Plasma-Introduced Oxygen Defects Confined in Li$_4$Ti$_5$O$_{12}$ Nanosheets for Boosting Lithium-ion diffusion

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Abstract

Although Li$_4$Ti$_5$O$_{12}$ (LTO) is considered as promising anode material for high-power Li-ion battery with high safety, the sluggish Li-ion diffusion coefficient restricts its wide application. In this work, oxygen vacancy was successfully incorporated into LTO by an eco-friendly and cost-effective plasma process. The deficient LTO delivers much higher capacity of 173.4 mAh g$^{-1}$ at 1 C rate after 100 cycles and 140.5 mAh g$^{-1}$ at 5 C after 1000 cycles than those of the pristine LTO. Meanwhile, even at high rate of 20 C it displays an ultrahigh capacity of 133.1 mAh g$^{-1}$ after 500 cycles with a Coulombic efficiency of 100%. Detailed analysis discovers that the lithium storage mechanisms in the oxygen-deficient LTO, especially at high rate, were dominated by the insertion behavior and dual-phases conversion due to the fast ion diffusion ability, rather than the widely reported surface capacitance by other approaches. This work highlights that the defect generation by plasma in nanomaterials is an effective way to promote the ion mobility, especially at high rate, thus can be extended to other electrode materials for advanced energy-storage applications.
1. Introduction

Electrochemical energy storage is of intensive interest to meet the increasing demands of electronic devices, vehicles and renewable energy commercialization. Among various techniques, lithium-ion batteries (LIBs) have not only dominated portable energy storage, but also attracted continuous research interests in pursuit of higher charge capacity and rate capability for upcoming large-scale applications. In general, the lithium storage ability strongly depends on the properties of electrode materials, and thus corresponding studies, especially of anode materials, stand out as the research core recently.\textsuperscript{1-2} Carbon-based materials have been widely used for commercial anodes, but suffer from large volume expansion and shrinkage during Li-ion intercalation/extraction and safety concerns owing to the lithium dendrite formation at low Li-ion intercalation potential. Therefore, it is significant to develop other alternative anodes.\textsuperscript{3-7}

The spinel Li$_4$Ti$_5$O$_{12}$ (LTO) has attracted wide attention as a potential intercalation-type anode candidate with long cycling stability and high safety. The preeminent performance is ascribed by a negligible volume change (often called as ‘zero-strain’) during the Li-ion insertion/extraction accompanied with one-electron transfer of Ti$^{4+}$ and Ti$^{3+}$ redox. A LTO lattice cell can accommodate three Li-ions with a theoretical specific capacity of 175 mAh g$^{-1}$ at comparatively high flat potential of 1.55 V, thus avoiding the formation of dendrites. Despite these superiorities, the rate capabilities of LTO are unsatisfactory due to the poor Li-ion diffusion coefficient ($\sim$10$^{-13}$ cm$^2$ s$^{-1}$).\textsuperscript{8-11} Various strategies have been proposed to improve the Li-ion diffusion of LTO, including reducing the particle size, doping heteroatoms (including cations and anions), fabricating distinctive nanostructure, coating carbon and other materials.\textsuperscript{12-18} In an attempt to overcome this challenge, the first question that arises is the origin of capacities at different rates, which may come from bulk (insertion/extraction) or surface (pseudocapacitance or double-layer capacitance), as different mechanisms require distinguishing strategies for optimizing Li-ion diffusion.\textsuperscript{19-23}

Introducing oxygen vacancies (OVs) has been proved as an efficient strategy to improve the capacities at high rates with the contributions of enhancing bulk capacities \textsuperscript{19-20} and surface capacitances \textsuperscript{21-24}. The preparation of the OVs is usually
realized by thermal treatments in reducing atmosphere and hydrothermal synthesis with discreet controls. However, these processes usually require long time and high energy consumption, and even with chemical pollution. Plasma treatments provide one promising option to circumvent these problems as an eco-friendly and energy-saving alternative to existing processes. In addition, plasma is ionized gas and contains charged particles with high kinetic energy, showing powers to functionalize, tailor and fabricate surfaces and nanomaterials.\textsuperscript{25-27}

With the interaction between the active particles in plasma and the bombarded subjects, it has been found that OVs can be effectively created in many anode materials such as Co\textsubscript{3}O\textsubscript{4}, TiO\textsubscript{2} and MoS\textsubscript{2}.\textsuperscript{28-30} For example, He \textit{et al} \textsuperscript{31} synthesized oxygen-deficient TiO\textsubscript{2} in Ar/H\textsubscript{2} plasma, which exhibited improved electrochemical performance. In addition, the OVs by plasma bombardment can boost the sodium-ion storage of TiO\textsubscript{2} as reported by Gan \textit{et al} \textsuperscript{32} owing to the improved ion diffusion coefficient and possible surface pseudocapacity process. Within the knowledge of the authors, there are few studies on plasma effects on LTO. Lan \textit{et al} \textsuperscript{33} only treated the as-fabricated electrode (the mixture of LTO, conductive carbon and binder) by atmospheric pressure plasma in Ar/N\textsubscript{2} and achieved improved capacity (132 mAh g\textsuperscript{-1}) and stability for 100 cycles at 10 C by the presence of OVs. Clearly the plasma effects on Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} as well as the storage mechanisms of introduced OVs, especially the Li-ion mobility at high rate, need be further explored.

Herein, the as-synthesized LTO nanosheets were treated by plasma process in a reducing atmosphere to produce oxygen defects in the spinel lattice. In comparison with the pristine LTO, the plasma-treated LTO (PLTO) shows significantly improved electrochemical energy storage with ultrahigh specific capacity (173.4 mAh g\textsuperscript{-1} at 1 C after 100 cycles), and remarkable rate capacity (133.1 mAh g\textsuperscript{-1} at 20 C after 500 cycles), which are 18\% and 48\% higher than those of the LTO, respectively. The electrochemical analysis fully evidence that the lithium storage of LTO nanosheets are diffusion-controlled mechanism rather than a capacitive process-dominated mechanism, even at the high rate of 5 C. Hence, introducing OVs by plasma into LTO to improve Li-ion diffusion in bulk is an effective strategy to deliver a high rate-performance. This study offers the highly efficient approach for targeted design for performance enhancement, and provides a new insight into the influence of plasma modulated OVs for intercalation-type anode materials.
2. Experimental

2.1 Material Synthesis

Li_4Ti_5O_12 nanosheets were synthesized through a facile strategy. In detail, 20 mM tetrabutyl titanate was added into 40 mL of anhydrous ethanol, fully stirring for 30 min. Meanwhile 18.4 mM LiOH•H_2O was dissolved into 40 mL of deionized water with complete dissolution. Then, the LiOH solution was dropwise added into the tetrabutyl titanate ethanol solution with vigorously stirring. The mixture was stirred for 2 h to fully mix the components. Subsequently, the solution was transferred to a 100 mL Teflon-lined autoclave, then heated at 180 ºC for 24 h. after cooled down to room temperature, the precipitates were centrifuged and washed with ultrapure water and ethanol, and then dried at 60 ºC for 12 h. Finally the obtained precursor was calcined at 600 ºC for 6 h in air. The Li_4Ti_5O_12 nanosheets were obtained.

2.2 Plasma Treatment

The deficient LTO nanosheets were prepared by treating the LTO precursor in a H_2/N_2 (the flow rate of H_2 and N_2 were both 100 sccm) plasma atmosphere. The process maintained at the pressure of 5 Pa and temperature of 150 ºC for 2 h.

2.3 Material Characterization

Phase analysis of as-prepared samples were initially characterized by X-ray diffraction (XRD) using an X-ray diffraction analyzer with Cu-Kα radiation (D8-Discover, Bruker). The morphology and microstructure of samples were analyzed using a field emission scanning electron microscope (FESEM, Sirion, FEI) and a high-resolution transmission electron microscope (HRTEM, Tecnai F20, FEI). The electronic state of samples were investigated by X-ray photoelectron spectroscopy (XPS) using a VG MultiLab 2000 system with a monochromatic Al Kα X-ray source (Thermo VG Scientific). The transmittance spectra of the anode materials were recorded using a diffuse reflectance UV-VIS spectroscopy with wavelength from 200 to 800 nm. Raman (Thermo Fisher DXRxi) measurement was conducted with a laser wavelength of 532 nm.
2.4 Electrochemical Measurements

The electrochemical performance of materials was examined using a CR2032-type coin cell assembled in an Ar-filled glove box. The working electrodes were prepared by evenly mixing the Li$_4$Ti$_5$O$_{12}$, super P and polyvinylidene difluoride (PVDF) in a weight ratio of 75:15:10. The uniform slurry was coated onto a pure Cu foil and dried at 80 °C for 12 h under vacuum. The working electrodes were punched into 13 mm diameter circular disks with an active-material loading of ~1.2 mg cm$^{-2}$. Pure lithium foil was used as the counter electrode and the Celgard 2400 was used as the separator. The 1M solution of LiPF$_6$ in ethylene carbonate and dimethyl carbonate (EC+DMC,1:1) was used as electrolyte. The galvanostatic charge/discharge measurements were implemented using a LAND battery test system in the voltage range of 1.0 to 2.5 V (vs. Li/Li$^+$) at different current densities. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed using a CHI660e electrochemical station. The EIS measurement was conducted in the frequency range of 0.1 Hz to 100 kHz at the open circuit voltage.

3. Results and discussion

3.1 Microstructure and phase constituents

The as-synthesized LTO by the hydrothermal fabrication was treated by plasma process at 150 °C in a mixture of hydrogen and nitrogen atmosphere (denoted as PLTO) as demonstrated in Figure S1. The SEM images in Figure 1a&1b show that both samples display similar nanosheet features, but the PLTO possesses smaller size due to the etching effects originating from the sputtering effects of the energetic particles in plasma. The particle size distribution curves of the two samples also confirm the reduced size of PLTO, as shown in Figure S2. The XRD patterns of both samples in Figure 1c show clear diffraction peaks indexed to cubic spinel LTO (JCPDS No. 49-0207) with trace amount of anatase TiO$_2$ (JCPDS No. 21-1272) and rutile TiO$_2$ (JCPDS No. 21-1276). Rietveld refinement analysis in Figure 1d&1e indicates that the phase constituents were similar and negligibly affected.
3.2 Oxygen vacancies

Notwithstanding, magnified diffraction peaks of (111) and (400) in Figure 2a&2b show clear shifts to lower diffraction angles due to the lattice expansion (~1%) after the plasma treatment. Meanwhile, the lattice expansion of plane (111) was also observed in HRTEM in Figure 2c&2d. This can be attributed to the formed defects in the lattice, especially the OVs, by bombardments of energetic particles in plasma, leading to the partial reduction of Ti$^{4+}$ ions to larger Ti$^{3+}$ ions to maintain the charge neutrality. The expanded lattice may facilitate the ion diffusion and is beneficial for improved electrochemical performance.$^{37-39}$
In order to confirm the existence of OVs, the surface chemical states of both samples were investigated by X-ray photoelectron spectroscopy (XPS) in Figure 3 and Figure S3. Figure 3a&3b show the fitting curves of O 1s spectra that are decomposed into three peaks, locating at 529.5, 532.3 and 531.6 eV corresponding to the Ti-O bonds, the hydroxyl species of surface-adsorbed water molecules, and the defects with low oxygen coordination, respectively. The peak area at 531.6 eV for PLTO is 11.59 % greater than that of LTO (8.02%), indicating more OVs. Compared to those of LTO, the Ti 2p peaks of PLTO shifted to the lower binding energy, from 458.4 and 464.1 eV to 458.0 and 463.9 eV respectively. Meanwhile, the fitted peak for Ti$^{3+}$ is shown in Figure S3c & 3d. It can be clearly observed that PLTO possesses more Ti$^{3+}$ (13.77%) than LTO (6.94%) after the introduction of OVs. The conversion of Ti from +4 to +3 valence state always companies with the formation of oxygen vacancy for the overall charge balance. 

**Figure 2.** Enlarged XRD patterns of (a) the (111) diffraction peak and (b) the (400) diffraction peak. HRTEM images of (c) LTO and (d) PLTO.
Electron paramagnetic resonance (EPR) results further consolidate the existence of OVs. As shown in Figure 3c, there is a high signal of $g$ at 2.003 in PLTO which originates from the unpaired electrons trapped in OVs. Meanwhile, the existence of Ti$^{3+}$ is also confirmed by EPR signal at $g=1.945$ assigned to Ti$^{3+}$ in Figure S4.\textsuperscript{31, 45-47} The variation of bandgap evidenced by UV-vis DRS spectra in Figure 3d and the blue-shifted Ti-O Raman peaks for PLTO in Figure S5 also agree with the existence of OVs.\textsuperscript{48-49}

Figure 3. High resolution of O 1s XPS spectra of (a) LTO and (b) PLTO, (c) EPR spectra and (d) UV-vis DRS spectra of LTO and PLTO.

3.3 Electrochemical performance

Figure 4a displays the first CV cycles of LTO and PLTO at 0.1 mV s$^{-1}$, in which both samples show a pair of redox peaks at ~1.5 V/~1.65 V, corresponding to the Li-ion insertion/desertion in Li$_4$Ti$_5$O$_{12}$.\textsuperscript{50-51} The PLTO shows lower polarization according to the voltage difference between the anodic and cathodic peaks (~210 mV) and higher peak currents. Moreover, the CV curves for 1st, 2nd and 3rd cycles in Figure S6 show the PLTO presented smaller polarization than LTO, suggesting its better electrochemical kinetics. Figure 4b shows the galvanostatic charge-discharge cycling
results at 1 C (175 mAh g\(^{-1}\)). In comparison with pristine LTO, PLTO exhibited the superior specific capacity of 173.4 mAh g\(^{-1}\) after 100 cycles. The rate capability in Figure 4c was 180.7, 177.8, 171.9, 170.4, 160 and 149.7 mAh g\(^{-1}\) at 1, 2, 5, 10, 20 and 30 C, respectively. When the rate returned 1 C, the discharge capacity recovered to \(\sim177.8\) mAh g\(^{-1}\), which was slightly higher than the theoretic value of Li\(_4\)Ti\(_5\)O\(_{12}\). Considering similar morphology features and other measurement parameters, the extraordinary capacity of PLTO may be attributed to the existence of OVs which can act as extra Li\(^+\) trapping sites during the electrochemical process.\(^{52-55}\)

Figure 4. (a) The first cycle of CV curves of LTO and PLTO at 0.1 mV s\(^{-1}\), (b) cycling performance of LTO and PLTO at 1 C, (c) rate performance of LTO and PLTO, (d) cycling performance of LTO and PLTO at 5 C, (e) cycling performance of PLTO at 20 C.
The long-term stability at high rates in Figure 4d&4e. At the rate of 20 C, a high capacity of 133.1 mAh g\(^{-1}\) can be reached for PLTO after 500 cycles, whereas the LTO exhibited a capacity of only 90.4 mAh g\(^{-1}\). At 5 C, PLTO delivered a high capacity of 140.5 mAh g\(^{-1}\) at 5 C after 1000 cycles, with a CE of ~100%. The initial CE of PLTO at 20 C and 5 C were 95.03% and 74.07% respectively. The relatively low initial CE of PLTO is ascribed to the absorbed trace water and surface defects as a common phenomenon of nanomaterials.\(^{50}\) In comparison with the pristine LTO, the specific capacity has been increased by 18% and 48% respectively indicating that the introduced OVs can greatly boost the kinetic properties of Li\(_4\)Ti\(_5\)O\(_{12}\).\(^{56}\) Meanwhile, the comparison of the electrochemical performance of the PLTO with the reported electrodes is shown in Table S2 and the PLTO shows significantly improved performance.

**Figure 5.** Discharge/charge curves of (a) PLTO and (b) LTO at various rates from 1 C to 30 C, discharge curves of LTO and PLTO at (c) 1 C and (d) 5 C, corresponding capacity contributions of different regions for LTO and PLTO at (e) 1 C and (f) 5 C.
Since the origin of capacities at different rates is important to understand the detailed influences of OVs, the charge/discharge curves of LTO and PLTO at different rates are further investigated to visualize the detailed contributions of different storage mechanism. Figure 5a&5b show the improved electrochemical performance of PLTO with higher specific capacities and less polarization than that of LTO in consistent with the CV results.\textsuperscript{57-58} Figure 5c&5d compare the discharge curves of LTO and PLTO at 1 C and 5 C which can be separated into three voltage regions: the decreasing voltage region from the open-circle voltage to $\approx$1.55 V (denoted as R1), the plateau at $\approx$1.55 V (denoted as R2) and a sloping region from $\approx$1.55 to 1 V (denoted as R3). The R1 is related to the Li-ion insertion into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ bulk by the formation of a solid solution domain. The R2 displays a dual-phase conversion region where $\text{Li}_4\text{Ti}_5\text{O}_{12}$ converts to $\text{Li}_7\text{Ti}_5\text{O}_{12}$, and the R3 is considered as the interfacial Li-ion storage in the solid-liquid and the solid-solid interface.\textsuperscript{35,43,59-61}

As presented in Figure 5e&5f, the increased capacity of PLTO was mainly introduced by the Li-ion stored through insertion in Region R1 and the phase transition in Region R2, which belong to the contribution of bulk storage. At Region R1, the contributed capacity for PLTO and LTO were 17.1 and 12.3 mAh g$^{-1}$ at 1 C, respectively. At 5 C, the PLTO displayed more significant contribution from R1 almost double of LTO (18.8 mAh g$^{-1}$ vs 9.8 mAh g$^{-1}$). At Region R2, the contributed capacities of PLTO were also higher, especially at the high rate at which the enhanced capacity reached 30%. In contrast, the contributed capacities of R3 are much lower and display negligible difference between LTO and PLTO, indicating interfacial capacity has much less contribution than the bulk capacity that is different from the dominant pseudocapacitive effects of OVs using non-plasma processes.\textsuperscript{28,57,62-63}
To confirm our hypothesis, cyclic voltammetry (CV) measurements at various sweep rates from 0.2 to 4 mV s\(^{-1}\) of LTO and PLTO were performed. It has been found that the redox peak current \(i_p\) increased with the increase of square root of sweep rate \(v\) with a linear relationship as presented in Figure 6b&6d, indicating that the charging mechanism was dominated by the lithium ion diffusion.\(^{40, 54, 63-65}\) The diffusion coefficient \((D_{\text{Li}})\) of lithium ion is calculated by the Randles-Sevcik equation:\(^{48, 66-67}\)

\[
i_p = (2.69 \times 10^5) n^{3/2} A D_{\text{Li}}^{1/2} C_{\text{Li}} v^{1/2}
\]

Equation 1

where \(n\) is the number of electrons involved in the electrode reaction, \(A\) is the area, \(C_{\text{Li}}\) is the concentration of lithium ions. The \(D_{\text{Li}}\) of lithiation and delithiation for PLTO are \(4.85 \times 10^{-7}\) and \(3.29 \times 10^{-7}\) cm\(^2\) s\(^{-1}\) respectively, about one order higher than those of LTO \((7.03 \times 10^{-8}\) cm\(^2\) s\(^{-1}\) and \(1.59 \times 10^{-8}\) cm\(^2\) s\(^{-1}\)).
Figure 7. Electrochemical impedance spectra of LTO and PLTO measured after (a) 1st cycle, (b) 20th cycle, (c) 50th cycle, (d) $Z'$ vs $\omega^{-1/2}$ at low frequency regions.

Electrochemical impedance spectra measurements (EIS) in Figure 7 were also performed to study the improved electrochemical performance. All the spectra were composed of a semicircle in the high- and medium-frequency range followed by a straight line at low frequency.\textsuperscript{50, 68-70} The PLTO prior to cycling possessed lower charge-transfer resistance ($R_{ct}$) (77.82 $\Omega$) than that of LTO (124.62 $\Omega$). Even after 20 cycles (Figure 7b) and 50 cycles (Figure 7c), the PLTO still displayed lower $R_{ct}$ as listed in Table S1, indicating that the charge transfer kinetic was significantly improved by introduction of OVs. The charge-transfer resistance displays a decreasing trend with the increase of the cycles as demonstrated in Figure 7 which can be ascribed by that the irreversible lithium insertion into the oxygen vacancy sites and grain boundaries in electrodes during activation process can increase the conductivity and also the enhanced wetting performance between electrode and electrolyte.\textsuperscript{71-73}
The diffusion coefficient $D_{Li}$ of Li-ion in bulk material can be also evaluated by Equation 2:50, 74

$$D_{Li} = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma^2} \quad \text{Equation 2}$$

where $R$, $T$, $F$, $A$ and $C$ are the gas constant, the absolute temperature, the Faraday's constant, the apparent area of the electrode and the molar concentration of Li-ions, respectively. The values of $\sigma$ can be obtained from the slopes of the lines in the graph of $Z'$ vs $\omega^{-1/2}$. As listed in Table S1, the PLTO also processed higher diffusion coefficient than that of LTO (~2-3 times), in agreement with the CV results.

Based upon, the plasma introduced OVs in LTO possess enhanced Li-ion diffusion coefficients by the CV and EIS measurements, leading to the improved superior electrochemical properties at high rates. As shown in Figure 5e&5f, the main contribution to the specific capacity of PLTO and LTO was the lithium insertion reaction and dual-phase conversion, corresponding to the region 1 and region 2 in Figure 5c&5d. The interfacial storage ability of the two samples shows almost negligible change. Moreover, when the rate increased to 5C, the capacities of both samples in region 3 were nearly the same with the capacities in region 3 at low rates, while the gap of the whole capacities at different rates result from the different contributions in region 1 and 2. This result indicated that the lithium storage mechanism of PLTO at high rates was still dominated by the lithium insertion and dual-phase conversion behavior. It is worth noting that the introduced OVs by many other approaches (e.g. thermal treatment and hydrothermal synthesis) are often accompanied with appreciable pseudocapacity effects 21-22 where charge storage occurs via Faradaic charge transfer at or near the surface of the material. The plasma process, therefore, offers a targeting approach to enhance the Li-ion diffusion of the LTO nanosheets. Through the bombardment by energetic particles in plasma, the lattice constant can be enlarged due to the synergistic effects of the defects and chemical variation as evidenced by the XRD and TEM analysis. In addition, the recent study 65, 75 demonstrates that the enhancement of Li-ion diffusion coefficient may be attributed to the local built-inside electric field originated from the unbalanced
charge distribution around the OVs.\textsuperscript{76-77} Thus, the oxygen defects introduced by plasma significantly enhanced the electrochemical performance of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} by boosting the Li-ion diffusion. Although oxygen vacancies (OVs) can significantly improve the electrochemical performance, it is a great challenge to stabilize the OVs especially under oxidizing conditions in which the OVs are very active. Within the knowledge of the authors, there are limited stabilizing strategies including the oxygen deficient atmosphere, heteroatom doping, the specific crystalline plane and the interfacial strain. Clearly, it is of great importance to understand the working mechanisms and evolution of OVs in electrochemical systems and more work need be carried out in this field.

4. Conclusion

In summary, this work brought forward a facile, low temperature, eco-friendly and cost-effective plasma approach to generate structural defects to improve the electrochemical properties of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}. Benefiting from the introduction of oxygen vacancies, the PLTO exhibited not only high lithium storage ability (a high capacity of 173.4 mAh g\textsuperscript{-1} at 1 C) but also impressive rate capacity (133.1 mAh g\textsuperscript{-1} after 500 cycles at 20 C with a Coulombic efficiency of 100%). The lithium storage mechanisms in the oxygen-deficient PLTO, especially at high rate, were dominated by the insertion behavior and dual-phases conversion due to the fast ion diffusion ability. Such results suggest that the defect generation by plasma in nanomaterials is an effective way to promote the ion mobility, especially at high rate, thus can be extended to other electrode materials for advanced energy-storage applications.

Supporting information

Supporting Information is available from the ACS Online Library or from the author.

Schematic of plasma treatment; Particle size distribution curves of PLTO and LTO; (a) XPS spectra of LTO and PLTO, (b) high solution of Ti 2p XPS spectra of LTO and PLTO, (c) Ti 2p fitted spectra of LTO, (d) Ti 2p fitted spectra of PLTO. EPR spectra of LTO and PLTO; Raman spectra of LTO and PLTO; The CV curves of PLTO and
LTO for 1st, 2nd and 3rd cycles; The $R_d$ value of LTO and PLTO; The elements obtained from the fitting EIS data; Comparison of the electrochemical performance of the plasma-treated LTO with the reported LTO electrodes.

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**Conflict of Interest**

The authors declare no conflict of interest.

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