

Research Article

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ Heattreated under Nitrogen Ambient with Outstanding Rate Capabilities

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The powders of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were prepared by heat treating the mixture of rutile TiO_2 and Li acetate at 800°C for 3 h under a nitrogen atmosphere and, for comparison, under air as well. The powders heated under N_2 show a remarkably higher-rate capability and better cycle stability. The discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under N_2 at 19°C (corresponding to a 3.2-minute total discharge) reached 107 mA h g^{-1} , 22 mA h g^{-1} higher than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air, which was 85 mA h g^{-1} . The former material also shows a much better cycle stability, with no discharge capacity loss after 300 cycles at 6°C or 16.3°C . The results indicate that heat treatment under low-oxygen partial pressure atmosphere such as N_2 could significantly improve the high-rate performance of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

1. Introduction

There has been increasing interest in developing spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) as a potential anode for application in lithium ion rechargeable batteries [1–14] due to its long cycle life, excellent lithium ion intercalation and deintercalation reversibility, and “zero-strain” intercalation characteristics. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a main discharge plateau of about 1.55 V versus lithium, which makes it a very promising anode material for many lithium ion batteries using high-voltage materials such as LiCoO_2 and LiMnO_2 as their cathodes. However, although spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits no structural change during charge/discharge process, its electron conductivity is low [15]. This affects its rate capability and cycle stability, for which the experimental values are not nearly as good as the theoretical ones. In order to increase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ conductivity, several strategies have been taken, including incorporating a conducting second phase such as Ag [16], Cu [17], CuO_x [18], or $\text{Li}_2\text{CuTi}_3\text{O}_8$ [19], doping with alien-valent metal ions such as Ta^{5+} [20] or Al^{3+} [21], and synthesizing nanosized [22, 23] $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Another effective method is heat treating $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under a reduced or low-oxygen partial pressure atmosphere [24].

In this work, the electrochemical characteristics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere were studied, with emphasis on their high-rate properties. X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) observations, and galvanostatic discharge/charge tests were used to characterize the material.

2. Experimental

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were prepared by using 9 g commercially available rutile TiO_2 (AR) and 12 g Li acetate (AR) [25]. The starting materials were thoroughly mixed in ethanol solvent and dried at 100°C for 7 h. The dried and mixed product was then heated at 800°C for 3 h under air or N_2 atmosphere, followed by natural cooling in the furnace.

The morphologies of the as-prepared powders were characterized by scanning electron microscopy (SEM) performed on Hitachi S4500. Powder X-ray diffraction (XRD) was performed on a Rigaku D/max-RB diffractometer operating in transmission mode with Cu K α radiation ($\lambda = 1.5418\text{ \AA}$). The BET-specific surface area was measured with a Quantachrome NOVA 4000 system, using the N_2 absorption-desorption method at liquid nitrogen temperature.

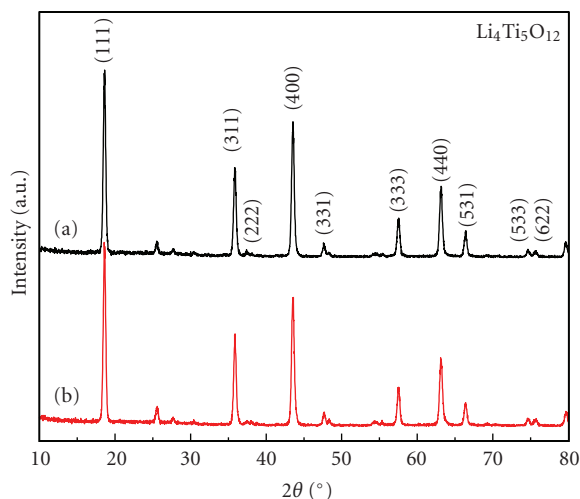


FIGURE 1: X-ray diffraction patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under (a) N_2 and (b) air.

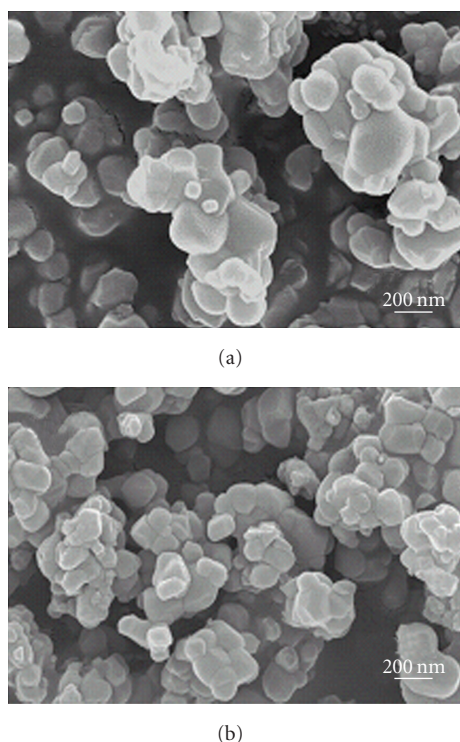


FIGURE 2: SEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under (a) air and (b) N_2 .

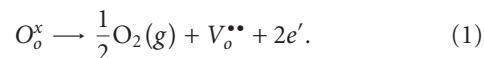
To fabricate the cathodes for the battery test cells, the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders, Super P carbon black, and polyvinylidene fluoride (PVDF) binder were mixed homogeneously in a weight ratio of 80:10:10 in an N-methyl pyrrolidinone (NMP) solvent. The electrode films, which used carbon-covered aluminum foil as the current collector, were fabricated using the tape-casting method [23]. The loading of active material was $1\text{--}2\text{ mg cm}^{-2}$. The coin-type half cell (CR2032 size) contained the as-fabricated electrode

film, a lithium metal counter electrode, a microporous polyethylene separator, and electrolyte of a 1 M solution of LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol %; Merck). The cell was constructed and handled in an Ar-filled vacuum glove box.

The discharge/charge tests were carried out using a LAND Celltest 2001 A (Wuhan, China) system between 2.5 and 1 V versus the Li counter electrode. First, the test cell was discharged for Li^+ ions to intercalate into the cathode, and then the test cell was charged and held at 2.5 V to fully charge before discharge. The constant current charge and discharge rates are the same. Cyclic voltammogram was recorded from 1.0 to 2.5 V at a scan rate of 10 mV s^{-1} , using IM6e electrochemical workstation (Germany).

3. Results and Discussion

Figure 1 shows the XRD patterns of as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders after heat treatment under air or N_2 atmosphere at 800°C for 3 h. The diffraction peaks of both samples can be indexed as spinel lithium titanate (cubic phase, space group $\text{Fd}\bar{3}\text{m}$ space group), except two small peaks at around 25° and 55° which probably correspond to remaining unreacted TiO_2 . The only difference between the two XRD patterns is that the diffraction peaks for the sample heated under N_2 are slightly shifted to the lower 2θ values compared to the one heated under air. This indicates that the lattice parameter of the former is larger than that of the latter. This is in good agreement with previous results of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under H_2/Ar atmosphere [24]. The larger lattice parameter for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders heat treated under N_2 atmosphere could be attributed to the reduction of some Ti^{4+} ions into Ti^{3+} when heated under low-oxygen partial pressure atmosphere, as the sizes of Ti^{3+} ions are larger than those of Ti^{4+} . The presence of Ti^{3+} ions could also explain the darker color of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders heat treated under N_2 atmosphere, which is light yellow (while the sample heated under air is white). It is believed that the reduction of some Ti^{4+} ions into Ti^{3+} is ascribed to the increase in electron concentration, which results from nonstoichiometry of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at low-oxygen partial pressures.



This relatively high electron concentration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ treated under reducing or low-oxygen partial pressure atmosphere compared to that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ treated under air has been noted in previous works [20, 24].

The SEM images of the two samples are shown in Figure 2. The diameter of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle treated under air (Figure 2(a)) was almost the same as that treated under N_2 atmosphere (Figure 2(b)), in agreement with BET-specific surface areas of the two samples, which are $3.70\text{ m}^2\text{ g}^{-1}$ and $3.78\text{ m}^2\text{ g}^{-1}$, respectively.

The charge/discharge properties and rate capabilities of the test cells containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under air or N_2 atmosphere as the electrode material were tested and analyzed. A comparison of the rate capabilities of the test cells is shown in Figure 3(a); the data shows that extremely

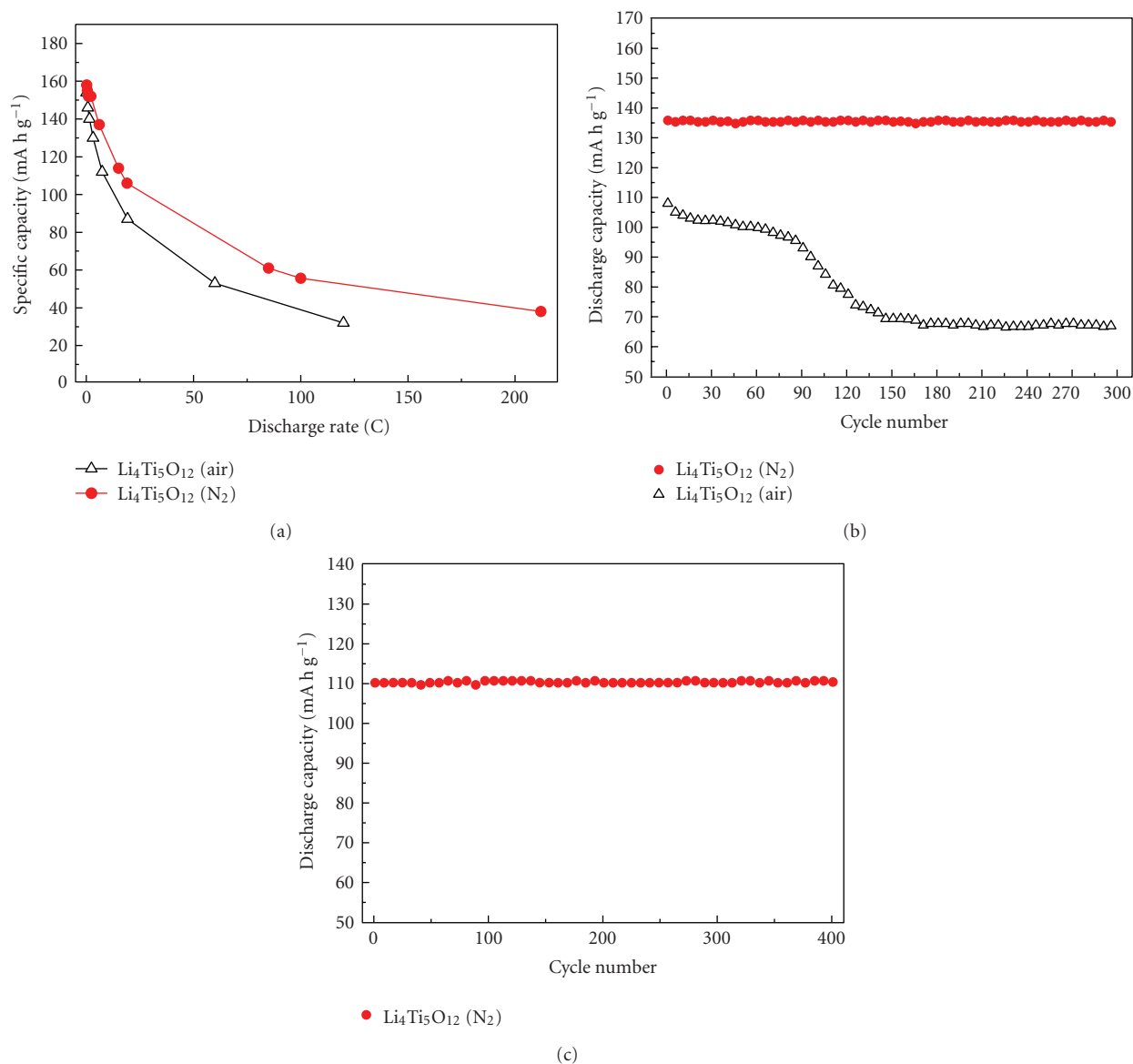


FIGURE 3: Electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under air or N_2 ambient. (a) Discharge capacity of the two samples under various rates. (b) Capacity retentions of the two samples when performing full charge/discharge cycles at 6 C. (c) Capacity retentions of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 ambient when performing full charge/discharge cycles at 16.3 C.

high rates can be achieved for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere. It can be seen that at low discharge rates (<0.5 C), the specific capacities of the two test cells are very close. As the discharge rate increases, the capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere is remarkably higher than that heated under air. The former could reach a discharge capacity of 107 mA h g^{-1} at 19 C (1680 mA g^{-1} of current density), 22 mA h g^{-1} higher than the latter, which had a discharge capacity of only 85 mA h g^{-1} . At a 85 C rate (4920 mA g^{-1} of current density), a capacity of more than 60 mA h g^{-1} could still be obtained, and a capacity of nearly 40 mA h g^{-1} was achieved at a 212 C (8240 mA g^{-1} of current density) rate for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere. This result is within expectations because

the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere has an increased electron concentration. The comparison of the rate capabilities of the test cells confirms that the heat treatment under N_2 atmosphere for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can largely improve its rate capability.

The change in discharge capacities with cycle numbers of the two samples at a 6 C rate (800 mA g^{-1} of current density) is shown in Figure 3(b), respectively. It shows that the cycling performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere is much better than that heat treated under air. After charging/discharging at 6 C for 300 cycles, the former sample still remains 100% in discharge capacity, showing 135 mA h g^{-1} , while the latter sample capacity slowly fades as the cycle number increases and quickly drops

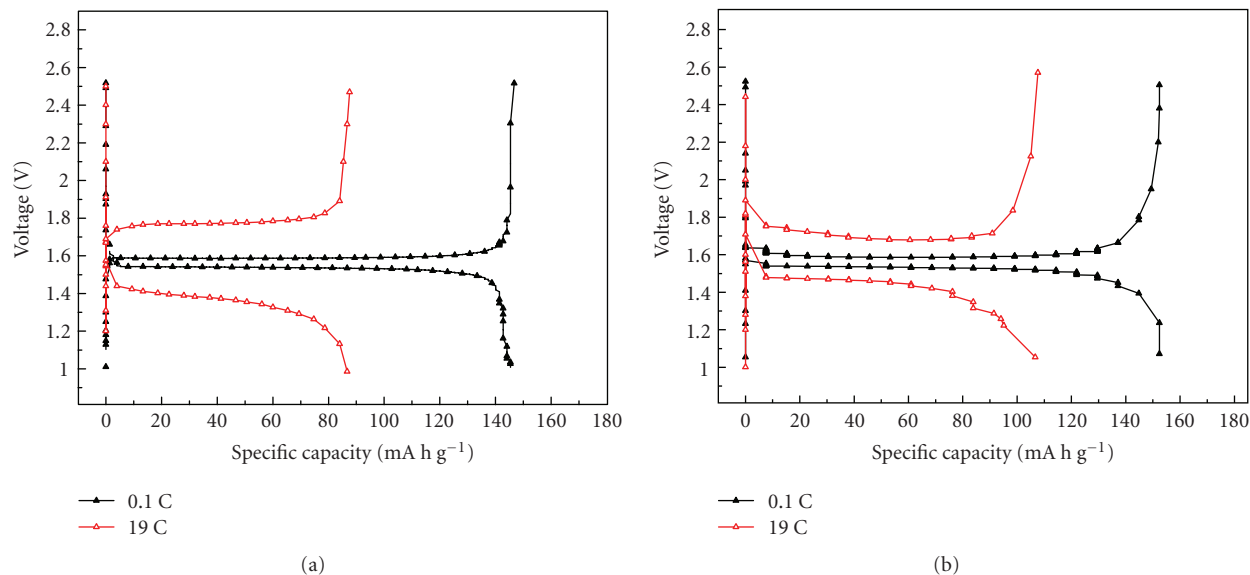


FIGURE 4: Charge discharge performance (0.1 C) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under (a) air and (b) N_2 .

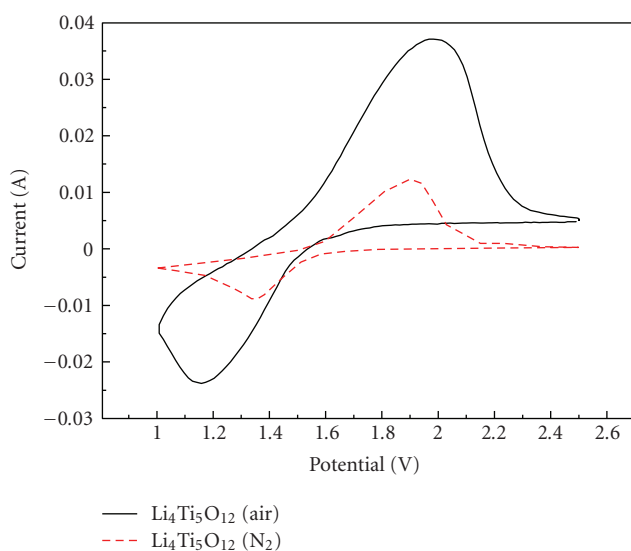


FIGURE 5: Cyclic voltammograms of test cells containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under air or N_2 atmosphere as cathode materials at scan rate of 10 mV s^{-1} .

after 90 cycles. After about 140 cycles, the discharge capacity retention of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under air is only 68%, showing 67 mA h g^{-1} . The high-rate cycling stability for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere at 16.3 C (1650 mA g^{-1} of current density) is also excellent. As shown in Figure 3(c), it keeps 100% in discharge capacity after 400 cycles, showing 109 mA h g^{-1} . From these results, it can be concluded that heat treatment under a reducing atmosphere such as N_2 could not only improve $\text{Li}_4\text{Ti}_5\text{O}_{12}$ high-rate capability significantly, but could also greatly enhance its cycling stability at high rates.

Figure 4 shows the charge/discharge curves for the test cells at 0.1 C (7 mA g^{-1} of current density) and 19 C (1680 mA g^{-1} of current density). When comparing the voltage profile of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere with the one of that heat treated under air, it can be seen that the former sample has more sloping charge/discharge curves. This indicates that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 has a more evident pseudocapacitive faradaic kinetics, which is due to its higher electron conductivity. From Figure 4, it can be observed that when charging and discharging at a rate of 0.1 C , the capacity and plateau voltage of the two cells were very close: around 150 mA h g^{-1} and 1.60 V , respectively. At 19 C , the capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under air was much smaller than that of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 . At 19 C , both test cells have more sloping voltage profiles than at 0.1 C , indicating a more evident surface-confined charge-transfer kinetics (known as the pseudocapacitive faradaic kinetics) existing along with diffusion-controlled kinetics as lithium intercalating/deintercalating in $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Due to their higher polarization under higher rates, both cells charge plateau voltages are higher than those charging at low rates, and meanwhile the discharge plateau voltages are lower.

Cyclic voltammogram was recorded, as shown in Figure 5, from 1.0 to 2.5 V at a scan rate as high as 10 mV s^{-1} . The two samples both have broad redox peaks under a high scan rate, which is in good agreement with the sloping voltage profile during the galvanostatic discharge/charge cycles at high rates, indicating a concurrence of both pseudocapacitive lithium intercalation mechanism and diffusion-controlled kinetics during the process. The two redox peaks of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere appear at 1.35 V and 1.9 V (versus Li^+/Li , depending on the scan rate), while those of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under air appear at 1.15 V and 2.0 V . The results show that under a high charge/discharge rate, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2

atmosphere has relatively low polarization compared to that heat treated under air, which results from its higher electron concentration. This lower polarization under high charge/discharge rates of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heat treated under N_2 atmosphere leads to its better rate capability.

4. Conclusions

The spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were prepared by heat treating the mixture of rutile TiO_2 and Li acetate under nitrogen atmosphere, and, for comparison, under air. The two samples have similar particle size and specific surface area, but the powders heated under N_2 showed better rate capability and cycle stability in comparison with those heated under air. The discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air at 19°C was 85 mA h g^{-1} , while the capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under N_2 reached 107 mA h g^{-1} . Meanwhile, the cycle stability of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under N_2 was also much better than that of the sample heated under air, indicating that heat treatment under reducing or low-oxygen partial pressure atmosphere such as N_2 could greatly improve the high-rate performance of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

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