# Porous Li$_4$Ti$_5$O$_{12}$ Coated with N-Doped Carbon from Ionic Liquids for Li-Ion Batteries

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With the increasing environmental problems caused by conventional energy sources and the gradual depletion of oil resources, clean energy is becoming an important topic for the whole world. As an electrochemical energy storage device, the lithium ion battery, which has the highest energy density among secondary batteries, has been widely used in portable electronic devices, and has also been proposed for use in electric vehicles and large-scale energy storage.[1–3] However, the performance of current lithium ion batteries cannot meet the requirements in these areas in terms of high power density, long cycle life, and safety. Graphite is widely used as the anode material for Li-ion batteries. The lithiation potential is below 0.2 V versus Li/Li$^+$. This voltage is close to the lithium stripping voltage, especially at high rate, which may cause a safety issue. In addition, a layer of electronically insulating solid-electrolyte interphase (SEI) is inevitably formed on the surface of graphite below 1.0 V versus Li/Li$^+$. Also the graphite anode undergoes a 9% volume variation during full lithium insertion and extraction. Spinel Li$_4$Ti$_5$O$_{12}$ has a relatively high lithiation voltage plateau at 1.54 V versus Li/Li$^+$, which can avoid the formation of the SEI and is very safe.[2,3] In particular, as a zero-strain insertion material,[4] it has excellent cycling performance. These features make it a promising anode material for large-scale long-life energy storage batteries. However, Li$_4$Ti$_5$O$_{12}$ has pretty low electronic conductivity (ca. 10$^{-13}$ S cm$^{-1}$) and moderate Li$^+$ diffusion coefficient (10$^{-9}$–10$^{-13}$ cm$^2$ s$^{-1}$);[5] thus the high rate performance is not satified for such applications.

The most commonly used strategies to solve this problem are to reduce the particle size[6,7] and to coat conductive materials on the Li$_4$Ti$_5$O$_{12}$ surface.[8–11] Reducing the particle size decreases the lithium diffusion length; therefore the electroactivity and/or rate capability of electrode materials can be improved. Coating conductive materials on the surface enhances the surface conductivity and the electrical contact in the electrode. Several methods of surface modification on Li$_4$Ti$_5$O$_{12}$ have been developed to increase its electrical conductivity and electrical contact, such as using highly conductive carbon, metal, or metal nitrides.[10–13] These methods significantly improved the electrochemical performance at high rate, however, most of the

processes are either complex or have to be performed at high temperature (>600 °C).

Recently, porous electrode materials have attracted much attention because of their large contact surface area with the electrolyte and the possibility of forming a 3D mixed conducting network in which metallized mesopores allow both Li$^+$ and e$^-$ to migrate rapidly, leading to a superior rate performance.[14] In the work reported here, an ionic liquid was used as a carbon precursor to form a 3D mixed conducting network in porous Li$_4$Ti$_5$O$_{12}$ particles for the first time. Ionic liquids were used as new precursors to obtain N-doped graphitized carbon.[15,16] Compared with conventional solid carbon precursors, ionic liquids can penetrate into porous materials easily, because of their fluidic properties. The pyrolysis of the specific ionic liquids with very low vapor pressure can occur in the wide temperature range of 400–1000 °C without drastic solvent evaporation. This is favorable for forming a thin uniform coating layer on the particle surface. In addition, the composition of the coating layer can be tuned by selecting different ionic liquids. An interphase between the active substrate and the coating layer could also be formed. For example, a metallic conductive TiN$_x$ layer may be formed for a titanium-based compound substrate. Therefore, using an ionic liquid as precursors has a significant advantage in tuning the composition and properties of the coating layer and the interphase, which is essential for material design and optimization.

The porous Li$_4$Ti$_5$O$_{12}$ sample was prepared by a spray-drying method as reported elsewhere.[17] The ionic liquid 1-ethyl-3-methylimidazolium dicyanamide (EMIm-dca) was chosen as the precursor, which is composed of only C, N, and H elements. Different amounts (165, 320, and 495 µL) of EMIm-dca were mixed with Li$_4$Ti$_5$O$_{12}$ powder (1 g) and then the mixtures were heated to 600 °C in Ar atmosphere; the obtained samples were named samples 1, 2, and 3, respectively. After heat treatment, the color of the initially white Li$_4$Ti$_5$O$_{12}$ powder varied from dark gray to black, depending on the amounts of ionic liquid (see Figure S1 in the Supporting Information). The morphology of the coated sample did not change obviously (Figure S2, Supporting Information). Furthermore, the Li$_4$Ti$_5$O$_{12}$ crystalline phase was well maintained after heat treatment (see the X-ray diffraction (XRD) patterns in Figure S3, Supporting Information). By comparing the Raman spectra of pristine and coated Li$_4$Ti$_5$O$_{12}$ (Figure S4, Supporting Information), we found that the G-band around 1590 cm$^{-1}$ and D-band around 1350 cm$^{-1}$, which are typical bands of carbonaceous materials,[16] appeared after coating, which confirmed the existence of carbon in the composite.

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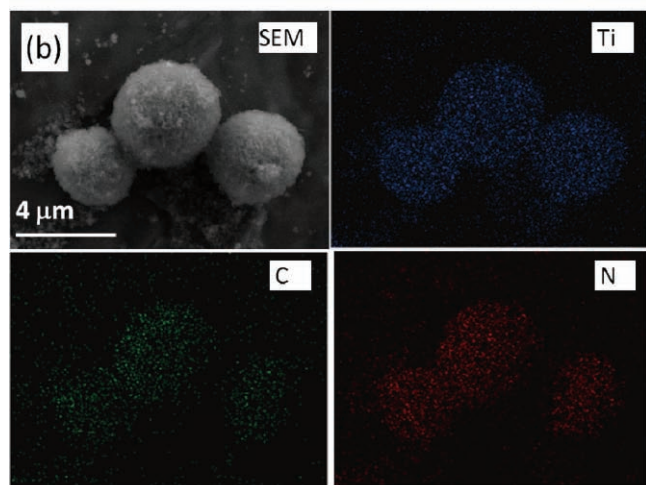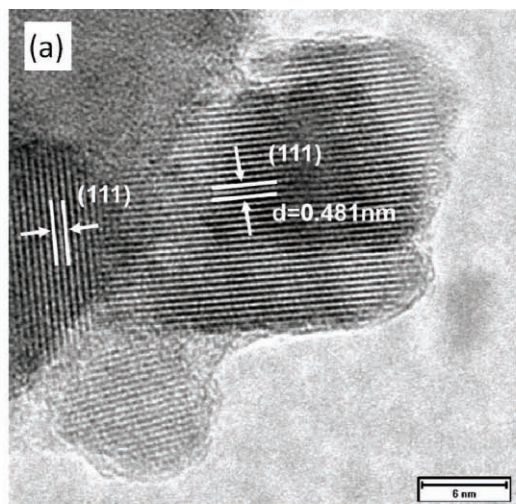**Figure 1.** a) HRTEM of coated $Li_4Ti_5O_{12}$ (sample 2). b) SEM image of coated $Li_4Ti_5O_{12}$ particles (sample 2) and the EDX mapping images of Ti, C, and N elements.

In order to investigate the distribution and composition of the surface coating layer, high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray (EDX) mapping analysis, Brunauer–Emmett–Teller (BET) absorption, and X-ray photoelectron spectroscopy (XPS) were carried out. From the HRTEM image in **Figure 1**a, it can be observed that a very thin uniform amorphous layer is formed on the surface. The EDX mapping images of Ti, C, and N elements are shown in Figure 1b. The distribution of C and N elements is consistent with that of Ti, which indicates that C and N distribute uniformly on/in the particles. The specific surface areas of pristine and coated $Li_4Ti_5O_{12}$ samples were calculated from $N_2$ isotherms by the Barrett–Joyner–Halenda (BJH) method and found to be 43.4 and 51.3 $m^2 g^{-1}$, respectively, indicating that the pore structure is maintained well after coating, which is consistent with the HRTEM results as shown in Figure 1a, where a very thin uniform layer coating on the particle surface was observed.

The XPS survey spectra of pristine and coated $Li_4Ti_5O_{12}$ are shown in **Figure 2**a. A new peak at around 399 eV for the coated sample can be seen clearly, which can be ascribed to N
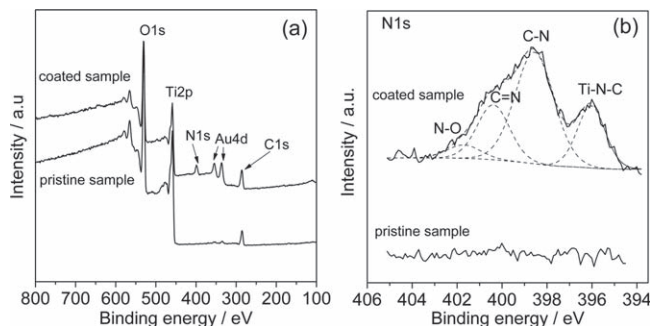


**Figure 2.** a) XPS survey spectra of pristine and coated $Li_4Ti_5O_{12}$. b) High-resolution XPS spectra of N 1s in pristine and coated $Li_4Ti_5O_{12}$ (sample 2).

1s, suggesting the presence of N in the coating layer. Typical high-resolution XPS spectra of N 1s for pristine and coated $Li_4Ti_5O_{12}$, acquired under the same conditions, are shown in Figure 2b. For the coated sample, the spectrum of N 1s contains multiple components due to the coexistence of different chemical states of N. It can be deconvoluted into four peaks: the peaks at binding energies of 398.5, 400.5, and 401.5 eV can be attributed to the C–N, C=N, and N–O bonds, respectively.[18] Besides, we cannot exclude the possibility of the existence of the C≡N bond, because its binding energy is close to that of the C–N bond. The existence of different C–N bonds indicates different configurations of N-doped carbon: pyridine-like nitrogen with a C–N bond together with a C=N bond and  graphite-like nitrogen with three C–N bonds.[19] Furthermore, a peak at 395.7 eV of N 1s can also be seen. The binding energy is close to TiN (397.0 eV), perhaps caused by a Ti-N-C-like compound. From the thermogravimetric (TG) results of the coated samples heated in air (Figure S5, Supporting Information), the carbon contents of the samples obtained from 1 g $Li_4Ti_5O_{12}$ and 165, 320, and 495 μL ionic liquid are about 3.6, 7.0, and 9.6 wt%, respectively.

**Figure 3**a compares the rate capability of the pristine sample and $Li_4Ti_5O_{12}$ sample coated with about 7.0 wt% N-doped carbon. At a low discharge/charge current rate of C/2 (1C means insertion of 3 mol Li into $Li_4Ti_5O_{12}$ in 1 h), the reversible capacity of the coated sample was 161 mAh $g^{-1}$, which was slightly lower than the pristine sample (169 mAh $g^{-1}$), owing to taking the mass of N-doped carbon into the total mass of active material. However, at high current rates of 5C and 10C, the coated sample shows much better rate capability. Capacities of 145 and 129 mAh $g^{-1}$ were achieved, respectively, while the capacities of the pristine sample were 60 and 15 mAh $g^{-1}$, respectively, at the same rates. Also, this result is better than the previously reported $Li_4Ti_5O_{12}$ by carbon-coating[11b] or surface nitridation[13] and is slightly lower than Shukla and co-workers' result on solution-combustion synthesized $Li_4Ti_5O_{12}$ followed by ball-milling with carbon black.[20] Other coated samples with different N-doped carbon contents also exhibit higher capacity at current rates of 5C and 10C than those of the pristine one, but lower capacity than those of the sample coated with about 7.0 wt% N-doped carbon (Figure 3b). For the 9.6 wt% N-doped carbon-coated sample, in addition to lower mass of effective active material, the thick coating layer formed may restrict the efficient charge transfer/transport; thus the specific capacity
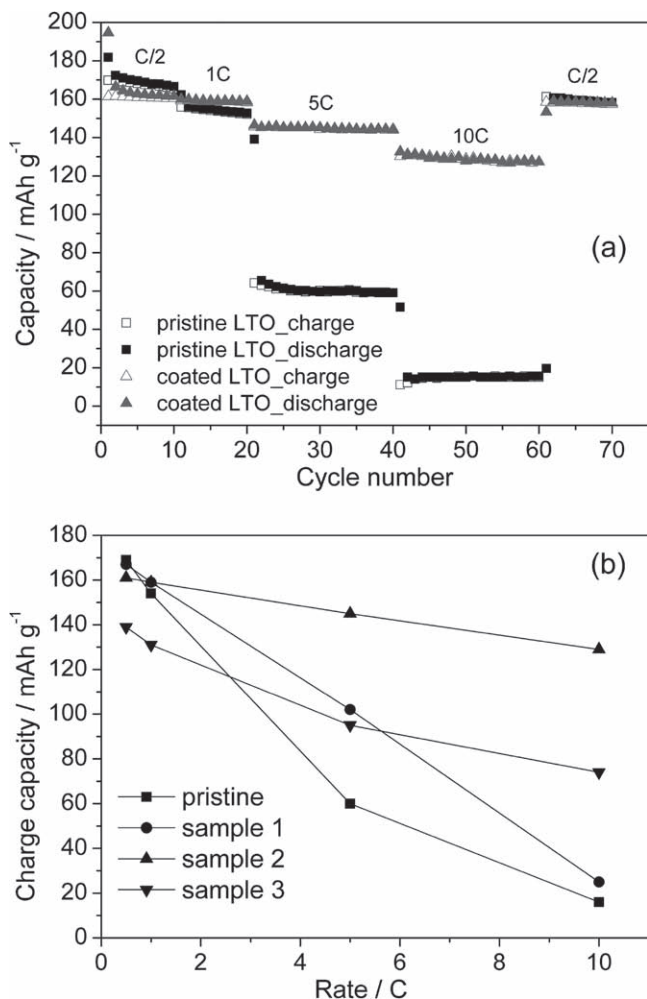
**Figure 3.** a) The discharge/charge capacities of pristine and coated $Li_4Ti_5O_{12}$ (sample 2) at different current rates. b) Specific capacities of pristine $Li_4Ti_5O_{12}$ and samples 1–3 at different current rates.

lower than those of the sample coated with N-doped carbon. In addition, a high polarization between discharge and charge curves was observed in Figure S6. These observations can be ascribed to the low electric conductivity of sugar-derived carbon at 600 °C. This result demonstrates that the N-doped carbon coating derived from an ionic liquid is quite effective in improving the rate capability and charge/discharge properties.

The other appealing feature of the coated sample is its excellent cycling performance. The cycling performance of the coated and pristine samples is shown in **Figure 4**. Both half cells were cycled at C/2 for 10 cycles and then turned to 2C. In the case of the coated sample, the initial capacity was 150 mAh g$^{-1}$ at 2C, which decreased to 124 mAh g$^{-1}$ after 2200 cycles at 2C, with very good capacity retention of 83%. However, for the pristine sample, the initial capacity was 135 mAh g$^{-1}$ at 2C, which decreased to 98 mAh g$^{-1}$ after 100 cycles, with moderate capacity retention of 73%. This excellent rate performance and cycling performance could result from a) the surface modification by N-doped carbon, which not only greatly enhances the electric conductivity but also remarkably increases the surface stability of $Li_4Ti_5O_{12}$; b) the formed interphase of a Ti-N-C-like compound between $Li_4Ti_5O_{12}$ and N-doped carbon, which might be helpful for charge transfer in the interface; and c) the 3D mixed conducting network[14] formed in the $Li_4Ti_5O_{12}$ particles, which makes the Li insertion/extraction more efficient.

In conclusion, this communication shows that ionic liquids can be used as new carbon precursors to decorate electrode material, in this case $Li_4Ti_5O_{12}$, by simply mixing the $Li_4Ti_5O_{12}$ and the ionic liquid EMIm-dca and then pyrolyzing at moderate temperature. The resulting material with a very thin and uniform N-doped carbon coating layer exhibits superior rate capability and excellent cycling performance versus Li. This synthetic approach is relatively simple, yet very effective, and owing to its versatility can also be extended to modify other electrode materials for electrochemical devices. The approach is not restricted to high-temperature treatment. Ongoing work shows
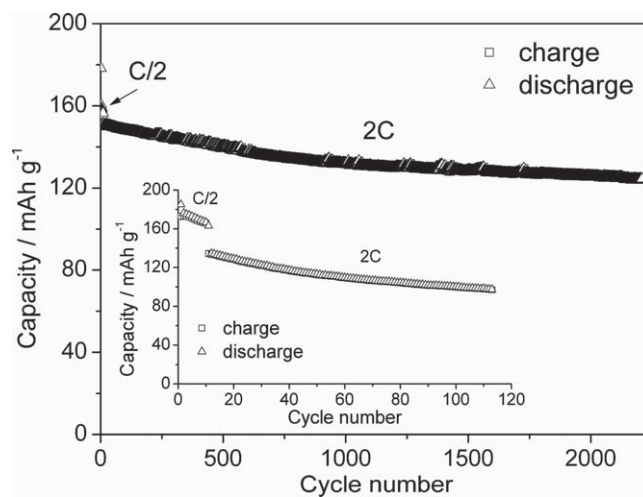
decreases, especially at high current rates. The relatively low capacity for the 3.6 wt% N-doped carbon-coated sample might be because such a small amount of ionic liquid cannot form a uniform absorbed precursor layer on the $Li_4Ti_5O_{12}$ surface, leading to a noncontinuous electronic conducting network being formed in the composite. Moreover, the charge voltage plateau of the coated sample can be still kept at the high charge rate; in contrast, for the pristine sample, the charge profile behaved as a slope because of the high polarization of the low conductivity $Li_4Ti_5O_{12}$ (see Figure S6, Supporting Information).

For comparison, a sample of porous $Li_4Ti_5O_{12}$ coated with carbon without nitrogen was prepared in the same way as ionic liquids, except that sugar, which does not contain N, was used as the carbon precursor: porous $Li_4Ti_5O_{12}$ was added to aqueous sugar solution; after stirring and evaporation of the water, the obtained $Li_4Ti_5O_{12}$-sugar mixture heated to 600 °C in Ar atmosphere. As shown in Figure S6 (Supporting Information), the capacities of porous $Li_4Ti_5O_{12}$ coated with 7 wt% carbon without nitrogen by sugar precursor were 71 mAh g$^{-1}$ and 18 mAh g$^{-1}$ at 5C and 10C, respectively, which were much



**Figure 4.** Cycling performance of coated $Li_4Ti_5O_{12}$ (sample 2). Inset: The cycling performance of pristine $Li_4Ti_5O_{12}$.

the possibility of pyrolyzing the mixture at rather low temperature, for example 450 °C, to form carbon-based composites that still exhibit improved performance compared with the pristine sample. Furthermore, the composition of the coating layer can be tuned for efficient charge transport by using different ionic liquids.

## Experimental Section

The structure of $Li_4Ti_5O_{12}$ was characterized using an X'Pert Pro MPD X-ray diffractometer (Philips, Netherlands) using Cu Kα radiation (1.5405 Å). The morphologies of $Li_4Ti_5O_{12}$ particles were observed using a scanning electron microscope (XL 30 S-FEG, FEI Co.). The HRTEM images were observed using a transmission electron microscope (JEOL 2010). The EDX mapping was done on a Hitachi S-4800 scanning electron microscope equipped with an energy dispersive X-ray analyzer (Horiba EMAX). The Raman spectra were acquired on a Renishaw inVia micro-Raman spectroscopy system equipped with an 514 nm Ar-ion laser. The TG curves of the ionic liquid and coated $Li_4Ti_5O_{12}$ were obtained using a Diamond TG/DTA thermoanalyzer. The elemental analysis was conducted on an XPS spectrometer (Escalab 250, Perkin Elmer Co.). The specific area of the samples was analyzed by a NOVA 2000e surface area analyzer (Quantachrome Instruments).

Both the pristine and coated sample electrodes were prepared with $Li_4Ti_5O_{12}$, carbon black, and poly(vinyl difluoride) (PVdF) at a weight ratio of 80:10:10. The slurry was cast on Al foil and dried at 100 °C in vacuum for 10 h. The coil cells CR2032 were assembled with pure lithium foil as the counter electrode, a glass fiber separator, and 1 M $LiPF_6$ EC:DMC (1:1) electrolyte in an argon-filled glove box. The discharge and charge measurements were carried out on a Land BT2000 battery test system (Wuhan, P. R. China). All the tests were performed in the range between 1.0 V and 2.2 V.

## Supporting Information

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

## Acknowledgements

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