Tunable Architectures of Niobium-doped Anatase TiO₂ for High Rate Capability Lithium-ion Batteries

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Abstract

Synthesis of metal doped nanostructures with special architecture is a quite considerable challenge in the field of energy storage materials. To promote the high rate capability and cyclability, architectures of anatase TiO₂ transformed from spherical-like to plate-like are controlled by niobium atoms. Large quantity of niobium atoms induce TiO₂ to expose (001) facets along the carbon spheres. In electrochemical performance, the plate-like niobium-doped TiO₂ displays a high specific capacity of ~220 mAhg⁻¹ at 0.5 C and still retains ~127 mAhg⁻¹ at 10 C. Using CV measurements reveals that the improvements of rate capability are beneficial from the Li-ion storage near the particle surface. It is demonstrated that the near-surface redox behaviors recognized as the pseudocapacitance plays a major role when increasing current density. This study helps to understand the importance of pseudocapacitive storage in the high rate capability anode materials.

Experimental procedure

1) glucose in 20 ml DI-water, hydrothermal process at 190 °C
2) Acetic acid, niobium oxalate, titanium chloride added into the solution
3) Transferred into autoclave and kept at 150 °C.
4) Calcination at 450 °C

Electrolyte: 1.0 M LiPF₆ in EC/DMC (1:1, vol. %)
Voltage range: 1 V and 3 V.
C-rate: 0.5, 1, 2, 5, 10, and 20 C.

Structure identification

Fig. 1. (a) XRD patterns and (b) magnified (101) peaks of TiₓNbₓO₂
- The X-ray diffraction patterns of Nb-TiO₂ can be all indexed as the pure anatase phase (ICPDs card no. 21-1272) except Nb50.
- No diffraction peaks observed for the impurities of niobium oxide or TiNb₂O₆.
- The (101) peaks gradually shifted to the lower incident angle, indicating that TiO₂ lattice is expanded by the larger ionic radius of Nb⁵⁺.

Morphology and microstructure

Fig. 2. SEM images of (a) pristine TiO₂, (b) Ti₀.75Nb₀.25O₂, (c) Ti₀.65Nb₀.35O₂.
TEM images of (d) pristine TiO₂, (e, f) Ti₀.65Nb₀.35O₂.
- The morphology of TiO₂ is gradually changed from spherical (pristine) to plate-like (Nb=0.35) and the coexistent morphology can be seen in Nb=0.25.
- The plate-like of Ti₀.65Nb₀.35O₂ is pieced by many nanorods with similar alignment direction along (101) planes.
- The d-spacing of Ti₀.65Nb₀.35O₂ shows a slight expansion due to the larger radius of Nb⁵⁺.

Table 1. d-spacing (Å) of pristine TiO₂ and Ti₀.65Nb₀.35O₂

<table>
<thead>
<tr>
<th>Sample name</th>
<th>pristine TiO₂</th>
<th>Ti₀.65Nb₀.35O₂</th>
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<tr>
<td>(001)</td>
<td>2.7</td>
<td>2.95</td>
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<tr>
<td>(001)</td>
<td>3.6</td>
<td>3.67</td>
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Cyclic voltammetry analysis

Fig. 4. Cyclic voltammetry of (a) pristine TiO₂ and (b) Ti₀.65Nb₀.35O₂ between 0.1 and 2 mV. (c) The kinetic study the power-law relationship between peak current and sweep rate
- Two shoulder peaks of Ti₀.65Nb₀.35O₂ located at 1.54 and 1.65 V have similar location as the electrochemical behavior of TiO₂(B), which is known for its highly exposed (001) facets.
- The b-value of pristine TiO₂ and Ti₀.65Nb₀.35O₂ is close to 0.52 and 0.72, respectively, suggesting that the kinetics of Ti₀.65Nb₀.35O₂ exhibit more surface storage process (pseudocapacitance) than pristine.

Conclusion

- The plate-like Nb-TiO₂ is assembled by nanorods with special orientation along (001) facets and the morphology is composed of relatively narrow pore size distribution and higher specific surface area.
- The cyclic voltammetry analysis reveals that the superior performance of Nb-TiO₂ is promoted by the surface storage.
- All of the results show that the benefits of doping Nb not only improve Li-ion diffusivity of TiO₂ but alter the morphology into more suitable for Li-ion transportation.

Fig. 3. (a) Rate capability between pristine TiO₂ and Ti₀.65Nb₀.35O₂. (b) The potential difference of phase transformation region for different current rate, (c) Ti₀.65Nb₀.35O₂ cycling at 20C.
- The capacity of Ti₀.65Nb₀.35O₂ is 220, 201, 187, 157, 127 mAhg⁻¹ at the rates of 0.5, 1, 2, 5, 10 C, respectively, while the pristine TiO₂ displays 170, 131, 90, 53, 31 mAhg⁻¹ at the corresponding rates.
- As compared to 0.5 C, Ti₀.65Nb₀.35O₂ can even maintain 60 % of capacity at 10C.
- Ti₀.65Nb₀.35O₂ exhibit less polarization than pristine TiO₂ (Fig. b), which is attributed to low ohmic resistance in Nb₃5 electrode.
- At a rate of 20 C, reversible capacity of 120 mAhg⁻¹ is retained after 8000 cycles. This proves that the structure of Ti₀.65Nb₀.35O₂ is considerably stable.

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