Electrolytic Reduction of Titanium Dioxide in Molten LiCl–Li₂O

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Abstract: The electrolytic reduction of TiO₂ in LiCl–Li₂O (1 wt.%) at 650 °C was investigated under a series of cathodic reduction potentials and applied charges to provide a mechanistic understanding of the electrochemical characteristics of the system. The optimal cathodic reduction potential was determined as being −0.3 V vs. Li/Li⁺. Li₂TiO₃ and LiTiO₂ were structurally identified as intermediate and partial reduction products of the TiO₂ electrolytic reduction. The reduction of LiTiO₂ was extremely slow and reversible due to its high stability and the detrimental effect of Li₂O accumulation within the solid particles. The most reduced product obtained in this study was LiTiO₂, which was achieved when using 150% of the theoretical charge under the optimal reduction potential. The highest reduction extent obtained in this study was 25%. Based on theoretical DFT modeling, a detailed multistep reduction mechanism and scheme were proposed for TiO₂ electrolytic reduction in LiCl–Li₂O (1 wt.%) at 650 °C.

Keywords: cathodic reduction; titanium dioxide; lithiothermic reduction; reduction mechanism; lithium titanate

1. Introduction

Titanates and titanium metal are valuable for batteries, coatings, and structural material applications [1–4]. Electrolytic reduction is a promising way for Ti metal and intermediates production directly from solid titanium dioxide through molten salt electrolysis. It has attracted extensive research effort that involves using various salt systems under various conditions with different setups [5–9]. The Fray–Farthing–Chen (FFC) Cambridge and calciothermic Ono–Suzuki (OS) processes are the two most well-studied processes utilizing CaCl₂ (melting point 772 °C) as electrolytes for electrolytic reduction between 850 and 950 °C. As an alternative electrolyte, LiCl can significantly decrease the reduction temperature to 650 °C for the electrolytic reduction of metal oxides due to its lower melting point [10–12]. The FFC process presumes that TiO₂ is reduced directly in CaCl₂ via electrons through multiple titanate intermediates, including CaTiO₃ and CaTi₂O₄, as well as titanium suboxides (TiOₓ, x < 2) [13–16]. Through the OS process, TiO₂ is reduced using in-situ-generated calcium metal from the CaCl₂ electrolyte at an overpotential when the applied potential is higher than the electrolyte decomposition potential [7–9,17,18]. Similarly, the reduction of TiO₂ in LiCl leads to the formation of lithium titanates, including Li₂TiO₃ and Li₂TiO₄ when the reduction potential is lower than the LiCl decomposition potential, that is, an underpotential. The complete reduction of TiO₂ to Ti is obtained at high cell potentials [10,19,20]. Regarding the electrolytic reduction of TiO₂ in molten LiCl–Li₂O, the oxides Li₂TiO₄, LiTiO₂, and suboxides have been identified using XRD and TEM under various temperatures and potentials (Table 1) [10,19–21]. Li₂TiO₃ was reported based on cyclic voltammetry (CV) results.
Table 1. Electrolytic reduction products for TiO$_2$ in LiCl salts.

| Reference | Temperature | Reduction Conditions | Products | Characterization |
|-----------|-------------|----------------------|----------|------------------|
| [19]      | 700 °C      | TiO$_2$ pellets, cell potentials 1.8 V and 3.2 V | Li$_2$TiO$_4$, LiTIO$_2$ | ICP, XRD, and TEM |
| [20]      | 650 °C      | TiO$_2$ powder, constant current at 1.2 A, cell potential 2.7 V | Li$_2$TiO$_4$, LiTIO$_2$, Ti | XRD and SEM |
| [10]      | 650 °C      | TiO$_2$ powder, cell potential 3.0 V | LiTIO$_2$, TiO, Ti$_2$O, Ti | XRD and SEM |
| [21]      | 850 °C      | Thin TiO$_2$ film, 0 to −2.0 V vs. Ni/NiO | Li$_2$TiO$_3$, TiO, Ti$_3$O$_5$, Ti$_2$O$_3$, Ti | CV |

However, the TiO$_2$ reduction mechanism in LiCl is not as well understood as in CaCl$_2$. The reduction pathways and mechanism of TiO$_2$ in LiCl have mostly been studied using two-electrode electrochemical cells. It is unclear whether the underpotential (lower than the electrolyte decomposition potential) or overpotential electrolytic reduction was employed under these conditions [10,22,23]. To elucidate the TiO$_2$ electrolytic reduction mechanism in LiCl, this work systematically investigated the electrolytic reduction of TiO$_2$ in LiCl–Li$_2$O (1 wt.%) at 650 °C using a three-electrode electrolysis cell by directly controlling the cathodic reduction potential under a series of applied charges. Reduction intermediates and products were analyzed and quantified using X-ray diffraction (XRD) with Rietveld refinement analysis. The CV and chronomperometry techniques, combined with density functional theory (DFT) calculations, were employed to obtain a detailed understanding of the TiO$_2$ reduction characteristics and mechanisms in the LiCl–Li$_2$O system.

2. Materials and Methods

A molten salt mixture, namely, LiCl–Li$_2$O (1 wt.%), for TiO$_2$ electrolytic reduction was made of ultra-high-grade lithium chloride (LiCl, 99.995% metals basis, ultra-dry, Alfa Aesar, Tewksbury, MA, USA) and lithium oxide (Li$_2$O, 99.5%, Alfa Aesar), which was used as received. Titanium dioxide powders (Rutile TiO$_2$, 99.995% metals basis, Alfa Aesar) were pelletized, grounded, and sieved between mesh 60 and 20 (particle sizes 0.25~0.85 mm). A total of 2.0 g of TiO$_2$ pellets were loaded in a basket for each TiO$_2$ reduction run immersed in a 150 g electrolyte salt bath at 650 °C.

A three-electrode electrochemical cell located in an argon glovebox (MBraun, Labmaster 200G, Stratham, NH, USA) with controlled moisture and oxygen levels (<1 ppm) was used for the electrochemical measurement and TiO$_2$ electrolytic reductions. The three-electrode electrochemical cell was composed of a working electrode, a Ni/NiO reference electrode, and a glassy carbon crucible, which was also used as the counter electrode (HTW GAZ30). VersaSTAT 4 Potentiostat (Princeton Applied Research, Oak Ridge, TN, USA), which interfaced with the glovebox, was employed for the electrochemistry measurement and electrolysis up to 2 amps using VersaStudio for controlling the parameters and for data acquisition. A Kerrlab electric furnace (Auto Electro Melt Maxi, Orange, CA, USA) was used to keep the electrolyte salt bath at 650 °C. This three-electrode electrochemical cell setup has shown high efficiency and reliability in a previous study for NiO electrolytic reduction [24].

Cyclic voltammetry (CV) was measured in the LiCl–Li$_2$O (1 wt.%) salts at 650 °C to determine the Li deposition potential ($E_{Li/Li^+}$) at a scan rate of 20 mV s$^{-1}$ using a Ni/NiO reference electrode and a 0.64 mm diameter stainless steel wire as the working electrode. A cathode basket assembly described in a previous work was used for the TiO$_2$ electrolytic reductions [24]. Briefly, the cathode basket assembly included a 1.59 mm diameter stainless steel rod as an electron collector and a stainless-steel cathode basket (height: 2.5 cm, diameter: 1 cm) made of double layers of 100 mesh stainless steel wire cloth, and the TiO$_2$ pellets were loaded and packed around the electron collector. The whole electrode assembly was soaked in the molten salt for 1~1.5 h before the electrolytic reduction started. Various cathodic reduction potentials, including −0.2 V, −0.3 V, and −0.4 V vs. Li/Li$^+$ were
applied on TiO$_2$, respectively, using 80% of the theoretical charge (i.e., the theoretical charge for the complete reduction of TiO$_2$ to Ti). The constant reduction potential was applied at an interval mode (the cell spent 8 min on and 2 min off) to minimize the excessive lithium metal generated on the working electrode. Higher theoretical charges, namely 130% and 150%, were also investigated for the TiO$_2$ reduction at the optimal potential, which was determined as being $-0.3$ V vs. Li/Li$^+$ in this study for further investigation. After the TiO$_2$ reductions, the electrode bundles were lifted out of the molten salt and cooled down to room temperature for further treatment and product analysis. To determine the starting composition for the electrolytic reduction, a soaking test was performed by immersing the TiO$_2$ in the LiCl–Li$_2$O (1 wt.%) salt at 650 °C for 5 h without electrolysis.

The cooled cathode basket assemblies were transferred out of the glovebox and rinsed with nanopure water to remove the extra LiCl–Li$_2$O salts. Then, the samples were retrieved out of the basket and rinsed in acetone for a quick dry. After that, the samples were kept vacuum dried at room temperature overnight. The completely dried samples were ground into fine powders using a pestle and mortar for the X-ray diffraction analysis (Rigaku SmartLab XRD, Wilmington, MA, USA, Cu Kα radiation at 40 kV and 30 mA). The scan range ($2\theta$) was from 10° to 80° at 4 deg min$^{-1}$. The XRD data were analyzed with Rietveld refinement using WPPF (whole powder pattern fitting) within PDXL 2 (Rigaku) for quantitative compositional analysis.

In this study, reduction intermediates, including Li$_2$TiO$_3$ and LiTiO$_2$, were identified and quantified, but LiTiO$_2$ was the only partial reduction product for TiO$_2$. Theoretically, the charge transfer for the reduction of TiO$_2$ to LiTiO$_2$ is 1, while the charge transfer for the reduction of TiO$_2$ to Ti is 4. The reduction extent of TiO$_2$ is defined as given in Equation (1):

$$\text{Reduction extent} = \frac{\frac{1}{4} \times m_{\text{LiTiO}_2}}{m_{\text{TiO}_2} + m_{\text{Li}_2\text{TiO}_3} + m_{\text{LiTiO}_2}} \times 100\% \quad (1)$$

The total applied charge is represented as a percentage of the theoretical charge, which for the complete reduction of TiO$_2$ to Ti metal is given as Equation (2):

$$\text{Theoretical charge} = 4m_{\text{TiO}_2}F \quad (2)$$

where $m$ is the number of moles of TiO$_2$, and $F$ is the Faraday constant (96,485 C mol$^{-1}$).

The Cottrell equation was employed to estimate the oxygen ion diffusion coefficients ($D$) during the TiO$_2$ electrolytic reduction using the chronoamperometry technique. The oxygen ion diffusion coefficients were calculated based on the I(t) data fit using Equation (3):

$$I(t) = \frac{nFA D^{1/2}}{\pi^{1/2}} C_0 \frac{1}{t^{1/2}} \quad (3)$$

where $I$ is the decay current during the cell-on interval, $n$ is the number of electrons transferred ($n = 2$), $A$ is the surface area of the working electrode, $C_0$ is the initial concentration of oxygen ions, and $t$ is the time in seconds.

3. Density Function Theory Modeling

Density function theory (DFT) modeling provides theoretical understanding that can be used to determine the TiO$_2$ reduction pathway and mechanism. Vienna Ab Initio Simulation Package (VASP) (Vienna, Austria) was used for the DFT calculation [25]. The Gibbs free energy of formation for titanate intermediates, such as Li$_2$TiO$_3$ and LiTiO$_2$, were calculated. The calculations of the total energies and structural relaxations were carried out using the projector augmented wave (PAW) method to model the core electrons (see the Supplementary Materials) [26]. The Helmholtz free energy, $F(V,T)$, which is a function of both crystal volume ($V$) and temperature ($T$), can be expressed using Equation (4):

$$F(V,T) = E(V) + F_{\text{ vib}}(V,T) + F_{\text{ el}}(V,T) \quad (4)$$
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. The \( E(V) \) of a given crystal can be described using the equation of state (EOS), and its values at different volumes were directly obtained from periodic DFT calculations. Here, the fourth-order Birch–Murnaghan (BM4) EOS, as expressed by Equation (5), was used:

\[
E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2}
\]  

(5)

4. Results and Discussion

4.1. Soaking Test for TiO\(_2\)

Soaking is a routine step for the electrolytic reduction of metal oxides and spent oxide fuels, which allows time for the system to reach stability and for salts to diffuse into the metal oxides matrix before the lithium metal is formed [11,27,28]. The soaked TiO\(_2\) sample in LiCl–Li\(_2\)O (1 wt.\%) at 650 \(^\circ\)C without electrolysis consisted of three phases, namely, 60.8 wt.% of TiO\(_2\), 38 wt.% of Li\(_2\)TiO\(_3\), and 1.2 wt.% of Li\(_{0.54}\)Ti\(_{2.86}\)O\(_6\), based on the XRD analysis (Figure 1). The Li\(_2\)TiO\(_3\) must be formed chemically via the insertion of Li\(_2\)O into TiO\(_2\) on the surface of TiO\(_2\) particles through Equation (6), which is analogous to the formation of perovskite CaTiO\(_3\) during the TiO\(_2\) reduction in calcium salt melt systems [13–15,23]. However, the formation of Li\(_2\)TiO\(_3\) is spontaneous in LiCl–Li\(_2\)O (1 wt.\%) at 650 \(^\circ\)C, while the formation of CaTiO\(_3\) is slow and regarded as the rate-limiting step for the FFC process [6].

**Figure 1.** XRD for fresh TiO\(_2\) (rutile) and soaked TiO\(_2\) in molten LiCl–Li\(_2\)O (1 wt.\%) for 5 h at 650 \(^\circ\)C (blue solid lines) and Rietveld refinement fittings (red dash lines, with rutile TiO\(_2\), Li\(_2\)TiO\(_3\), and Li\(_{0.54}\)Ti\(_{2.86}\)O\(_6\)).

A total of 60.8 wt.% of TiO\(_2\) remained after 5 h of soaking, which suggested that the diffusion of Li\(^+\) and O\(^{2-}\) ions through the increasing thickness of the Li\(_2\)TiO\(_3\) layer had slowed down. The minor Li\(_{0.54}\)Ti\(_{2.86}\)O\(_6\) phase also indicated that Li\(_2\)O non-stoichiometrically reacted with the bulk TiO\(_2\) phase, possibly because only a very small portion of the Li\(_2\)O reached the fresh TiO\(_2\) core due to the slow diffusion through the surface of the Li\(_2\)TiO\(_3\) layer. This was the first time that the Li\(_2\)TiO\(_3\) phase was structurally identified for the TiO\(_2\) electrolytic reduction in LiCl salts, which was previously reported only based on the CV measurement of TiO\(_2\) in molten LiCl (Table 1) [21].

4.2. Effect of the Reduction Potential on the Electrolytic TiO\(_2\) Reduction

To understand the effect of the reduction potential on the TiO\(_2\) electrolytic reduction, various cathodic potentials that were controlled directly using the reference electrode were applied for the TiO\(_2\) reduction in LiCl–Li\(_2\)O (1 wt.\%) at 650 \(^\circ\)C using 80% of the theoretical charge. The lithium deposition potential was determined at −1.75 V vs. Ni/NiO, as discussed in a previous study [24]. Figure 2a shows the XRD results with Rietveld refinement analysis for TiO\(_2\) electrolytic reductions at cathodic potentials of −0.2 V, −0.3 V, and −0.4 V vs. Li/Li\(^+\). For all three reduced samples, three phases were identified, including unreacted TiO\(_2\), Li\(_2\)TiO\(_3\), and LiTiO\(_2\) compared with the standard XRDs (Figure 2a). No other reduced
product or metallic Ti was detected. Lithium titanates, including \( \text{LiTiO}_2 \) and \( \text{Li}_2\text{TiO}_4 \), were reported for the \( \text{TiO}_2 \) electrolytic reduction in LiCl salts under various conditions, but no \( \text{Li}_2\text{TiO}_3 \) was formed in this study [10,19–21]. The quantitative compositional results based on the Rietveld refinement analysis for the three samples reduced at different cathodic potentials were compared with the soaked only \( \text{TiO}_2 \) sample (Figure 2b). Compared with the soaked only \( \text{TiO}_2 \) sample, the unreacted \( \text{TiO}_2 \) content at \(-0.2\) V decreased from 60.8 to 14.5 wt.% while \( \text{Li}_2\text{TiO}_3 \) remained at a similar level around 35.7 wt.%. The partial reduction product \( \text{LiTiO}_2 \) accounted for 49.8 wt.%. These results indicate that \( \text{TiO}_2 \) may have been directly reduced to \( \text{LiTiO}_2 \) by the in-situ-generated Li metal at \(-0.2\) V vs. Li/Li\(^+\) (Equation (7)).

![Figure 2](image)

Figure 2. (a) XRD results (blue solid lines) and Rietveld refinement analysis (red dash lines) of the reduced \( \text{TiO}_2 \) samples at \(-0.2\) V, \(-0.3\) V, and \(-0.4\) V vs. Li/Li\(^+\) with 80% of the theoretical charge; (b) reduced sample compositions and reduction extents for the \( \text{TiO}_2 \) reductions at \(-0.2\) V, \(-0.3\) V, and \(-0.4\) V vs. Li/Li\(^+\).

The \( \text{TiO}_2 \) content further decreased to 1.69 wt.% at \(-0.3\) V, which lay under the XRD detection limit (~2%). The \( \text{Li}_2\text{TiO}_3 \) decreased from 35.7 to 28.3%, while the partial reduction product, \( \text{LiTiO}_2 \), increased from 49.8 to 70.4%. This suggested that both \( \text{Li}_2\text{TiO}_3 \) and \( \text{TiO}_2 \) were transformed into \( \text{LiTiO}_2 \) at a higher reduction potential (Equation (8)) and \( \text{TiO}_2 \) was more reducible than \( \text{Li}_2\text{TiO}_3 \). The reduction of \( \text{Li}_2\text{TiO}_3 \) to \( \text{LiTiO}_2 \) is a reversible reaction [29,30]. As the cathodic reduction potential further increased to \(-0.4\) V vs. Li/Li\(^+\), \( \text{LiTiO}_2 \) stayed almost the same, while both \( \text{TiO}_2 \) and \( \text{Li}_2\text{TiO}_3 \) only changed slightly within the XRD limit.

Increasing the cathodic reduction potential could promote the \( \text{TiO}_2 \) electrolytic reduction to \( \text{LiTiO}_2 \) to a certain extent, then it started to reduce the current efficiency. A previous study also showed that a high Li metal concentration impeded the \( \text{O}^{2-} \) diffusion and led to a lower reduction extent of \( \text{Ti}^{4+} \) [31]. A similar trend was also observed in CaO/CaCl\(_2\) for the \( \text{TiO}_2 \) electrolytic reduction [13]. In this study, the highest achieved \( \text{TiO}_2 \) reduction extent was 18.6% at \(-0.3\) V vs. Li/Li\(^+\) using 80% of the theoretical charge (Figure 2b). The optimal reduction potential for \( \text{TiO}_2 \) reduction in the LiCl–Li\(_2\)O (1 wt.%) salt was determined as being \(-0.3\) V vs. Li/Li\(^+\).

The \( I(t) \) curves for the \( \text{TiO}_2 \) reduction at all three cathodic reduction potentials showed a similar three-stage pattern, namely, a sharp current peak in the very beginning (<20 min), a current decrease, and a steady state remaining between 0.4 and 0.6 A (Figure 3). The \( I(t) \) curves for the \( \text{TiO}_2 \) electrolytic reduction were significantly different from the \( I(t) \) curves for the \( \text{NiO} \) and \( \text{Cr}_2\text{O}_3 \) reductions, which showed high current plateaus for an extended time until the reduction finished [24,32,33]. The same interval operation mode was used in our previous NiO study to prevent the excessive accumulation of in-situ-generated Li metal [24]. The overall current magnitude increased when the reduction potential increased from \(-0.2\) to \(-0.4\) V (vs. Li/Li\(^+\)), which decreased the experimental time for completing
80% of the theoretical charge for 2 g TiO\textsubscript{2} from 6.5 to 5 h. The FFC process of TiO\textsubscript{2} reduction also produced a similar I(t) profile \cite{14,34}. The first stage of the current increase was attributed to the transformation of the insulator TiO\textsubscript{2} to lithium titanate LiTiO\textsubscript{2}, which has a conductivity of 0.5 S cm\textsuperscript{-1} \cite{35}. According to the three-phase interlines (three PIs) reaction mechanism, the conductive LiTiO\textsubscript{2}, insulator TiO\textsubscript{2}, and electrolyte LiCl can form three PIs \cite{36–38}. As the three PIs expanded from contacting points to a large area, the charge transfer reactions occurring at the three PIs led to an increasing current flow \cite{36}. With more LiTiO\textsubscript{2} generated, the interline moved inward to the inside of the TiO\textsubscript{2} core. The longer diffusion distance for the three PIs resulted in a sharp current decrease at the beginning of the second stage (Figure 3). When the current continued to decrease at a slower rate, the Li\textsubscript{2}TiO\textsubscript{3} shell started being reduced to the more conductive LiTiO\textsubscript{2} and three new PIs of LiTiO\textsubscript{2} | Li\textsubscript{2}TiO\textsubscript{3} | electrolyte were formed. The continuous propagation of the three newly formed three PIs increased the material transfer distance, leading to the continuously decreasing current. The following stage varied little with time (around 0.4 A), indicating that either the reaction at the three PIs was limited by the slow diffusion of reactive species or it had reached equilibrium. For the TiO\textsubscript{2} electrolytic reduction at \(-0.2\) V vs. Li/Li\textsuperscript{+}, the final product still contained TiO\textsubscript{2}, while the Li\textsubscript{2}TiO\textsubscript{3} remained the same, suggesting that the final charge transfer was more relevant with reactions at the three PIs of LiTiO\textsubscript{2} | TiO\textsubscript{2} | electrolyte, where the O\textsuperscript{2–} diffusion coefficient was estimated as being \(1.12 \times 10^{-5}\) cm\textsuperscript{2} s\textsuperscript{-1}. At \(-0.3\) V and \(-0.4\) V vs. Li/Li\textsuperscript{+}, the reaction stopped at the reduction of Li\textsubscript{2}TiO\textsubscript{3} at the three PIs of LiTiO\textsubscript{2} | Li\textsubscript{2}TiO\textsubscript{3} | electrolyte, where the O\textsuperscript{2–} diffusion coefficients were estimated as being \(1.46 \times 10^{-6}\) cm\textsuperscript{2} s\textsuperscript{-1} and \(1.68 \times 10^{-5}\) cm\textsuperscript{2} s\textsuperscript{-1}, respectively \cite{21,36–38}. The I(t) curves of the TiO\textsubscript{2} reduction were a clear indication of the multistep reaction mechanism, which was limited by the O\textsuperscript{2–} diffusion from the three PIs to the bulk salts \cite{13,15}.

![Figure 3](image)

**Figure 3.** Current–time profiles for the 2 g TiO\textsubscript{2} reductions at cathodic reduction potentials of \(-0.2\) V, \(-0.3\) V, and \(-0.4\) V vs. Li/Li\textsuperscript{+} with intervals using 80% of the theoretical charge.

4.3. **Effect of the Applied Charges on the TiO\textsubscript{2} Reductions at \(-0.3\) V vs. Li/Li\textsuperscript{+}**

Using 80% of the theoretical charge only led to an 18.6% reduction of TiO\textsubscript{2}. Thus, further investigation was carried out for TiO\textsubscript{2} electrolytic reductions by employing increased charges, namely 130% and 150% of the theoretical charge, at the optimal cathodic potential, namely, \(-0.3\) V vs. Li/Li\textsuperscript{+}.

The XRD analysis showed that no metallic Ti was formed for the TiO\textsubscript{2} electrolytic reduction when using 130% and 150% of the theoretical charge at \(-0.3\) V vs. Li/Li\textsuperscript{+} (Figure 4a). The TiO\textsubscript{2} reduction extent increased from 22.3 to 25% when using 130% and 150% of the theoretical charge, respectively; meanwhile, the 13.4 wt.% of Li\textsubscript{2}TiO\textsubscript{3} was completely converted to LiTiO\textsubscript{2} (Figure 4b). The 28.3 wt.% of Li\textsubscript{2}TiO\textsubscript{3} remained under 80% of the theoretical charge and required 70% more of the theoretical charge to be reduced completely to LiTiO\textsubscript{2}, suggesting the passivation behavior and stability of Li\textsubscript{2}TiO\textsubscript{3}. 
Furthermore, the formation of Li$_2$TiO$_3$ in the soaking stage may have slowed down the reduction process in several ways: (1) Li$_2$TiO$_3$ slowed down the outward diffusion of O$^{2-}$ and (2) the reduction of Li$_2$TiO$_3$ was a reversible process, which could be controlled by the O$^{2-}$ concentration [21,39].

![Figure 4](image_url)

Figure 4. (a) XRD results (blue solid lines) and Rietveld refinement analysis (red dash lines) of the reduced TiO$_2$ samples at $-0.3$ V vs. Li/Li$^+$ using 80%, 130%, and 150% of the theoretical charge; (b) reduced sample compositions and reduction extents for the TiO$_2$ reductions at $-0.3$ V vs. Li/Li$^+$ using 80%, 130%, and 150% of the theoretical charge.

These results show that the TiO$_2$ electrolytic reduction was very refractory, with LiTiO$_2$ being the most reduced product using 150% of the theoretical charge within 9 h, which was most likely due to the stability of Li$_2$TiO$_3$ and LiTiO$_2$. The sample geometry played an important role, as the adverse effect of Li$_2$TiO$_3$ and LiTiO$_2$ on the TiO$_2$ reduction is less pronounced in thin-film and fine powder TiO$_2$ [10,32]. The FFC process also shows that the electrolytic reduction of TiO$_2$ in CaCl$_2$ was challenging with a current efficiency that was typically less than 20%, although the much higher temperatures are more kinetically favorable for electrolytic reduction [40]. For the FFC process, the major products obtained within 8 h were a mixture of TiO, CaTiO$_3$, and CaTi$_2$O$_4$, and it took 120 h to completely reduce 8 g TiO$_2$ to Ti in CaO/CaCl$_2$ at 900 °C [14]. The electrochemical or chemical formation of various more thermodynamically stable perovskite phases as the intermediate products is one of the main problems contributing to the low current efficiency. The formation of lithium titanates is much easier and faster because the smaller Li$^+$ ion leads to faster and deeper intercalation chemical reactions. However, LiTiO$_2$ is more thermodynamically stable than LiCl [40].

Similar I(t) profiles with a three-stage pattern are observed for TiO$_2$ reductions at $-0.3$ V vs. Li/Li$^+$ using 130% and 150% of the theoretical charge but with an extended time (Figure 5). It took 8.2 h to apply 150% of the theoretical charge as the longest experiment among all the TiO$_2$ electrolytic tests in this study, with the highest reduction extent of 25% of 2 g TiO$_2$. The steady stage reflects the final charge transfer for the conversion of Li$_2$TiO$_3$ at the three PIs of LiTiO$_2$ | Li$_2$TiO$_3$ | electrolyte [21]. The O$^{2-}$ diffusion coefficient in the steady state for 130% and 150% of the theoretical charge were estimated as being $8.98 \times 10^{-7}$ cm$^2$ s$^{-1}$ and $4.35 \times 10^{-7}$ cm$^2$ s$^{-1}$, which were about one order smaller than that for the steady state when using 80% of the theoretical charge. The smaller O$^{2-}$ diffusion coefficients at higher theoretical charges indicates that the conversion of Li$_2$TiO$_3$ to LiTiO$_2$ was very refractory in the steady stage, which explains the extended reduction process, and hence, the time taken.
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Figure 5. Current–time profiles for the TiO$_2$ reductions at $-0.3$ V vs. Li/Li$^+$ using 80%, 130%, and 150% of the theoretical charge for 2 g TiO$_2$.

4.4. TiO$_2$ Reduction Mechanism

By employing a systematically controlled cathodic potential reduction and charges, reactions (6)–(8) were revealed and discussed for the TiO$_2$ electrolytic reduction process.

The DFT modeling was calculated based on the optimized bulk structures of the relevant compounds, including Li and Ti (Table S2). Gibbs free energy changes for the possible reactions involved during the TiO$_2$ reduction (Equations (6)–(13)) were calculated (Table 2).

Table 2. Gibbs free energy change and reaction potentials for reactions at 650 °C using DFT calculations.

| Reaction | Equation  | $\Delta G_r$ (kJ mol$^{-1}$) | Theoretical Potential (V) |
|----------|-----------|-------------------------------|---------------------------|
| TiO$_2$ + Li$_2$O → Li$_2$TiO$_3$ | (6) | $-125.0$ | $-$ |
| Li + TiO$_2$ → LiTiO$_2$ | (7) | $-113.0$ | $-$ |
| Li$_2$TiO$_3$ + Li ↔ LiTiO$_2$ + Li$_2$O | (8) | $-11.0$ | $-$ |
| LiTiO$_2$ + Li → TiO + Li$_2$O | (9) | $0.8$ | $-0.01$ |
| TiO + 2Li → Ti + Li$_2$O | (10) | $-22.3$ | $-$ |
| TiO → Ti + 1/2O$_2$ | (11) | $227.0$ | $-1.18$ |
| Li$_2$TiO$_3$ → LiTiO$_2$ + 1/2Li$_2$O + 1/4O$_2$ | (12) | $222.0$ | $-2.30$ |
| LiTiO$_2$ → TiO + 1/2Li$_2$O + 1/4O$_2$ | (13) | $212.0$ | $-2.20$ |

The negative Gibbs free energy $\Delta G_{650 \degree C} = -125$ kJ mol$^{-1}$ for the insertion reaction of Li$_2$O to TiO$_2$ indicates that the formation of Li$_2$TiO$_3$ was spontaneous at 650 °C (Equation (6)), which is consistent with the TiO$_2$ soaking only testing result. The $\Delta G_{650 \degree C}$ for the TiO$_2$ reduction with Li metal was more negative than that for the reduction of Li$_2$TiO$_3$ with Li metal, suggesting that the reduction of TiO$_2$ with Li was more favorable than Li$_2$TiO$_3$ (Equation (7) vs. Equation (8)). The remaining core of the TiO$_2$ was most likely reduced to LiTiO$_2$ before the Li$_2$TiO$_3$ shell reduction, which could be slowed down by the Li$_2$TiO$_3$ passivation layer. The unit cell volume of Li$_2$TiO$_3$ was three times as much as the one for TiO$_2$, which not only reduced the pore volume for the transport of O$^{2-}$ ions but was more thermodynamically stable (Figure 6) [6,40]. The reduction of Li$_2$TiO$_3$ by the Li metal generated Li$_2$O (Equation (8)), which needed to diffuse through the LiTiO$_2$ layer to the bulk molten salts. The slow diffusion of O$^{2-}$ through the LiTiO$_2$ layer led to the accumulation of trapped Li$_2$O in the solid particle, which limited the reversible reduction of Li$_2$TiO$_3$. The further reduction of LiTiO$_2$ by the Li metal also generated Li$_2$O (Equation (9), $\Delta G_r = 0.8$ kJ mol$^{-1}$). The direct electrolytic reductions of Li$_2$TiO$_3$ and LiTiO$_2$ were alterna-
tive pathways for the titanium dioxides’ reduction at underpotentials (Equations (12) and (13)), for which the Gibbs free energies were much higher. Both reduction pathways of LiTiO$_2$ were most likely halted due to the high local Li$_2$O concentration (Equations (9) and (13)), which became the key limiting step for further reduction and caused the extended time. The DFT analysis was consistent with the experimental TiO$_2$ electrolytic reduction results obtained in this study showing that the LiTiO$_2$ was the most reduced product achieved, even when using 150% of the theoretical charge. The passivation and refractory behaviors of LiTiO$_3$ were witnessed for the electrolytic reduction of TiO$_2$ in the LiCl molten salts using underpotentials before the formation of the Li metal [19,40].

![Figure 6. Unit cell volumes for the related chemicals during the TiO$_2$ electrolytic reduction in the molten LiCl–Li$_2$O (1 wt.%) at 650 °C.](image)

By combining the experimental and DFT results, a three-step reaction mechanism for the TiO$_2$ electrolytic reduction at overpotentials in the LiCl–Li$_2$O (1 wt.%) salt at 650 °C was proposed for this study:

- **Step 1:** Li$_2$O + TiO$_2$ → Li$_2$TiO$_3$;
- **Step 2:** TiO$_2$ + Li → LiTiO$_2$;
- **Step 3:** Li$_2$TiO$_3$ + Li ↔ LiTiO$_2$ + Li$_2$O (reversible).

As illustrated in Figure 7, the soaking process followed a shrinking core mechanism, where the insertion of Li$_2$O and TiO$_2$ formed a stoichiometric Li$_2$TiO$_3$ layer on the external surface of the TiO$_2$ particles [16]. The Li$_2$TiO$_3$ layer became thicker and slowed down the O$^{2-}$ diffusion, leading to unstoichiometric Li$_{0.54}$Ti$_{2.86}$O$_6$ formation with the unreacted TiO$_2$ core.

![Figure 7. Shrinking core model for (a) the TiO$_2$ soaking process and (b) for the electrolytic reduction of the TiO$_2$ process with a passivation layer.](image)

The Li$_2$TiO$_3$ | TiO$_2$ | electrolyte interline initially formed on the surface of the oxide particle and gradually moved to the interior of the particle.
In the second step, the Li metal diffused through the Li$_2$TiO$_3$ and reduced the TiO$_2$ core directly into LiTiO$_2$. The three PIs of Li$_2$TiO$_3$ | TiO$_2$ | electrolyte were formed. The lithium metal continuously moved to the center of the TiO$_2$ core until the core was fully converted to LiTiO$_2$. This step was controlled by the Li diffusion through the Li$_2$TiO$_3$ and newly formed LiTiO$_2$ layer. The second reaction also followed a shrinking-core model. When the TiO$_2$ was completely reduced to LiTiO$_2$, the Li$_2$TiO$_3$ shell started to be reduced to a mixture of LiTiO$_2$ and Li$_2$O, which was different from the inner LiTiO$_2$ core. The reaction occurred at the external layer of Li$_2$TiO$_3$ and formed a new three PIs of Li$_2$O+LiTiO$_2$ | Li$_2$TiO$_3$ | electrolyte. It stopped when the interline approached the LiTiO$_2$ core. In the I(t) curves, the second current reduction session took a long time and the data presented in Figure 4a shows that the conversion of Li$_2$TiO$_3$ to LiTiO$_2$ was not completed until 150% of the theoretical charge was applied. This indicates that Li$_2$TiO$_3$ was stable and the reduction of Li$_2$TiO$_3$ was refractory. Therefore, the third step was the rate-limiting step in the TiO$_2$ reduction in the molten LiCl–Li$_2$O.

Important physical variables determine the electrolytic reduction process, including the diffusion coefficient of oxygen in various phases, the applied current density, the radius of the grains, and the density of the phase [16]. In this study, the most reduced product obtained for the electrolytic reduction of TiO$_2$ was LiTiO$_2$ with 150% of the theoretical charge in 8.2 h. Previous studies on TiO$_2$ electrolytic reduction using the pellet form (thickness ≈ 0.2 cm) at cell potentials of 1.8 V and 3.2 V also only achieved LiTi$_2$O$_4$ and LiTiO$_2$ within several hours [19]. In contrast, the complete reduction of the TiO$_2$ powder in LiCl was achieved with both CV techniques and potentiostamperometry [10,21]. Li$_2$O accumulation within the pellet may alternate the conductivity of the mixtures and slow down the direct electrolytic reduction of Li$_2$TiO$_3$ and LiTiO$_2$, which was observed for other metal oxide reductions [27].

The key to improving the TiO$_2$ reduction in LiCl–Li$_2$O molten salts is to reduce the Li$_2$O local concentration and promote the diffusion of O$^{2−}$ out of the solid phase. Strategies to achieve this include lowering the Li$_2$O concentration in the molten salts, reducing the pellet size, and applying sonication or mechanical stirring to accelerate the O$^{2−}$ diffusion [41]. Furthermore, as the Ti species valence reduced to 0 step by step according to the DFT analysis for the multistep reduction, the $ΔG$ changed from negative to positive. This indicates that the stepwise reduction of TiO$_2$ with the in-situ-generated Li metal reached thermodynamic equilibrium and gradually became more refractory, although the overall $ΔG$ for the TiO$_2$ reduction was negative and the reaction was spontaneous. Another promising way to improve the TiO$_2$ electrolytic reduction in LiCl is to avoid the intermediate steps, such as removing the soaking step or decrease it to a reasonably short time.

5. Conclusions

Electrolytic TiO$_2$ reduction in LiCl–Li$_2$O salts at 650 °C was examined in terms of a soaking only test, the effect of a reduction potential, and the effect of applied charges. The soaking without electrolysis showed the spontaneous formation of Li$_2$TiO$_3$, which is a unique intermediate for TiO$_2$ electrolytic reduction. The increasing reduction potential promoted TiO$_2$ reduction only to a certain extent. The optimal cathodic reduction potential was determined as being −0.3 V vs. Li/Li$^+$. The highest charge, i.e., 150% of the theoretical charge, was applied for 8.2 h and caused the partial reduction of TiO$_2$ through to the full conversion of LiTiO$_2$, which was the most reduced product obtained in this study. Accordingly, the highest reduction extent was 25%.

Combined with the DFT modeling, the electrolytic reduction of TiO$_2$ in molten LiCl–Li$_2$O was proposed to follow a multistep reaction mechanism. The external surface of the TiO$_2$ particles was converted to Li$_2$TiO$_3$ via the chemical insertion of Li$_2$O during the soaking stage. Then, the TiO$_2$ core was partially reduced to LiTiO$_2$ before Li$_2$TiO$_3$ was electrocally reduced to LiTiO$_2$. The reduction of Li$_2$TiO$_3$ was reversible and led to the formation of Li$_2$O. Due to the accumulation of Li$_2$O at the three PIs, the reduction of
Li$_2$TiO$_3$ to LiTiO$_2$ was very slow and the rate-limiting step. Further reduction of LiTiO$_2$ was paused as more Li$_2$O was generated and accumulated.

Based on the understanding of the TiO$_2$ electrolytic reduction mechanism in molten LiCl–Li$_2$O, the key to increasing the efficiency of electrolytic TiO$_2$ reduction is to reduce the O$^{2-}$ ions concentration at the three PIs. Strategies to achieve this include promoting the O$^{2-}$ diffusion at the three PIs, using smaller TiO$_2$ particles or powder, using a lower concentration of Li$_2$O for the bulk salts, and reducing the soaking time to avoid the excessive formation of Li$_2$TiO$_3$.

**Supplementary Materials:** The followings are available online at https://www.mdpi.com/article/10.3390/electrochem2020016/s1. Figure S1: Optimized bulk crystal structures for the Li system, TiO$_2$, TiO, and Ti. Table S1: Rietveld refinement results for the soaked and reduced products. Table S2: Optimized bulk lattice parameters. Table S3: Equation of state, equilibrium volumes (V$_0$) determined from corresponding BM4 EOS, bulk moduli, and electronic potentials for the materials modeled from DFT.

**Author Contributions:** Conceptualization, S.L. and H.Z.; methodology, S.L. and H.Z.; software, B.L.; validation, M.S., B.L., S.L. and H.Z.; formal analysis, M.S. and H.Z.; resources, S.L. and B.L.; data curation, M.S.; writing—original draft preparation, M.S.; writing—review and editing, H.Z.; visualization, B.L.; project administration, S.L. and H.Z.; funding acquisition, S.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported through the INL Laboratory Directed Research and Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

**Institutional Review Board Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors would like to thank the staff at the Center for Advanced Energy Studies for their assistance and the use of their facilities.

**Conflicts of Interest:** The authors declare no conflict of interest.

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