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Improved electrochemical performance of nitrogen doped TiO₂-B nanowires as anode materials for Li-ion batteries†

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N-doped TiO₂-B nanowires are prepared by the solvothermal method using TiN nanoparticles as the starting material. X-ray photoelectron spectroscopy shows that the N dopants preferentially occupy the interstitial sites of TiO₂-B up to a content of ~0.55 at%. Above this critical value, the N dopants will substitute the oxygen atoms which improve the electronic conductivity of TiO₂-B. The maximum proportion of substituted-N in the TiO₂-B nanowires is ~1.3 at%. Raman scattering shows that the substituted-N strengthens the Ti(1)–O₁–Ti(2) and O₁–Ti(1)–O₃ bonds of TiO₂-B. This improves the stability of the corresponding local structures, thus reducing the distortion of the Li⁺ diffusion channel along the *b*-axis of TiO₂-B. As a result, the substituted-N has more of an impact on the electrochemical properties of TiO₂-B than the interstitial-N does. The TiO₂-B nanowires containing substituted-N dopants exhibit a remarkably enhanced electrochemical performance compared to pure TiO₂-B. They show a discharge capacity of 153 mA h g^{−1} at the 20 C rate with a capacity retention of 76% after 1000 cycles. In addition, they can deliver a discharge capacity of 100 mA h g^{−1} at an ultra-high rate of 100 C, indicating their great potential in high power lithium ion batteries.

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1. Introduction

Lithium ion batteries are considered as one of the most prominent energy storage devices due to their high energy densities and long cycle life. Conventional lithium ion batteries use graphite as the anode material which is cheap, abundant and stable for cycling. However, both natural graphite and artificial graphite have severe safety concerns because they operate close to the Li⁺/Li redox couple with a risk of metallic lithium plating and dendrite formation at an overcharged state.¹ In addition, they suffer from a high irreversible capacity loss during the initial cycles due to the formation of a solid electrolyte interphase (SEI) film.² As a consequence, searching for alternative anode materials is strongly required for the development of next generation lithium ion batteries.

Among various new anode materials under consideration, titanium dioxides (TiO₂) including anatase, rutile and bronze (TiO₂-B) have attracted particular attention because of their long cycle life, high safety and minimum environmental impact.^{3–10} The higher redox potential of titanium dioxides (~1.6 V vs. Li/Li⁺) endows them with greater overcharge protection than graphite. In addition, the material can be easily made in nanostructured forms thus permitting access to fast charge–discharge rates. A major problem for the TiO₂ anodes is their high working voltages compromising the cell voltage and hence the energy density. This shortcoming can be partly overcome by coupling with high voltage cathode materials such as LiNi_{0.5}Mn_{1.5}O₄ (4.7 V vs. Li/Li⁺), or high capacity cathode materials such as Li-excess layered oxides Li[Li_xM_{1–x}]-O₂ (M = Mn, Ni, Co).^{11–13}

Among different titanium dioxides, TiO₂-B is the most attractive one due to its large specific capacity and excellent rate capability. TiO₂-B can store more than 250 mA h g^{−1} in its nanostructured forms.^{14–16} In contrast, the practical specific capacities of anatase and rutile TiO₂ are limited to 168 mA h g^{−1}. However, the electrochemical performance of TiO₂-B is seriously restricted by its low electronic conductivity and small lithium diffusion coefficients. These problems can be overcome by preparing nanostructured TiO₂-B combined with carbonaceous additives such as carbon nanotubes, carbon fibers,

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graphene, *etc.*^{17–22} But, the carbonaceous additives can only tailor the electron transport on the particle surface and between adjacent particles; the intrinsic electronic conductivity of the TiO₂-B bulk is still poor. In addition, the carbonaceous additives in the composite anodes decrease the tap density of the materials and thus sacrifice the energy density of the battery.

Recently, it has been shown that the intrinsic electronic conductivity of TiO₂ can be improved by doping of some aliovalent ions such as Nb⁵⁺, V⁵⁺, P⁵⁺, Fe³⁺, Zn²⁺, N^{3–}, S^{2–} and F[–].^{23–31} In addition, slight modification of the TiO₂ lattice can be achieved by the dopant atoms which may improve the diffusion of lithium ions. For example, J. G. Kim *et al.* prepared N-doped TiO₂ nanofibers by the electrospinning method. The N-doped nanofibers showed a discharge capacity of 185 mA h g^{–1} at the 0.1 C rate, which was much higher than that of the un-doped counterpart.³² H. K. Han *et al.*, reported that the discharge capacity of N-doped TiO₂ hollow nanofibers (85 mA h g^{–1}) at the 2 C rate was nearly two times higher than that of ordinary TiO₂ nanoparticles.²⁹ G. Liu *et al.* prepared N and S co-doped TiO₂ nanocrystals. The material showed superior rate performance due to its high electronic conductivity.³⁰ Y. M. Li *et al.* reported that the N-doped anatase TiO₂ and N-doped graphene nanocomposites showed much better electrochemical performance than that of pristine TiO₂.³³ In addition, our recent work showed that the lithium diffusion coefficients of N-doped anatase TiO₂ were increased about 13 times with respect to its un-doped counterpart.³⁴ These studies suggest that N doping could be a suitable method for improving the electrochemical properties of TiO₂-B. However, to the best of our knowledge, there is no study reported on the effects of N-doping on the electrochemical properties of TiO₂-B. In this work, for the first time, we prepared N-doped TiO₂-B nanowires by the solvothermal method. The material shows good cycling stability and excellent rate capability for Li ion storage which indicates its potential applications in high power lithium ion batteries. In order to reveal the origin of the excellent electrochemical performance, the physical and structural properties of the materials were studied by X-ray photoelectron spectroscopy and Raman scattering. Their electrochemical kinetic properties were studied by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic intermittent titration technique.

2. Experimental section

2.1 Synthesis of N-doped TiO₂-B nanowires

The N-doped TiO₂-B nanowires were prepared by using commercial TiN nanoparticles (T110281, Aladdin) as the starting materials. The TiN nanoparticles were heat treated at 400 °C in air to obtain the N-doped TiO₂ precursors. The contents of N in the precursors were adjusted by changing the heat treatment time from zero minute to 30 minutes. To prepare pure TiO₂-B nanowires, the heat treatment temperature was increased to 500 °C and the heating time was increased to

10 h. The pure and N-doped TiO₂-B nanowires were synthesized by the hydrothermal reaction of the above precursors. As a typical procedure, 0.4 g of the precursor powders was dispersed in 40 mL of 10 mol L^{–1} NaOH solution. The suspension was transferred into a 50 mL autoclave. The autoclave was then sealed and heat treated at 170 °C for 60 h. After cooling to room temperature, the obtained precipitates were isolated from the solution, followed by constant stirring in 0.1 mol L^{–1} of HCl solution for 4 h to obtain a proton exchanged titanate precipitate. The precipitate was then centrifuged and washed completely with deionized water. Afterwards, the material was freeze-dried at –30 °C for 20 h. Finally, the material was heat treated at 450 °C for 4 h under N₂ flow to improve the crystallization of the products.

2.2 Material characterization

The crystal structure of the materials was studied by X-ray diffraction (XRD) on a Bruker AXS D8 X-ray diffractometer with Cu K α radiation. The lattice parameters were calculated by the Celref 3 Program. The morphology of the materials was studied by using a JSM-6700F field emission scanning electron microscope (FESEM). High-resolution transmission electron microscopy (HRTEM) images were obtained using a FEI Tecnai G2 electron microscope coupled with an X-ray energy dispersive spectroscopy (EDS, BRUKER AXS). Raman scattering of the products was collected on a Thermo Scientific FT-Raman spectrometer using an Nd-line laser source (λ = 532 nm). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB spectrometer using a Mg-K α light source. The binding energy was corrected using the C 1s peak at 284.6 eV. For measurement of electronic conductivity, the samples were prepared to thin film electrodes on a copper substrate with the thickness about 30 μ m. Then, dc conductivity measurement was performed by the two-electrode method.

Electrochemical experiments were performed using 2032 coin cells with a metallic lithium foil as the anode. The cathode was composed of a 70 wt% active material, a 15 wt% super P conductive additive and a 15 wt% poly(vinylidene fluoride) (PVDF) binder which was pasted on a copper current collector. The loading mass of the active material was 1–2 mg cm^{–2}. The anode and cathode were separated by using a Celgard 2320 membrane. A 1 mol L^{–1} lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC : DMC = 3 : 7) was used as the electrolyte. Galvanostatic charge–discharge cycling was conducted on a LAND-2010 automatic battery tester in the voltage window of 1.0–3.0 V. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) were performed on a Bio-Logic VSP multichannel potentiostatic–galvanostatic system. The impedance data were recorded by applying an *ac* voltage of 5 mV in the frequency range from 1 MHz to 5 mHz. GITT measurement was performed throughout the first discharge process. For each GITT step, the battery was discharged with a current flux of 30 mA g^{–1} for 0.5 h, followed by an open circuit stand for 4 h to reach the quasi-equilibrium state.

3. Results and discussion

3.1 X-ray diffraction

As the first step for material preparation, the TiN nanoparticles were heat treated at 400 °C in air to obtain the precursors. X-ray diffraction shows that the precursor is a mixture of anatase, rutile and TiN due to incomplete reaction of TiN with oxygen (ESI, Fig. S1†). The amount of N in the precursors could be adjusted by changing the heat treatment time. In order to prepare pure TiO₂-B nanowires, the heat treatment temperature should be increased to 500 °C and the heating time should be increased to 10 h. Thereafter, the final products could be obtained by the hydrothermal reaction of the precursors. Altogether, five samples were prepared in this work and their crystal structures were examined by XRD. Fig. 1 shows the XRD patterns of the pure TiO₂-B and two typical N-doped TiO₂-B samples. All patterns exhibit the elaborate diffraction peaks of TiO₂-B having a monoclinic structure with the space group *C2/m*. The diffraction peaks are broad indicating that the products are nanosized materials. The framework

of TiO₂-B is constructed by using corrugated sheets of edge- and corner-sharing TiO₆ octahedra that are linked by bridging oxygen atoms to form a three-dimensional network.³⁵ This structure is more open than those of rutile and anatase TiO₂, making the material a more effective host for lithium storage. The lattice parameters of the pure TiO₂-B nanowires are calculated to be $a = 12.288 \text{ \AA}$, $b = 3.759 \text{ \AA}$, $c = 6.482 \text{ \AA}$, $\beta = 107.06^\circ$, and $V = 286.23 \text{ \AA}^3$ which fit well with those recorded in JCPDS 74-1940. The lattice parameters of the N-doped TiO₂-B samples are similar to those of pure TiO₂-B. The diffraction peaks of these nanomaterials are weak and broad. In addition, the N doping contents are small and the size of N³⁻ ($r = 1.46 \text{ \AA}$) is similar to that of O²⁻ ($r = 1.36 \text{ \AA}$). Due to these reasons, it is difficult to discern the slight changes of the N-doped TiO₂-B materials from the present XRD patterns.

3.2 Morphology and microstructure characterization

The morphologies of the pure and N-doped TiO₂-B samples are studied by SEM as shown in Fig. 2. All the samples are composed of nanowires showing a high aspect ratio with 50–200 nm width and several micrometers length. Owing to the freeze-drying treatments, the samples show good dispersion without significant agglomeration and twinning. These features are conducive to electrode materials soaking in the electrolyte more effectively, thus resulting in satisfying battery performance. The pure TiO₂-B is further studied by TEM as shown in Fig. 3. In the HRTEM image, the lattice fringes with spaces of 0.586 nm and 0.355 nm are due to the (200) and (110) planes of TiO₂-B, respectively. In addition, fast Fourier transform (FFT) of the HRTEM image shows that the TiO₂-B nanowire grows along the [010] direction. The N-doped TiO₂-B samples show similar TEM and HRTEM images to those of pristine TiO₂-B indicating that N doping does not change the atomic structure of TiO₂-B. In order to confirm doping of N in the TiO₂-B nanowires, we carried out EDX analysis for a single nanowire. Fig. 4 shows the dispersive mapping of Ti, O, and N elements which indicates that the N element is uniformly distributed in the material.

Fig. 1 XRD patterns of the P-TiO₂, I-TiO₂ and I/S-TiO₂ samples.

Fig. 2 SEM images of the P-TiO₂ (a), I-TiO₂ (b) and I/S-TiO₂ (c) samples.

Fig. 3 (a) TEM and (b) HRTEM images of the pure $\text{TiO}_2\text{-B}$ nanowires. Inset in (b) shows the fast Fourier transform of the HRTEM image.

Fig. 4 HAADF-STEM image and mapping of the Ti, O and N elements of the I/S- TiO_2 sample. The elemental map signals were obtained by scanning the inset of the HAADF-STEM image.

3.3 X-ray photoelectron spectroscopy

XPS analysis was performed to study the chemical states of Ti, O and N of the materials. All samples show very similar Ti 2p

and O 1s XPS as shown in Fig. 5a and b, respectively. The Ti 2p_{3/2} binding energy is observed at 458.4 eV which fits well with that of Ti^{4+} .³⁶ The O 1s binding energy at 529.6 eV confirms the O^{2-} state of the materials.³⁶ As shown in Fig. 5c, no N 1s XPS is observed for the pure $\text{TiO}_2\text{-B}$ nanowires, but the appearance of N 1s XPS for the N-doped $\text{TiO}_2\text{-B}$ samples confirm the successful doping of N in $\text{TiO}_2\text{-B}$. The N 1s peak at 399.8 eV is due to the interstitial-N with the O-Ti-N linkage, and the other one at 395.6 eV is due to the substituted-N with the direct Ti-N linkage.³⁷ The interstitial O-Ti-N bond shows a higher binding energy than that of the substituted Ti-N because the high electro-negativity of oxygen reduces the electron density on nitrogen. The amounts of interstitial/substituted-N in the samples are calculated to be 0.57/0.72 at% and 0.52/0 at%, respectively. According to the N 1s XPS results of all the prepared samples (ESI, Fig. S2†), it can be concluded that the N dopants preferentially occupy the interstitial site of $\text{TiO}_2\text{-B}$ up to a content of ~ 0.55 at%. Above this critical value, the N dopants will substitute the oxygen atoms of $\text{TiO}_2\text{-B}$. In addition, the maximum substituted-N in the samples is evaluated to be ~ 1.3 at%; otherwise, the TiN impurity will be formed in the material. It has been reported that the substituted-N is more effective than the interstitial-N for improving the electronic conductivity of TiO_2 because it could narrow the band gap of TiO_2 by elevating the valence band maximum, while the interstitial-N can only introduce some localized N 2p states in the band gap, as shown in Fig. 6.³⁰ Accordingly, the interstitial/substituted-N co-doped $\text{TiO}_2\text{-B}$ (hereafter denoted as I/S- TiO_2) is expected to possess a higher electronic conductivity than those of the interstitial-N doped $\text{TiO}_2\text{-B}$ (hereafter denoted as I- TiO_2) and pure $\text{TiO}_2\text{-B}$ (hereafter denoted as P- TiO_2). As shown in Table 1, dc conductivity measurement shows that the electronic conductivity of the pure $\text{TiO}_2\text{-B}$ nanowires is $3.01 \times 10^{-11} \text{ S cm}^{-1}$. The I- TiO_2 sample which contains only interstitial-N shows a larger electronic conductivity of $3.81 \times 10^{-9} \text{ S cm}^{-1}$. Significantly, the I/S- TiO_2 sample containing both interstitial and substituted-N possesses the largest electronic conductivity of $4.61 \times 10^{-8} \text{ S cm}^{-1}$.

Fig. 5 Ti 2p (a), O 1s (b), and N 1s (c) XPS of the P- TiO_2 , I- TiO_2 and I/S- TiO_2 samples.

Fig. 6 Scheme of the band structures of the pure and N-doped $\text{TiO}_2\text{-B}$.

Table 1 Electronic conductivity of the P- TiO_2 , I- TiO_2 and I/S- TiO_2 samples

	P- TiO_2	I- TiO_2	I/S- TiO_2
Electronic conductivity [S cm^{-1}]	3.01×10^{-11}	3.81×10^{-9}	4.61×10^{-8}

3.4 Raman scattering

As mentioned above, the substituted-N is very important for improving the electronic conductivity of $\text{TiO}_2\text{-B}$. In order to know the possible substituted positions of N, we carried out Raman scattering to study the local structure of the samples. The Ti atoms in $\text{TiO}_2\text{-B}$ have different local environments, namely Ti(1) and Ti(2). Both of them are surrounded by six oxygen atoms as shown in the inset of Fig. 7. Group theory calculations have shown 18 Raman active modes for $\text{TiO}_2\text{-B}$ most of which can be observed in Fig. 7.³⁸ In general, the Raman patterns of the three samples are similar except for two major differences. First, the peak intensities of P- TiO_2 and

I- TiO_2 are much stronger than those of I/S- TiO_2 . Even though multiple factors can affect the intensities of Raman peaks, here we can rule out the effects of measurement conditions because all the experiments were performed under the same conditions (including the sample amount, laser power, scattering time, *etc.*). Therefore, the differences in Raman intensities could be attributed to the intrinsic properties of the samples. One of the possible reasons may be the higher electronic conductivity of I/S- TiO_2 . It is known that the material with a high electronic conductivity could reduce the skin depth of the incident photons, thus resulting in low Raman scattering intensities. Second, the positions of all peaks are very stable, only the one located at around 145.6 cm^{-1} (dash line) being an exception. This Raman peak is attributed to the Ti(1)- O_1 -Ti(2) and O_1 -Ti(1)- O_3 vibrations of $\text{TiO}_2\text{-B}$.³⁸ For the I- TiO_2 sample, this Raman peak is still located at 145.6 cm^{-1} which is the same as that of P- TiO_2 . This indicates that the interstitial-N has little impact on the local structure of $\text{TiO}_2\text{-B}$. However, for I/S- TiO_2 having both interstitial and substituted-N, this peak shifts to a higher wavenumber of 154.3 cm^{-1} . This indicates that the substituted-N replaces the O atoms at the O_1 and/or O_3 positions. In addition, the local structures related to the Ti(1)- O_1 -Ti(2) and O_1 -Ti(1)- O_3 bonds are strengthened by the substituted-N atoms.

3.5 Galvanostatic charge-discharge cycling

Fig. 8a compares the first charge-discharge curves of the samples at the 0.5 C rate ($1\text{C} = 300 \text{ mA g}^{-1}$). All the samples display a pair of S-shaped voltage profiles, which are different from the characteristic voltage plateaus at $\sim 1.7 \text{ V}$ for anatase TiO_2 . This is due to the different Li ion intercalation mechanisms of $\text{TiO}_2\text{-B}$ and anatase. It has been reported that the Li^+ intercalation into $\text{TiO}_2\text{-B}$ is a pseudo-capacitive process, rather different from the two-phase diffusion process of anatase.^{39,40} This makes $\text{TiO}_2\text{-B}$ very attractive for fast Li ion transport. The initial discharge/charge capacities for the pure $\text{TiO}_2\text{-B}$ nanowires are $240.9/217.4 \text{ mA h g}^{-1}$ resulting in a coulombic efficiency of 90.2%. The initial capacity loss could be due to Li ion storage at irreversible sites. Also, a part of the capacity loss could be caused by the formation of a solid electrolyte interface (SEI) film as recently reported by P. G. Bruce *et al.*⁴¹ The initial discharge/charge capacities of the samples increase with N-doping. In particular, I/S- TiO_2 ($277.8/249.0 \text{ mA h g}^{-1}$) shows larger specific capacities than those of I- TiO_2 ($252.0/225.5 \text{ mA h g}^{-1}$).

Fig. 8b shows the rate performance of the pure and N-doped $\text{TiO}_2\text{-B}$ samples. The corresponding charge-discharge curves at each current rate are displayed in Fig. 8d-f. At each charge-discharge rate, I- TiO_2 only shows slightly higher capacities than those of P- TiO_2 . In contrast, the discharge capacities of I/S- TiO_2 are much higher than those of I- TiO_2 and P- TiO_2 . When the charge-discharge rate increases to 100 C (30 A g^{-1}), I/S- TiO_2 still has a high discharge capacity of 100 mA h g^{-1} , whereas that of P- TiO_2 is only 75 mA h g^{-1} . In addition, compared to the big fluctuations of pure $\text{TiO}_2\text{-B}$, the specific capacities of I/S- TiO_2 are very stable at this extremely

Fig. 7 Raman spectrum of the P- TiO_2 , I- TiO_2 and I/S- TiO_2 samples. (Inset): scheme of the local structure of $\text{TiO}_2\text{-B}$.

Fig. 8 (a) The first charge–discharge curves, (b) rate-dependent cycling performance, and (c) long term cycling stability of the samples. (d–f) Charge–discharge curves of the samples at different current rates.

high charge–discharge rate. Further, the normalized discharge capacities (ESI, Fig. S3†) also show that the rate capability of the N-doped samples, especially I/S-TiO₂, are better than that of P-TiO₂ especially at high current rates. The cycling stability is also important for the practical applications of lithium-ion batteries.

Here the long term cycling stability of the pure and N-doped TiO₂-B samples are tested at the 20 C rate as shown in Fig. 8c. The pure TiO₂-B nanowires exhibit fast capacity fading in the initial 100 cycles. Then the discharge capacity gradually decreases which is only 85 mA h g^{−1} after 1000 cycles. The corresponding capacity retention is 60%. I-TiO₂ shows slightly improved cycling performance but the capacity retention is still unsatisfying. More excitingly, I/S-TiO₂ shows much better capacity retention. A high discharge capacity of

116 mA h g^{−1} can be obtained after 1000 cycles, and the capacity retention increases to 76%. This indicates that the substituted-N is much more effective than the interstitial-N for improving the electrochemical performance of TiO₂-B. We also studied the long term cycling performance (ESI, Fig. S4†) and rate performance (ESI, Fig. S5†) of all the prepared samples. Overall, the interstitial/substituted-N co-doped samples show much better rate capability and cycling stability than those of the other samples. This further demonstrates that the substituted-N is very important for improving the electrochemical properties of TiO₂-B.

3.6 Cyclic voltammetry

Fig. 9 shows the CV curves of the pure and N-doped TiO₂-B nanowires at different scan rates. The peak-S1 and -S2 are due

Fig. 9 CV curves of the P-TiO₂ (a), I-TiO₂ (b) and I/S-TiO₂ (c) samples at different scan rates. (Inset): linear fitting of the cathodic current vs. scan rate.

Table 2 Slopes of the fitted lines for the S1, S2 and A current peaks

	S1 ^a	S2 ^a	A ^b
I/S-TiO ₂	−1.54	−1.27	−0.43
I-TiO ₂	−1.36	−1.08	−0.41
P-TiO ₂	−1.24	−1.05	−0.40

^a Linear fitting of the cathodic current *versus* (scan rate). ^b Linear fitting of the cathodic current *versus* (scan rate)^{1/2}.

to Li extraction from the TiO₂-B phase. At present there are two different point-of-views regarding the origin of peak-A. Some people think that this peak is due to an anatase impurity phase because TiO₂-B is metastable, so that a part of the material could be transformed to anatase during the heat treatment process.^{42–44} On the other hand, recent theoretical and experimental studies have shown that the peak-A is attributed to Li⁺ intercalation into the interstitial octahedral site of TiO₂-B.^{45,46} Even though there is no definite conclusion up to now, this peak is always observed for TiO₂-B samples. At the scan rate of 0.1 mV s^{−1}, the electrode polarizations (*i.e.* the voltage splitting between the anodic and cathodic peaks) for the pure TiO₂-B nanowires are 0.08 V for peak-S1 and 0.09 V for peak-S2 which are smaller than that of 0.36 V for peak-A. This indicates that the electrochemical kinetics during the peak-S1 and -S2 processes are better than that during peak-A. The corresponding electrode polarizations for I/S-TiO₂ (*i.e.*, 0.04 V, 0.06 V, 0.34 V) and I-TiO₂ (*i.e.*, 0.07 V, 0.08 V, 0.35 V) are smaller than those of P-TiO₂ indicating that N-doping improves the electrochemical kinetics of the electrode.

CV analysis was further used to study the Li ion storage mechanisms of the pristine and N-doped TiO₂-B samples. For all the three samples, the peak-S1 and -S2 display linear relationships against the scan rate (inset of Fig. 9), which is characteristic for the capacitive behaviour:⁸

$$I_p = dQ/dt = CdE/dt = Cv \quad (1)$$

where Q is the voltammetric charge, C is the capacitance and dE/dt is the scan rate (v). The small peak-to-peak splitting (*i.e.* electrode polarization) is a typical feature of faradaic pseudo-capacitance which is different from the ideally rectangle CV curves of double-layer capacitance. On the other hand, the peak-A shows a linear relationship against the square root of the scan rate ($v^{1/2}$) which corresponds to a typical feature of the diffusion-controlled process:^{47,48}

$$I_p = 2.69 \times 10^5 \cdot ACD_{Li}^{1/2} n^{3/2} v^{1/2} \quad (2)$$

where I_p is the peak current, A is the electrode surface area, C is the concentration of Li ions in the electrode, n is the number of electrons involved in the redox process, and v is the scan rate. The specific faradaic pseudo-capacitance behaviour of TiO₂-B is much favourable for fast Li ion intercalation and de-intercalation thus resulting in its excellent rate capability. Table 2 shows the slopes of the fitted lines. For each current

peak, the N-doped samples always show a larger slope than that of pure TiO₂-B nanowires. In particular, I/S-TiO₂ possesses the largest slopes in all the three samples. This indicates that the substituted-N is more effective than the interstitial-N for improving the electrochemical kinetics of TiO₂-B.

3.7 Electrochemical impedance spectroscopy

The electrochemical process of lithium ion batteries involves charge transfer reactions at the electrode/electrolyte interface and Li ion diffusion in the electrode bulk. In order to study the electrochemical kinetics of the materials, ac impedance spectroscopy was conducted at 3.0 V and 1.0 V of the first discharge. Fig. 10 shows the Nyquist plots of the pristine and N-doped TiO₂-B materials. All samples show a semicircle in the high to medium frequency region which is attributed to the charge transfer process. The Nyquist plots are simulated by the equivalent circuit shown in the inset of Fig. 10 where R_s represents the ohmic resistance of the battery cell, R_{ct} and CPE represent the charge transfer resistance and the correlated constant phase element, while W is related to the diffusion of Li ions in the active materials. The fitted kinetic parameters are displayed in Table 3. All samples show very small ohmic resistances (<2.0 Ω). The N-doped TiO₂-B, especially I/S-TiO₂, show smaller ohmic resistances than that of P-TiO₂ which could be attributed to their high electronic conductivities, assuming that all battery cells were assembled in the same way. For each sample, the charge transfer resistance slightly increases with the cell discharged from 3.0 V to 1.0 V. The N-doped TiO₂ samples show smaller charge transfer resistances than the pristine one. In particular, the charge transfer resistances of I/S-TiO₂ are much smaller than those of P-TiO₂ and I-TiO₂. This indicates that the substituted-N significantly improves the charge transfer reactivity of TiO₂-B.

The Warburg data of Nyquist plots were used to determine the lithium diffusion coefficients (D_{Li}) of the materials by using the following equation,⁴⁹

$$D_{Li} = \frac{1}{2} \left[\left(\frac{V_m}{FS\sigma} \right) \left(\frac{dE}{dx} \right) \right]^2 \quad (3)$$

where V_m is the molar volume of TiO₂-B, S is the surface area of the electrode, F is the Faraday constant, dE/dx is the first order derivative of the discharge profile. σ is the Warburg coefficient which obeys the following relationship,

$$\sigma = \frac{dZ'}{d\omega^{-1/2}} \quad (4)$$

σ can be obtained from the slope of the linear fitting of Z' *vs.* $\omega^{-1/2}$ plots (ESI, Fig. S6†). Based on this, the lithium diffusion coefficients of the samples are calculated and displayed in Table 3. It is seen that the lithium diffusion coefficients are improved by N-doping, especially by the substituted-N. In addition, the lithium diffusion coefficient decreases about one order of magnitude with the cell discharged from 3.0 V to 1.0 V. Detailed discussion of the lithium diffusion kinetic

Fig. 10 Nyquist plots of the P-TiO₂, I-TiO₂ and I/S-TiO₂ samples at 3.0 V (a) and 1.0 V (b) of the first discharge. (Inset): equivalent circuit of the Nyquist plots.

Table 3 The fitted electrochemical kinetic parameters of the P-TiO₂, I-TiO₂ and I/S-TiO₂ samples

	R_s (Ω)		R_{ct} (Ω)		D_{Li} (cm ² s ⁻¹)	
	3.0 V	1.0 V	3.0 V	1.0 V	3.0 V	1.0 V
I/S-TiO ₂	1.3	1.1	129.2	135.0	1.06×10^{-8}	1.14×10^{-9}
I-TiO ₂	1.4	1.2	286.7	320.9	9.58×10^{-9}	8.14×10^{-10}
P-TiO ₂	1.8	1.7	327.1	376.1	4.50×10^{-9}	7.34×10^{-10}

properties will be given in the following section according to the GITT analysis results.

3.8 Galvanostatic intermittent titration technique

GITT has been widely used to determine the lithium diffusion coefficients (D_{Li}) of electrode materials with highly reliable data. Fig. 11 shows the GITT curves of the samples during the first discharge as a function of Li⁺ content (x). The plots of dE/dx vs. x are presented in the inset of Fig. 11. Considering that the Li⁺ intercalation in TiO₂-B obeys a solid solution behaviour, the lithium diffusion coefficients can be calculated by the following equation,^{50,51}

$$D_{Li} = \frac{4}{\pi} \left(I_0 \frac{V_m}{FS} \right)^2 \left(\frac{dE/dx}{dE/dt^{1/2}} \right)^2 \quad (5)$$

where I_0 is the applied current, V_m is the molar volume of the active material, F is the Faraday constant and S is the surface area of the electrode. Fig. S7 (ESI[†]) shows a typical titration step of the samples at $x = 0.49$. It is seen that I/S-TiO₂ and I-TiO₂ show smaller ohmic polarizations and overpotentials than those of P-TiO₂ due to their high electronic conductivities. Fig. S8 (ESI[†]) shows the E vs. $t^{1/2}$ plots of the materials

Fig. 11 GITT curves of the P-TiO₂, I-TiO₂ and I/S-TiO₂ samples. (Inset): dE/dx values of the GITT curves.

at $x = 0.49$ where a linear relationship can be obtained in the time range of 10–100 s. Thus, the lithium diffusion coefficient can be calculated by eqn (5) using the values of dE/dx and $dE/dt^{1/2}$. Fig. 12 shows the lithium diffusion coefficients of the samples as a function of Li⁺ content. It is noticed that the GITT results at 3.0 V and 1.0 V are about one order of magnitude lower than those obtained by the EIS analysis. The discrepancy between GITT and EIS results has been clarified by Bruce *et al.*⁵² and some other groups.^{50,53} According to these literature studies, GITT could provide more precise lithium diffusion coefficients as compared to EIS. All samples show

Fig. 12 D_{Li} values of the P-TiO₂, I-TiO₂ and I/S-TiO₂ samples as a function of Li⁺ content.

Fig. 13 (a) Li⁺/e⁻ transport pathway for the TiO₂-B nanowires. (b) Scheme of the lattice structure for N-doped TiO₂-B.

similar D_{Li} of $\sim 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ in the x range of $0 < x < 0.68$. The D_{Li} of P-TiO₂ gradually decreases with further Li⁺ intercalation and reaches a minimum value of $2.69 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at $x = 0.82$. Afterwards, the D_{Li} values are almost unchanged until a maximum Li⁺ content of ~ 0.92 is obtained. According to K. Hoshina *et al.* the small D_{Li} for $x > 0.68$ could be attributed to the distortion of the Li⁺ diffusion channel along the b -axis of TiO₂-B.⁵⁴ This diffusion channel is constructed by the Ti(1) and Ti(2) atoms and the linkage O₁ and O₃ oxygens (Fig. 13). Raman scattering shows that the substituted-N in I/S-TiO₂ strengthens the Ti(1)–O₁–Ti(2) and O₁–Ti(1)–O₃ bonds. This will improve the stability of the corresponding local structures and thus reduces the distortion of the Li⁺ diffusion channel. Therefore, the material can possess a large D_{Li} in a wider x range thus resulting in a larger discharge capacity. As can be seen from Fig. 12, the D_{Li} of I/S-TiO₂ could be kept at $\sim 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ until $x = 0.83$. In addition, the maximum Li⁺ intercalation amount increases to 1.07 which is much larger than that of P-TiO₂. In fact, the interstitial-N also improves the lithium diffusion to some extent. But it plays a less important role in the diffusion kinetics of TiO₂-B than the substituted-N

does. As seen from Fig. 12, the D_{Li} of I-TiO₂ begins to decrease at $x = 0.73$. In addition, even though the total Li⁺ intercalation of I-TiO₂ (~ 0.97) is larger than that of P-TiO₂, it is still much less than that of I/S-TiO₂. Therefore, the substituted-N is much more effective than the interstitial-N for improving the electrochemical performance of TiO₂-B.

4. Conclusions

In summary, N-doped TiO₂-B nanowires have been prepared by the solvothermal method using TiN nanoparticles as the starting material. The N dopants preferentially occupy the interstitial sites of TiO₂-B. The maximum amount of interstitial-N is about 0.55 at%. Above this critical value, the N dopants will substitute the oxygen atoms at the O₁ and/or O₃ positions. The maximum substituted-N in TiO₂-B is ~ 1.3 at%; otherwise, TiN impurity will be formed in the material. The interstitial-N has little impact on the structure and physical properties of TiO₂-B. In contrast, the substituted-N is very important for improving the electronic conductivity and local structural stability of TiO₂-B. This significantly improves the electrochemical properties of the TiO₂-B nanowires. As a result, the practical specific capacities, rate capability and cycling stability of the material are overall improved by the substituted-N dopants. The material shows a discharge capacity of 153 mA h g^{-1} at the 20 C rate with a capacity retention ability of 76% after 1000 cycles. In addition, it can deliver a discharge capacity of 100 mA h g^{-1} at an ultra-high rate of 100 C ($I = 30 \text{ A g}^{-1}$), indicating its great potential in high power lithium ion batteries.

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