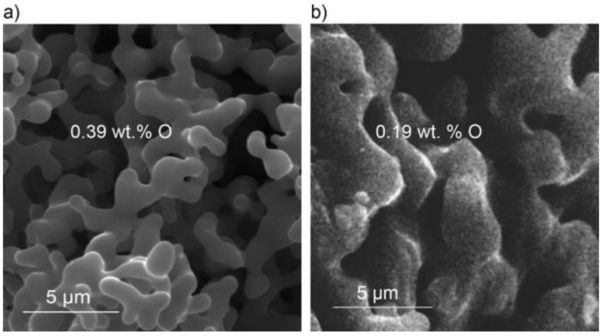

Figure 2. SEM images of products from electrolysis of TiO_2 pellets of 68 % porosity. a) 3.2 V, 5 h. b) 3.2 V, 3 h + 2.6 V, 3 h.

Clearly, the micrometer-sized nodules in Figure 2 a are far larger than what would be expected from electroreduction of the submicrometer TiO_2 powder, apparently due to sintering. According to Table 2, the O content of the product from electrolysis under the same conditions for 3 h was 0.68 wt %, corresponding to a particle size of about 1 μm, that is, the particle size grew by a factor of about two in the additional 2 h of electrolysis at 3.2 V. This suggests that the additional 2 h of electrolysis may have not contributed significantly to further O removal, but mostly to growth of the particles. To further confirm this postulate, electrolysis was carried out for 3 h at 3.2 V, and then for 3 h at 2.6 V. The thermodynamic decomposition voltages of CaO and TiO at 850 °C are 2.680 and 2.254 V, respectively.[9b] Thus, the additional time of electrolysis at 2.6 V would not contribute very much to O removal, but could prevent re-oxidation of the Ti metal at the cathode, and encourage more sintering.

During electrolysis, it was observed that when the voltage changed from 3.2 to 2.6 V, the current dropped from 0.7 to 0.2 A, and was stable in the remaining time of electrolysis (see Supporting Information). The benefits are increased current efficiency and decreased energy consumption, as shown in Table 2. The measured O content of 0.19 wt % in the product corresponds to particle sizes larger than 4 μm, which compare well with the SEM image in Figure 2 b, which shows both significant growth and sintering of the nodular particles. The current efficiency, energy consumption, and O content in the product from the two-voltage electrolysis listed in Table 2 are the best results among all reported studies on solid-state electroreduction of TiO_2 to Ti in $CaCl_2$ based molten salts.

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