**Preparation and Characterization of Oxygen-Deficient Li$_4$Ti$_5$O$_{12}$ Anode Material in Reducing Atmosphere for Lithium Ion Batteries**

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**Abstract.** The poor electrical conductivity of Li$_4$Ti$_5$O$_{12}$ has limited its practical application as high rates performance anode for lithium ion batteries. An oxygen deficient Li$_4$Ti$_5$O$_{12}$ is investigated by a reducing atmosphere for lithium ion batteries in this work. Compared with pristine Li$_4$Ti$_5$O$_{12}$ calcined at argon and air, the oxygen deficient Li$_4$Ti$_5$O$_{12}$ exhibits significant improvement of electrochemical performance, it could deliver a specific capacity of 114.8 mAh g$^{-1}$ even at a high charge/discharge rate of 10C and exhibit excellent cycling performance at low rates. However, more oxygen vacancies will increase the distortion of the lattice, causing serious deterioration in anode performance. Herein, an appropriate concentration of oxygen deficiency in oxygen-deficient Li$_4$Ti$_5$O$_{12}$ is obtained by controlling the reducing atmosphere flow of ~170 mL/min to possess optimal electrochemical performance.

1. **Introduction**

The spinel cubic structure Li$_4$Ti$_5$O$_{12}$ has demonstrated outstanding cyclability and safety as an anode electrode material for lithium ion batteries (LIBs) [1, 2]. Li$_4$Ti$_5$O$_{12}$ has zero-strain properties and relatively high potential range (1.55 V vs Li$^+/\text{Li}$) in the charge/discharge process, which give a long cycle life and results in no dendrite formation [3, 4]. However, Li$_4$Ti$_5$O$_{12}$ has relatively low conductivity (<10$^{-13}$ S cm$^{-1}$) [5]. This is one of the main reasons leading to its poor high rate performance and limiting its commercial application [6-8]. The most common problem-solving strategy employed in the literature is to enhance electronic conductivity with a surface conductive coating [9, 10] and to tailor the particle size of electroactive materials to the nanometer-scale [10-13]. Yet, it is still challenging to fabricate higher-rate Li$_4$Ti$_5$O$_{12}$. The oxygen deficiency method has been attracting more and more attention to improve the electrical conductivity of materials [14, 15]. For example, the oxygen-deficient Li$_4$Ti$_5$O$_{12}$ is obtained via first preparing oxygen-deficient TiO$_2$ by Liu et al. [16] has excellent lithium storage performance delivering a capacity of 143 mAh g$^{-1}$ at a current density of 100C. H. Song et al. [15] combined with the doping of Mo prepared a high conductivity (10$^{-2}$ S cm$^{-1}$) oxygen-containing defect Li$_4$Ti$_5$O$_{12}$ in a reducing atmosphere, which achieved an excellent capacity at a high C-rate (167 mAh g$^{-1}$ at 10C). Unfortunately, this complicated methods and expensive costs limit their practical application and production, although many researchers have made good progress in the study of oxygen-deficient Li$_4$Ti$_5$O$_{12}$. 
In the present study, we used a simple and practical method of high temperature solid phase to prepare an oxygen-deficient Li$_4$Ti$_5$O$_{12}$ in a reducing atmosphere that has excellent rate performance and the discharge specific capacity. Moreover, the reducing atmosphere flow rate is controlled to obtain an appropriate amount of oxygen defects, which the problem of serious lattice deterioration in the oxygen-deficient Li$_4$Ti$_5$O$_{12}$ material caused by excessive oxygen defects can be solved.

2. Experimental
The mixture was prepared by the following steps adopting TiO$_2$-anatase and Li$_2$CO$_3$ as raw material in appropriately stoichiometric ratio were mixed by ball-milling for 4h in amount absolute ethanol. A white powder precursor was obtained after follow by drying. The precursor material was first calcined at 450°C for 3h and then calcined at 800°C for 10h in a reducing atmosphere (5% H$_2$, 95% N$_2$), denoted as H$_2$-LTO. For comparison, we also prepared Ar-LTO and Air-LTO materials using the same procedure, but calcined in argon and air atmosphere, respectively.

Powder X-ray diffraction (XRD, RIGAKUD/MAX-3B) using Cu Kα radiation in steps of 0.02° was used to identify the crystalline phase and crystal lattice parameters of the powders. To calibrate the lattice parameters more accurately, high purity silicon (99.999 wt %) is selected as the internal standard. Morphologies were characterized by scanning electron microscopy (SEM, Tecnai G2 TF30 S-Twin). A UV-visible spectrophotometer (U-4100) was used to record the optical absorption spectra. Surface chemical composition of the prepared samples were investigated by X-ray photoelectroscopy (XPS, PHI 5000, and Versa Probe-II). All core level XPS spectra were calibrated using C 1s photoelectron peak at 284.8 eV as the reference. The electrochemical characterizations were carried out using CR2032 coin-type half cells. Cells were cycled Galvanostatically using a LAND-BT2013A battery testing system.

3. Result and discussion

3.1. Analysis of structure and morphology

![Figure 1. XRD patterns of three samples prepared at different atmosphere.](image)

**Table 1.** The cell parameters of the three samples prepared at different atmosphere.

| Sample    | a (Å)    | esd (Å) |
|-----------|----------|---------|
| Air-LTO   | 8.3609   | 0.00028 |
| Ar-LTO    | 8.3607   | 0.00021 |
| H$_2$-LTO | 8.3598   | 0.00022 |

Figure 1 shows XRD patterns of three samples prepared at different atmosphere. As displayed, the most major peaks of the three samples are in accordance with the cubic spinel Li$_4$Ti$_5$O$_{12}$ (JCPDS NO.49-
The cell parameters of Air-LTO, Ar-LTO and H$_2$-LTO were calculated by refining XRD data, as shown in Table 1. The cell parameters of Air-LTO (a = 8.3609 Å), Ar-LTO (a = 8.3607 Å) and H$_2$-LTO (a = 8.3598 Å) gradually decrease. This may be due to the gradual increase of the concentration of oxygen defects in the three samples, especially in H$_2$-LTO. Moreover, it can be seen that the cell parameters of Air-LTO and Ar-LTO do not change much within the standard error range, according to the calculation results. This may indicate that Air-LTO and Ar-LTO contain less oxygen than H$_2$-LTO.

![Figure 2](image1.png)

**Figure 2.** SEM images of three samples prepared at different atmosphere. (A and d) H$_2$-LTO; (B and E) Ar-LTO; (c and f) Air-LTO.

The morphology of the prepared H$_2$-LTO, Ar-LTO and Air-LTO powders is determined by SEM. As shown in Figure 2, it can be seen that the three pure materials prepared at different atmosphere maintain relatively good homogeneity. And the primary particle sizes of all three samples are 200-400 nm and are both spinel type. It is indicated that the spinel structure and particle size growth of composite materials have not been effected at different atmospheric conditions in this study.

![Figure 3](image2.png)

**Figure 3.** Ti 2p XPS spectra of (a) H$_2$-LTO, (b) Ar-LTO and (c) Air-LTO, (d) a UV-visible absorption spectra and actual color of three samples in insert.
Table 2. Integral area of Ti $^{4+}$2p and Ti $^{3+}$2p of three samples

| Sample       | H$_2$-LTO Position (eV) | Ar-LTO Position (eV) | Air-LTO Position (eV) |
|--------------|-------------------------|----------------------|-----------------------|
| Ti $^{4+}$2p3/2 | 13301.11               | 7302.71              | 15713.59              |
| Ti $^{3+}$2p3/2 | 7213.50                | 7322.46              | 1323.659             |
| Ti $^{4+}$2p1/2 | 6650.55                | 3651.36              | 7856.80              |
| Ti $^{3+}$2p1/2 | 3606.76                | 3661.23              | 661.83               |
| $\chi^2$       | 10.1546                | 2.9477               | 13.5624              |

In order to confirm whether the different atmosphere will influence the oxidation state of the transition metal species in the synthesized H$_2$-LTO, Ar-LTO and Air-LTO materials, XPS was carried out. Figure 3a-c shows XPS results of Ti 2p3/2 and Ti 2p1/2 binding energy. The high resolution of Ti 2p spectrum presents two main peaks at approximately 458.3 eV (Ti 2p1/2) and 458.3 eV (Ti 2p3/2) in both three samples, indicating the binding energies of Ti $^{4+}$. Taking a further look, the spectra curve of Ti 2p can be fitted into a distinct part of Ti $^{3+}$ peaks at 455.9 eV and 461.6 eV corresponding to Ti $^{3+}$ 2p3/2 and Ti $^{3+}$ 2p1/2 in sample of H$_2$-LTO. This indicates that a part of Ti $^{4+}$ ions were reduced to the Ti $^{3+}$ state by the generation of oxygen vacancies in the reducing atmosphere. What’s more, similar result was also fitted in Ar-LTO, demonstrating that Ar-LTO also contained a small amount of oxygen deficiency binding calculations of peak area (Table 2). It is interesting to note that for Air-LTO, only a single peak set of Ti $^{3+}$2p3/2 can be seen, despite the binding energy of Ti $^{4+}$2p was intermediate between those of the Ti $^{3+}$ and Ti $^{4+}$ states. Hence, this strongly suggests that material preparation in the reducing atmosphere led to the partial reduction of Ti $^{4+}$ ions, similar to that of H$_2$-LTO. According to the peak area, it can be seen that H$_2$-LTO contains more Ti $^{3+}$ (oxygen vacancies), followed by Ar-LTO, and finally Air-LTO.

The expected of XPS analysis in oxygen vacancies in H$_2$-LTO, Ar-LTO and Air-LTO were further verified using UV-visible absorption spectra, which is known to be a powerful tool for determining the concentration of oxygen vacancies based on the absorption of ultraviolet light by the oxygen in material. Comparing the UV-visible absorption spectrum in Figure 3d, the spectral absorption of H$_2$-LTO in the ultraviolet region was clear further confirming the existence of oxygen defects, while the samples Ar-LTO and Air-LTO had a little absorption in this region. The colors of the different samples were distinct in different atmospheres, despite the XRD and SEM results showed that the structure and morphology were not significantly different. As shown in the inset of Figure 3d, the color of H$_2$-LTO was much bluer than that of Ar-LTO and Air-LTO from the more redox reaction of Ti$^{3+}$/Ti$^{4+}$ existence. The difference in electronic conductivity was also clearly identified by measuring the band gaps using UV-visible spectroscopy [15]. The band gap energies were measured to be 3.58 eV, 3.66 eV and 3.67 eV for H$_2$-LTO, Ar-LTO and Air-LTO, respectively. It is expected that their electronic conductivity would be significantly greater and electrochemical performance would be better due to a reduction in the band gap.
3.2. Electrochemical performance

Figure 4. The charge/discharge curves of (a) H₂-LTO, (b) Ar-LTO and (c) Air-LTO; (d) Rate capacity of three samples

Figure 4 a-c shows the charge/discharge curves of H₂-LTO, Ar-LTO and Air-LTO composite at particular rates in a voltage of 1.0-2.2 V. The discharge capacity of H₂-LTO composite changes from 168.4 mAh g⁻¹, 162.1 mAh g⁻¹, 156.2 mAh g⁻¹, 139.4 mAh g⁻¹, 114.8 mAh g⁻¹ at the rate of 0.2, 1, 2, 5 and 10C, respectively. Compared to the H₂-LTO composite, the electrochemical performance of Ar-LTO and Air-LTO composite is slightly poor. The rate capacity of the samples at different current densities were measured shown in Figure 4 d. Compared to Ar-LTO and Air-LTO, H₂-LTO composite display higher capacity and better rate performance. But the cycle stability is poor than Ar-LTO, this may be due to the presence of more oxygen vacancies will increase the distortion of the lattice, which will result in a decrease in Li ion mobility [15].

Figure 5. Cycle performance of H₂-LTO, Ar-LTO and Air-LTO composite at 1C
Encouraged by the excellent rate capacity of H2-LTO, the long-term cycle performance of all three samples were measured shown in Figure 5. The initial discharge capacity of H2-LTO composite is 162.1 mAh g\(^{-1}\) and still maintains 147 mAh g\(^{-1}\) with the retention of 90.7 % after 200 cycles at 1C, while the capacity of Air-LTO is 158.8 mAh g\(^{-1}\) with the 88.4 % reservation (140.4 mAh g\(^{-1}\)). Also we noticed that the initial discharge capacity of Ar-LTO composite is 152.4 mAh g\(^{-1}\) and still maintains 142.7 mAh g\(^{-1}\) with the retention reach up to 93.6 % at the same test condition. This is presumably because the calcined in an argon atmosphere is beneficial to the stability of Ar-LTO material structure and contains a small amount of oxygen vacancies, which is reflected in the charge and discharge cycle. Therefore, the control of the concentration of oxygen defects in the material is particularly important.

3.3. Control the concentration of oxygen defects in H2-LTO

![Figure 6](image_url)

**Figure 6.** (a) XRD patterns of H2-LTO with different gas flows. (b) Cycleability of H2-LTO with different gas flows at different rates. (c) Rate capability of second discharge of H2-LTO with different gas flows in a C-rate range from 0.2 to 10C.

**Table 3.** The electrochemical performance of H2-LTO with different gas flows at different rates.

| Sample       | Discharge capacity (mAh g\(^{-1}\)) |
|--------------|-----------------------------------|
|              | 0.2C  | 1C     | 2C     | 5C     | 10C    |
| 65 mL/min    | 167.0 | 157.0  | 147.7  | 117.5  | 74.7   |
| 100 mL/min   | 177.5 | 167.5  | 156.8  | 125.5  | 83.2 |
| 135 mL/min   | 177.1 | 165.5  | 156.2  | 129.4  | 90.4 |
| 170 mL/min   | 168.5 | 163.9  | 157.4  | 141.4  | 116.3 |
| 200 mL/min   | 167.8 | 158.7  | 140.3  | 103.1  | 68.9 |
In view of the results discussed above that too much oxygen defect content can cause structural defects in the material, for which effective control of the oxygen defect concentration is achieved. The materials of H2-LTO with 65, 100, 135, 170, 200 mL/min gas flows were prepared using the same calcination procedure. The impurity peak of TiO2 appears in the material synthesized with the low concentration (65 and 100 mL/min) of the reducing atmosphere, as shown in Figure 6a. When further increased of the concentration of the reducing atmosphere, the XRD patterns can be indexed on the basis of the spinel structure and no remarkable secondary phase can be observed in the patterns. Figure 6b shows the cycle performance of H2-LTO at various concentrations of reducing atmosphere. Compared to the high concentration (200 mL/min) and low concentration (65 mL/min), the three kinds of 100, 135, 170 mL/min display higher capacity and better rate performance especially for the 170 mL/min sample. Figure 6c shows the discharge curves of H2-LTO at various concentrations of reducing atmosphere at each rates. 100 mL/min sample has the highest discharge capacity at low rates (0.2C, 1C and 2C), as shown in table 3. In contrast with the value tested at 5C and 10C, 170 mL/min sample has a higher discharge capacity (table 3) than all other samples, even reaching 116.3 mAh g⁻¹ at 10C (table 3). Therefore, through the comparative research above, the oxygen defects in the oxygen-deficiency material can be effectively controlled to synthesize a lithium ion battery anode material excellent in performance when the gas flows of a reducing atmosphere (5% H2, 95% N2) is controlled in ~170 mL/min.

4. Conclusion
The preparation of pure Li4Ti5O12 composite at different atmospheres did not change its spinel structure and not affect the growth of particle size. The XPS and UV-visible absorption spectra results show that the synthetic (H2-LTO) at reducing atmosphere contains the maximum concentration oxygen defects. This could lead to an increase of electronic conductivity. The oxygen deficient Li4Ti5O12 (H2-LTO) shows enhanced lithium ion insertion/extraction kinetics, especially the discharge specific capacity can reach 114.8 mAh g⁻¹ at high rates (10C) than that of samples by calcined in argon (Ar-LTO) and in air (Air-LTO); however, the cycle stability is poor than Ar-LTO. In particular, the cycle performance of Ar-LTO at 10C is not better than Air-LTO because of the oxygen vacancies will increase the distortion of the lattice, despite the Ar-LTO also contains small amount concentration oxygen defects as identified from the XPS and UV-visible absorption spectra results. The oxygen defect in the oxygen-deficiency material can be well controlled when the gas flow is controlled at around 170 mL/min, so that obtains excellent electrochemical performance, 116.3 mAh g⁻¹ at 10C.

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