$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2\text{-SiO}_2$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SiO}_2$ composites as an anode material for Li-ion batteries

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Abstract The commercial electrode $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was modified with SiO_2 and $\text{TiO}_2\text{-SiO}_2$. All samples were characterized by scanning electron microscope (SEM), particle size distribution (PSD), porous structure parameters (low-temperature N_2 sorption), galvanostatic charge–discharge test, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). Appropriate amount of $\text{TiO}_2\text{-SiO}_2$ and SiO_2 could effectively reduce the electrochemical polarization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and enhance electrochemical reaction kinetics of Li^+ insertion/deinsertion. Moreover, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2\text{-SiO}_2$ provides a high rate capacity of 165 mAh g^{-1} at the high current density of 0.5 C. To investigate cycle stability of the electrode materials at high current density, the measurements were directly carried out at 3 C. SEM images of the LTO/ $\text{TiO}_2\text{-SiO}_2$, LTO, and LTO/ SiO_2 particles after galvanostatic charging/discharging show that they were coated by a uniform layer (the SEI layer).

Keywords Lithium titanate · $\text{TiO}_2\text{-SiO}_2$ oxide composite · Silica · Galvanostatic charge–discharge · Cyclic voltammetry

Introduction

As practical lithium-ion battery, high security and energy storage are important, long cycle life and good rate performance also directly determine their application prospects [1]. However, the current commercial lithium-ion battery based on graphite systems cannot satisfactorily meet the increasing

demands of modern power systems because of their poor rate capability and cycle life [2]. Recently, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has aroused intense research interests as a new anode for lithium-ion battery owing to its some appealing features such as high stability, safety, and excellent cycling performance [3–5]. Despite many advantages associated with $\text{Li}_4\text{Ti}_5\text{O}_{12}$, low electric conductivity prohibits its use in large-scale applications [6, 7]. In order to overcome the problem, surface coating method has been devoted to the exploration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, such as doping $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with metals or metal oxides [8–10] and coating $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with conductive carbons [11–13]. Wang et al. [14] synthesized the rutile- TiO_2 -terminated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets by a facile method through adjusting the molar ratios of starting reactants. The rutile- TiO_2 layer at the edges of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets inherits the advantage of nanosheet morphology for fast lithium-ion transportation from liquid electrolyte into the nanosheets, which improves surface stability and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In contrast to the common graphite anodes, Li intercalation into TiO_2 and LTO takes place at potentials around 1.8 and around 1.55 V vs. Li/Li^+ , respectively. Thus, TiO_2 and LTO anodes operate within the electrochemical stability window of typical battery electrolytes, so that the formation of solid electrolyte interphase (SEI) layers on top of the active TiO_2 /LTO particles should not take place. SEI layers may, however, form on the surface of conductive additives. Anodes containing TiO_2 nanoparticles have been extensively studied in order to increase the interfacial area between TiO_2 particles and the battery electrolyte and in order to reduce the diffusion length for Li^+ ions within the TiO_2 particles [15, 16]. The mechanism of Li storage in nanocrystalline TiO_2 has been examined by means of charge/discharge experiments and cyclic voltammetry.

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material has an excellent reversibility of Li-ion intercalation and de-intercalation with a theoretical

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capacity of 175 mAh g⁻¹, and it also exhibits no volume changes during charge and discharge cycles combined with an excellent safety performance [17–19]. However, the power performance of Li₄Ti₅O₁₂ is greatly limited by its low electronic conductivity (ca. 10⁻¹³ S cm⁻¹) and moderate Li diffusion coefficient (10⁻⁸–10⁻¹¹ cm² s⁻¹) [20–24]. In order to improve the electrochemical performance of the Li₄Ti₅O₁₂ anode, extensive works concentrated on forming nanoparticles [25–28], doping [29–34] with metal cations, and composing with carbon or metal powders [35, 36].

In many publications, Li₄Ti₅O₁₂ is synthesized by the sol-gel method with addition of TiO₂ or graphene. In this work, for the first time, the cheaper method of adding inorganic oxides by mixing in the preparation of the electrode is described.

Experimental

Materials

The materials used were lithium titanate Li₄Ti₅O₁₂ powder (Aldrich, BET surface area 32.6 m² g⁻¹, mean diameter 940 nm), carbon black (CB, Fluka), poly(vinylidene fluoride) (PVdF, Fluka), lithium foil (Aldrich, 0.75-mm thick), *N*-methyl-2-pyrrolidinone (NMP, Fluka), propylene carbonate (PC, Aldrich), dimethyl carbonate (DMC, Aldrich), and lithium hexafluorophosphate (LiPF₆, Fluka). Solid LiPF₆ salt was dissolved in the liquid solution: a classical electrolyte (1 M LiPF₆ in PC + DMC, 1:1) was prepared in a dry argon atmosphere in a glovebox. Tested anodes were prepared on a copper foil (Hohsen, Japan) by a casting technique, from a slurry of Li₄Ti₅O₁₂, carbon black, and PVdF in NMP. The ratio of the components was Li₄Ti₅O₁₂:CB:PVdF = 85:5:10 (by weight). A total of 3 wt% TiO₂-SiO₂ and SiO₂ were added. The composition of the electrodes is given in Table 1.

Based on the study and optimization of the composition of the electrodes, selected 3% of the composites were added to electrode with Li₄Ti₅O₁₂ spinel. After solvent (NMP) vacuum evaporation at 120 °C, a layer of the carbon electrode was formed, containing the active material (Li₄Ti₅O₁₂), an electronic conductor (CB), and the binder (PVdF).

Table 1 The ratio of components to prepare electrodes (by weight/wt%)

Electrodes	Li ₄ Ti ₅ O ₁₂	CB	PVdF	TiO ₂ -SiO ₂	SiO ₂
LTO	75	5	10	—	—
LTO/SiO ₂	72	5	10	—	3
LTO/TiO ₂ -SiO ₂	72	5	10	3	—

Preparation of TiO₂-SiO₂ and SiO₂

TiO₂-SiO₂

TiO₂-SiO₂ oxide composite was obtained in an emulsion system. Two emulsions were prepared: Firstly, emulsion E2, made of cyclohexane as the organic phase, titanium sulfate, and nonylphenylpolyoxyethyleneglycol ethers (NP3 and NP6) in appropriate quantities. Then, emulsion E1 was made from a 5% solution of sodium silicate to which cyclohexane and NP3, NP6 emulsifiers were introduced.

Both emulsions were subjected to homogenization for 20 min (IKA®T25 homogenizer made by IKA WERKE). Then, using a PP1B-05A peristaltic pump, emulsion E1 was introduced in doses to E2. As a result of dispergation, a white precipitate of TiO₂-SiO₂ was obtained, which was destabilized at 80 °C in order to separate the organic phase. The precipitate was filtered off from the post-reaction mixture. The filter cake obtained was washed a few times with hot water and then with methanol in order to remove the residues of surfactants. Subsequently, the TiO₂-SiO₂ composite was dried by the convection method to eliminate moisture. Finally, the dried TiO₂-SiO₂ precipitate was calcined in a type AWF 115/5 furnace made by Lenton Furnaces, at 1000 °C for 3 h, to obtain a stable form.

SiO₂

Two types of emulsions were prepared. The first one labeled as E2 and referred to as acidic was composed of the organic phase (cyclohexane POCh SA) and a 5% solution of hydrochloric acid (POCh SA). It also included nonylphenylpolyoxyethyleneglycol ethers (NP3 and NP6, PCC ROKITA SA). The second emulsion labeled E1 was referred to as the basic one. It contained a fixed volume of a 20% solution of sodium silicate (VITROSILICON SA) into which cyclohexane and emulsifiers (NP3 and NP6) were introduced in appropriate amounts. The emulsions were obtained by dissolving weighted portions of non-ionic surfactants in cyclohexane. The mixture obtained was applied in small doses into the water phase being a water solution of sodium silicate for E1 and a water solution of hydrochloric acid for E2. The E2 emulsion was homogenized in the next step for 20 min at the rate of 8800 rpm and placed in a reactor (QVF MiniPlant Pilot-Tec) of 10 dm³ in capacity (under continuous stirring at the rate of 760 rpm). Then, E1 was homogenized at the rate of 8800 rpm for 20 min. After this stage, E1 was introduced in doses into E2 at the rate of 20 cm³ min⁻¹ using a peristaltic pump. As a result of dispergation, a white sediment of silica appeared, which was later destabilized at 80 °C in order to separate the organic phase. The sample was filtered off under reduced pressure. The filtration residue obtained was washed a few times with hot water and then with methanol in order to remove

possible residues of surfactants. The last phase of the process was the removal of humidity from the silica by spray drying in a GeoNiro A/S.

Procedures and measurements

Particle size of $\text{TiO}_2\text{-SiO}_2$, SiO_2 , and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was determined with Zetasizer Nano ZS (Malvern Instruments Ltd., UK). Specific surface areas of the powders were determined by N_2 adsorption (BJH method) using an ASAP 2020 instrument (Micromeritics Instrument Co.). The performance of the cells was characterized using galvanostatic charge–discharge tests, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). Cycling efficiency of $\text{Li}_4\text{Ti}_5\text{O}_{12}|\text{Li}$ systems was measured in two compartment cells. Electrodes (metallic-lithium foil and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) were separated by the glass microfiber GF/A separator (Whatman, 0.4-mm thick), placed in an adopted Swagelok® connecting tube. Typically, the mass of electrodes was as follows: Li ca. 45 mg (0.785 cm^2) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 2.5–3.5 mg. Cells were assembled in a glove box in the dry argon atmosphere. Cycling measurements were taken with the use of the ATLAS 0461 MBI multichannel electrochemical system (Atlas-Sollich, Poland) at different current rates (0.5–5 C). Cyclic voltammetry and ac impedance measurements were performed using the $\mu\text{Autolab FRA2}$ type III electrochemical system (Ecochemie, Netherlands). The thermal behavior of electrolytes in the temperature range of 30–600 °C was studied by TG-DSC. A differential scanning calorimeter model DSC XP-10 (THASS GmbH) was used. After electrochemical measurements, cells were disassembled in a glove box and the electrodes were washed with DMC and dried in vacuum at room temperature. The morphology of the $\text{TiO}_2\text{-SiO}_2$, SiO_2 , and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (pristine and after electrochemical cycling) was observed under a scanning electron microscope (SEM, Tescan Vega 5153).

Results and discussion

Physicochemical properties of $\text{TiO}_2\text{-SiO}_2$ and SiO_2

$\text{TiO}_2\text{-SiO}_2$ hybrid obtained by the effective method of precipitation from an emulsion system is characterized by a monomodal particle size distribution with diameters in the range 342–1110 nm (Table 2). As evidenced by the SEM image (Table 2), the particles have spherical shape. The hybrid is highly homogeneous, as is confirmed by the low polydispersity index of 0.226.

At the next stage of study, the adsorptive properties of $\text{TiO}_2\text{-SiO}_2$ composite were characterized using a method based on nitrogen adsorption/desorption (Table 2). The isotherm obtained had the shape typical for mesoporous

adsorbents (type IV in the IUPAC classification) [37]. The mean pore diameter of 3.8 nm was also typical for mesoporous substances. The surface area of the $\text{TiO}_2\text{-SiO}_2$ hybrid was $12.5\text{ m}^2/\text{g}$, which implies an intermediate level of surface activity.

The spherical silica was precipitated and subjected to dispersion analysis. The particle size distribution (Table 2) revealed a single band corresponding to the particles of diameters covering the range 164–295 nm, with the maximum volume of 37.2% corresponding to the particles of 220 nm in diameter. The SEM of the silica (Table 2) confirmed the above result as the sample showed high uniformity and a few agglomerates. The polydispersity index of this silica material was 0.250.

Furthermore, N_2 sorption experiments were carried out to determine the structural properties of the silica fillers (Table 2). The surface area (A_{BET}) of unmodified silica SiO_2 is much larger ($48\text{ m}^2\text{ g}^{-1}$) than for modified silicas ($15\text{--}37\text{ m}^2\text{ g}^{-1}$) [38]. The pore volume (V_p) of the unmodified silica is greater than the silane-grafted silicas. However, the average pore diameter (S_p) of silica modified slightly greater than the unmodified sample, which can be explained by the migration of modifier into the pores.

TG-DSC of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Figure 1 presents the TG-DSC curves of the precursor LTO over a temperature range from 30 to 600 °C in air. The results suggest a four-stage reaction process.

The initial 5 wt% weight loss below 180 °C is owing to the removal of surface water. The following 10 wt% weight loss below 280 °C can be attributed to the dehydration of crystal water, and a sharp endothermic peak is examined in this stage.

Moreover, an exothermic reaction occurs at 280 °C, which relates to a sharp decrease in the sample weight. However, this reaction is not exothermic enough to trigger the complete conversion of the precursor sample, since this step only accounts for a mass loss of ~15% of the initial sample weight. The sample is left with 65% of its initial weight, while theoretically, a complete conversion would lead to a residual mass of 23.8%. This means that the fuel is not completely degraded and the sample is left with amounts of incompletely oxidized fuel.

In the stage below 450 °C, the layered hydrous lithium titanate transforms to spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ accompanied by the pyrolysis of titanium glycerol and a large quantity of heat was released.

BET of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Figure 2 shows the N_2 adsorption/desorption isotherms of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the Barrett–Joyner–Halenda (BJH) pore-size distribution curve (inset). The isotherms reveal type IV with

Table 2 Parameters of porous structure, PSD, and SEM images of unmodified titania/silica and silica support

Parameters	Additives	
	TiO ₂ -SiO ₂	SiO ₂
$A_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	12.5	48
$V_p / \text{cm}^3 \text{g}^{-1}$	0.12	0.59
S_p / nm	3.8	12.43
PSD	342–1110 nm (531–23.8%)	164–295 nm (220–37.2%)
SEM

a representative H1-type hysteresis loop, which is characteristic of mesoporous materials [39]. The pore-size distribution indicates that the narrow distribution of the micropores is around 5 nm. The Brunauer–Emmett–Teller (BET) specific surface area of the Li₄Ti₅O₁₂ obtained is 56 m² g^{−1}. It is well-known that a large specific surface area can provide more locations and channels for lithium to insert into the electrode material, which also decreases the irreversible capacity associated with the concentration polarization [40].

Cyclic voltammetry

Figure 3 shows the CVs of the LTO/TiO₂-SiO₂ hybrid as a LIB anode at different scan rates (0.2, 0.5, and 1.0 mV s^{−1}) in the voltage range of 0.0–3.0 V (vs Li/Li⁺). Each curve clearly demonstrates that there is one pair of redox peaks in the range of 1.0–2.5 V, which is in accordance with the typical CV characteristics of spinel Li₄Ti₅O₁₂. Oxidation peaks at about ~1.85 V and the reduction peak at ~1.2 V may be attributed to the

Fig. 1 TG-DSC curves of the Li₄Ti₅O₁₂

Fig. 2 BET of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$

oxidation/reduction reactions of the $\text{Ti}^{3+}/\text{Ti}^{4+}$ couple in the spinel structure, compensated by lithium extraction–insertion [41]. However, no distinct cathodic peaks are observed from 0.9 to 1.3 V. A visible peak between 0.4 and 0.7 V is responsible probably for the presence of introduced $\text{TiO}_2\text{-SiO}_2$ groups.

The nanostructured $\text{LTO}/\text{TiO}_2\text{-SiO}_2$ apparently behaves differently from the bulk crystals that show clear crystalline phase transitions during the lithium insertion/extraction process involving one Li^+ per $\text{TiO}_2\text{-SiO}_2$. The CV curves are almost identical in the first 3 cycles at each scan rate, indicating good reversibility of these electrochemical reactions. At higher scan rates, the relative contribution by the capacitive component decreases. The Li^+ insertion/extraction waves become broader and shift to lower/higher potentials, respectively.

Impedance spectroscopy

As seen from the Nyquist plots, it can be found that the radius of the semicircle of $\text{LTO}/\text{TiO}_2\text{-SiO}_2$ electrode is smallest and

that of commercial LTO is the largest among the three samples. And the resistances were calculated on the base of fitting circuit (inset of Fig. 4). This experiment demonstrated that the charge-transfer resistance of LTO electrode can be lowered through doping of $\text{TiO}_2\text{-SiO}_2$ and combination with SiO_2 . Although the mechanism of effects of $\text{LTO}/\text{TiO}_2\text{-SiO}_2$ should be further studied, these experiments have proved that fabricated $\text{LTO}/\text{TiO}_2\text{-SiO}_2$ electrode possessed superior electrochemical performance as anode material in LIB.

This result validates that $\text{TiO}_2\text{-SiO}_2$ phase in $\text{LTO}/\text{TiO}_2\text{-SiO}_2$ has better effect to improve the conductivity of the electrode at low charge/discharge current density. That may explain why $\text{LTO}/\text{TiO}_2\text{-SiO}_2$ electrode with active process shows better cycling stability than LTO/SiO_2 electrode without active process.

The EIS results of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ half cells after 5 cycles are plotted in another research [42]. In the publication, the authors analyze the addition of carbon to the $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It is interesting to note that the EIS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ without and with 3 wt% carbon addition is composed of one depressed semicircle at high to middle frequency and a slope line at low frequency, while the EIS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with 5 wt% carbon addition is composed of two partially overlapped and depressed semicircles at high to middle frequency and a slope line at low frequency [43–46]. There is no SEI formation on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material surface during the charge and discharge processes, since the reaction of SEI formation occurs below 0.8 V (vs. Li/Li^+) [47, 48]. The slope line at low frequency corresponds to the Warburg impedance (Z_w), which is related to the Li-ion diffusion in the electrodes [45]. The authors also show that the R_{ct} of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with 3 wt% carbon addition is the least and that with 5 wt% carbon addition the largest. The larger R_{ct} is mainly attributed to the agglomeration of carbon resulting in a great decrease of ionic conductivity. It is seen that the EIS results are consistent with those of the CV.

Fig. 3 The comparison of CV plots at different scanning rates for the commercial $\text{LTO}/\text{TiO}_2\text{-SiO}_2$ electrode

Fig. 4 Electrochemical impedance spectra of the commercial LTO, as prepared LTO/SiO₂ and LTO/TiO₂-SiO₂ electrodes

Galvanostatic charging/discharging

Charge and discharge processes in Li₄Ti₅O₁₂ take place in a two-phase system via transformation between a spinel structure of Li₄Ti₅O₁₂ and a rock-salt type structure of Li₄Ti₅O₁₂ determining a flat potential plateau of 1.55 V (vs. Li⁺/Li) [49]. Moreover, changes in its cubic unit cell parameter are very small (8.3595–8.3538 Å [50]), thus providing an excellent cycling stability and reversibility of this material. A promising approach to improve the performance of electrode materials is concerned with the use of nanosized materials [51–53]. Another approach is concerned with the formation of composites with oxides such as SiO₂ and TiO₂. This leads to the sorption of mobile ions at grain boundary [54–56].

The charge–discharge curves of Li₄Ti₅O₁₂/TiO₂-SiO₂ at the current density of 0.5 C are shown in Fig. 5a. As the same as Li₄Ti₅O₁₂, the two composites provide a pair of distinct and flat potential plateau around 1.53 and 1.60 V [57].

Charge plateau is attributed to low polarization of the composites containing TiO₂-SiO₂. Rate discharge capability and cycle stability of the prepared materials were investigated at different current densities from 0.5 to 5 C (Fig. 5b). All the capacity calculations are based on the total mass of the active materials.

Here, reversible capacity of additives can be neglected due to the high discharge cut-off potential (1.0 V) and the small content in the electrode materials (~3 wt%). The initial discharge capacity of Li₄Ti₅O₁₂/TiO₂-SiO₂, Li₄Ti₅O₁₂, and Li₄Ti₅O₁₂/SiO₂ is 158, 140, and 132 mAh g⁻¹, respectively, which is lower than the theoretical capacity of Li₄Ti₅O₁₂ (175 mAh g⁻¹). This is not surprising in view of irreversible Li insertion, surface defects, and trace water adsorbed on the active materials during the first discharge process [57]. At the low current density of 0.5 C, Li₄Ti₅O₁₂/TiO₂-SiO₂, Li₄Ti₅O₁₂, and Li₄Ti₅O₁₂/SiO₂ deliver stable discharge capacities of 170, 150, and 146 mAh g⁻¹, respectively, in the 10th cycle. The values of Li₄Ti₅O₁₂/SiO₂ and Li₄Ti₅O₁₂ are very close, while the capacity of Li₄Ti₅O₁₂/TiO₂-SiO₂ is obviously higher.

When current density is increased to 1 C, the discharge capacities of all the three samples have a close decrease of about 5 mAh g⁻¹. With increasing current density to 3 C, the discharge capacities of Li₄Ti₅O₁₂/TiO₂-SiO₂ and Li₄Ti₅O₁₂ decrease around 4 mAh g⁻¹, while that of Li₄Ti₅O₁₂ decrease about 8 mAh g⁻¹. An obvious difference in capacity change occurs when current density increases to 5 C. The discharge capacity of Li₄Ti₅O₁₂ decreases to 121.7 mAh g⁻¹. However, Li₄Ti₅O₁₂/TiO₂-SiO₂ keeps a relatively stable value of 145 mAh g⁻¹. Li₄Ti₅O₁₂ delivers a capacity of 130 mAh g⁻¹ with a small proportion off all. At the high current density of 5 C, superior high rate performance of Li₄Ti₅O₁₂/TiO₂-SiO₂ is more remarkably shown. Li₄Ti₅O₁₂/TiO₂-SiO₂, Li₄Ti₅O₁₂, and Li₄Ti₅O₁₂/SiO₂ deliver discharge capacities of 136, 122, and 80 mAh g⁻¹, respectively. The comparison based on the above results indicates evidently that the addition of TiO₂-SiO₂ in Li₄Ti₅O₁₂ can improve rate capability of the electrode materials. In particular, Li₄Ti₅O₁₂/TiO₂-SiO₂ still provides a high rate capacity of 140 mAh g⁻¹ at the high current density of 5 C. To investigate cycle stability of the electrode materials at high current density, the measurements were directly carried out at 3 C. The results are shown in the inset in Fig. 5b. The discharge capacities of the three materials reach stable values after 10 cycles. For Li₄Ti₅O₁₂/TiO₂-SiO₂, Li₄Ti₅O₁₂, and Li₄Ti₅O₁₂/SiO₂, the capacities are 155, 140, and 118 mAh g⁻¹, respectively. Clearly, though the addition of SiO₂ can improve rate capability of Li₄Ti₅O₁₂, it is not ideal for long cycle stability at high current density. Li₄Ti₅O₁₂/TiO₂-SiO₂ has not only outstanding high rate capability but also excellent cycle stability [58].

A very thin layer of TiO₂-SiO₂ was found on the outmost surface of LTO, which indicates composite maybe chemically-inert when facing with such kind of electrolyte. Therefore, the introduction of the TiO₂-SiO₂ groups into the spinel causes significant stabilization of the capacitance, which positively influences the working life of the electrode.

Xu et al. used a nanocomposite of Li₄Ti₅O₁₂ particles coated with polythiophene (PTh) as advanced anode for

Fig. 5 Discharge capacity at 0.5 C for LTO/TiO₂-SiO₂ (a), and cycle performance at various rates of (○) Li₄Ti₅O₁₂, (□) Li₄Ti₅O₁₂/TiO₂-SiO₂, and (△) Li₄Ti₅O₁₂/SiO₂ (b)

rechargeable LIBs. The conducting PTh layer was successfully coated on the surface of Li₄Ti₅O₁₂ through the in situ oxidative polymerization method. Specific capacities of 172, 168, and 151 mA h g⁻¹ at 0.2, 1, and 10 C were obtained in the Li₄Ti₅O₁₂/PTh composite. The electrochemical results also show that the Li₄Ti₅O₁₂/PTh exhibits remarkably improved cycling performance as compared with the Li₄Ti₅O₁₂ anode. Moreover, the charge-transfer resistance of Li₄Ti₅O₁₂/PTh electrode was much lower than that of the bare Li₄Ti₅O₁₂, revealing that the PTh coating can significantly increase the electron conductivity between the Li₄Ti₅O₁₂ particles [59].

Wang in your research fabricated the spinel Li₄Ti₅O₁₂/rutile-TiO₂@carbon (LTO-RTO@C) composites via a hydrothermal method combined with calcination treatment employing glucose as carbon source. The carbon coating layer and the in situ-formed rutile-TiO₂ can effectively enhance the electric conductivity and provide quick Li⁺ diffusion pathways for Li₄Ti₅O₁₂. When used as an anode material for lithium-ion batteries, the rate capability and cycling stability of LTO-RTO@C composites were improved in comparison with those of pure Li₄Ti₅O₁₂ or Li₄Ti₅O₁₂/rutile-TiO₂. The galvanostatic discharge curves of as-assembled full lithium-

ion cells at different rates have a very flat voltage plateau around 1.8 V, implying an ideal battery system [60].

Zhou et al. showed Ce-doped Li₄Ti₅O₁₂ anode materials which were prepared via a solid state reaction. The Ce is designed to replace Ti (Li₄Ti_{5-x}Ce_xO₁₂) or take the place of octahedral interstice (Li₄Ti₅Ce_xO₁₂). The structure analysis results show that it is difficult for Ce to dope into the lattice of Li₄Ti₅O₁₂, because only few Ce can dope in the lattice of Li₄Ti₅O₁₂ and CeO₂ impurity is inevitable in Ce-doped Li₄Ti₅O₁₂ materials. As per their design, Li₄Ti₅Ce_{0.1}O₁₂ with Ce interstitial doping has the bigger lattice volume than Li₄Ti_{4.9}Ce_{0.1}O₁₂ with Ce substitution doping and pristine Li₄Ti₅O₁₂. As for the electrochemical performance, Li₄Ti₅Ce_{0.1}O₁₂ delivers the highest capacity at 0.2 C (over 170 mA h g⁻¹) and best rate performance among the pristine and Ce-doped Li₄Ti₅O₁₂ materials [61].

Lou et al. have synthesized mesoporous LTO hollow spheres and observed relatively high rate performance of 104 mA h g⁻¹ at 20 °C [62]. Additives (e.g., Br⁶⁺, Zr⁴⁺, V⁵⁺, Zn²⁺, Al³⁺, and Sc³⁺) have been observed to increase the electronic conductivity of LTO [63–70]. Various carbon-modified spinel LTO composites have attained more than 90% of the

Fig. 6 SEM images of the electrodes after galvanostatic charging-discharging: (a) LTO, (b) LTO/SiO₂, and (c) LTO/TiO₂-SiO₂

theoretical capacity and superior rate capability [71–86]. In particular, by using flexible current collectors such as carbon nanotubes and fibers, flexible LTO composite electrodes have been obtained [71, 86]. In addition, combining LTO with conducting metallic nanoparticles can also improve the rate performance of LTO electrodes [87–94]. These improvements are noteworthy but still insufficient for power and flexibility-oriented applications.

SEM

The morphology evolution of the samples after galvanostatic process was observed by SEM. Images show that the precursor (Li₄Ti₅O₁₂) has an irregular morphology. But high-resolution image displays that the precursor is assembled by nanoparticles with a homogeneous particle size distribution of

about 300 nm. The nanoparticles agglomerate into a relatively dense and smooth surface with mesopores formed among the interconnected particles. The hierarchical porous structure is formed due to a large amount of mesopores formed among the irregular particles. Such a porous structure plays a vital role in enhancing the power density via reducing the diffusion path length of lithium-ion [50]. However, SEM images of the LTO/TiO₂-SiO₂ (Fig. 6b), LTO (Fig. 6a), and LTO/SiO₂ (Fig. 6c) particles after galvanostatic charging/discharging show that they were coated by a uniform layer. Probably this film can be identified as the SEI layer.

The TiO₂-SiO₂ layer at the edges of the LTO nanosheets inherits the advantage of nanosheet morphology for fast lithium-ion transportation from liquid electrolyte into the nanosheets, which improves surface stability and electrochemical properties of LTO.

Conclusions

The amorphous TiO₂-SiO₂ and SiO₂ nanoparticles were prepared by emulsion method, and then, they were used as additive to the Li₄Ti₅O₁₂ anode. The oxide addition plays a significant influence in the structure, morphology, and electrochemical performances of the anode. The sample with 3 wt% TiO₂-SiO₂ shows highest specific capacity, and they are 166, 150, and 120 mAh g⁻¹ at 0.5, 1, and 5 C rate, respectively. Whereas, the sample with 3 wt% TiO₂-SiO₂ addition shows best cycling performance and the capacity retention after 50 cycles at 1 and 5 C is respectively 99 and 92%. Its capacitive behavior is beneficial for the improvement of the cycling performance. The sample with 3 wt% SiO₂ shows the smallest specific capacity, and they are 120, 110, and 100 mAh g⁻¹ at 0.1, 1, and 5 C rate, respectively.

The Li₄Ti₅O₁₂ has large capacity of 176 mAh g⁻¹ and the best cycling stabilities. It has a large specific surface area, and the porous structure has advantages for lithium diffusion and contact with the electrolyte.

Through the combination of TiO₂/Li₄Ti₅O₁₂ and TiO₂-SiO₂/Li₄Ti₅O₁₂ composites have exhibited greatly improved electrochemical performances including the superior rate performance and excellent cycle life.

It suggests that this novel electrode would be an alternative material for rechargeable lithium-ion batteries.

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References

- Wilamowska M, Pradeep VS, Graczyk-Zajac M, Riedel R, Soraru GD (2014) Tailoring of SiOC composition as a way to better performing anodes for Li-ion batteries. *Solid State Ionics* 260:94–100
- Li Y, Xu GJ, Yao YF, Xue LG, Yanilmaz M, Lee H, Zhang XW (2014) Coaxial electrospun Si/C–C core–shell composite nanofibers as binder-free anodes for lithium-ion batteries. *Solid State Ionics* 258:67–72
- Liu J, Song KP, Aken PAV, Maier J, Yu Y (2014) Self-supported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -C nanotube arrays as high-rate and long-life anode materials for flexible Li-Ion batteries. *Nano Lett* 14:2597–2601
- Hasegawa G, Kanamori K, Kiyomura T, Kurata H, Nakanishi K, Abe T (2015) Hierarchically porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials for Li- and Na-Ion batteries: effects of nanoarchitectural design and temperature dependence of the rate capability. *Adv Energy Mater* 8:1–8
- Yu L, Wu HB, Lou XW (2013) Rational construction of a metal core for smart combination with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as integrated arrays with superior high-rate Li-ion storage performance. *Adv Mater* 25:2296–2300
- Chen SL, Wu HB, Hu HH, Mo YH, Yin JL, Wang GL, Cao DX, Zhang YM, Yang BF, She PL (2013) High rate performance of the composites of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Ketjen Black and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -Ketjen Black–multi-walled carbon nanotubes for Li-ion batteries. *Solid State Ionics* 233:1–5
- Wang JQ, Yang ZZ, Li WH, Zhong XW, Gu L, Yu Y (2014) Nitridation Br-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for high rate lithium ion batteries. *J Power Sources* 266:323–327
- Wu HB, Chang S, Liu XL, Yu LQ, Wang GL, Cao DX, Zhang YM, Yang BF, She PL (2013) Sr-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as the anode material for lithium-ion batteries. *Solid State Ionics* 232:13–17
- Kim JG, Park MS, Hwang SM, Heo YU, Liao T, Sun ZQ, Park JH, Kim KJ, Jeong G, Kim YJ, Kim JH, Dou SX (2014) A tailored catalyst for the sustainable conversion of glycerol to acrolein: mechanistic aspect of sequential dehydration. *Chem Sus Chem* 7:1490–1495
- Hu MJ, Jiang YZ (2014) Electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C anode material prepared with a stearic acid carbon source. *J Alloys Compd* 603:202–204
- Wang Y, Rong HB, Li BZ, Xing LD, Li XP, Li WS (2014) Microemulsion-assisted synthesis of ultrafine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C nanocomposite with oleic acid as carbon precursor and particle size controller. *J Power Sources* 246:213–215
- Fang W, Cheng XQ, Zuo PJ, Ma YL, Liao LX, Yin GP (2013) A novel electrospun PVDF/PMMA gel polymer electrolyte with in situ TiO_2 for Li-ion batteries. *Solid State Ionics* 244:52–56
- Wang Y, Zou W, Dai XY, Feng LD, Zhang HQ, Zhou AJ, Li JZ (2014) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C anode material with high-rate performance using phenanthroline as carbon precursor. *Ionics* 20:1377–1380
- Wang YQ, Gu L, Guo YG, Li H, He XQ, Tsukimoto S, Ikuhara Y, Wan LJ (2012) Rutile- TiO_2 nanocoating for a high-rate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode of a lithium-ion battery. *J Am Chem Soc* 134:7874–7877
- Ferg E, Gummow RJ, Kock AD, Thackeray MM (1994) Spinel anodes for Li-ion battery. *J Electrochem Soc* 141:L145–L147
- Ohzuku T, Ueda A, Yamamoto N (1995) Zero-strain insertion material of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ for Rechargeable Lithium Cells. *J Electrochem Soc* 142:1431–1435
- Aldon L, Kubiak P, Womes M, Jumas JC, Olivier-Fourcade J, Tirado JL, Corredor JI, Vicente CP (2004) Chemical and electrochemical Li-insertion into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Spinel. *Chem Mater* 16:5721–5725
- Zhang SS, Xu K, Jow TR (2006) EIS study on the formation of solid electrolyte interfaces in Li-Ion battery. *Electrochim Acta* 51:1636–1640
- Schranzhofer H, Bugajski J, Santner HJ, Korepp C, Möller KC, Besenhard JO, Winter M, Sitte W (2006) Electrochemical impedance spectroscopy study of the SEI formation on graphite and metal electrodes. *J Power Sources* 153:391–395
- Zhang SS, Xu K, Jow TR (2004) Optimization of the forming conditions of the solid-state interface in the Li-ion batteries. *J Power Sources* 130:281–285
- Chen CH, Vaughney JT, Jansen AN, Dees DW, Kahaian AJ, Goacher T, Thackeray MM (2001) Studies of Mg-Substituted $\text{Li}_{4-x}\text{Mg}_x\text{Ti}_5\text{O}_{12}$ Spinel Electrodes ($0 \leq x \leq 1$) for Lithium Batteries. *J Electrochem Soc* 148:A102–A104
- Doi T, Iriyama Y, Abe T (2005) Ogumi electrochemical insertion and extraction of Lithium Ion at uniform nanosized $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ particles prepared by a spray pyrolysis method. *Chem Mater* 17:1580–1583
- Guerfi A, Sevigny S, Lagace M, Hovington P, Kinoshita K, Zaghib K (2003) Nano-particle $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel as electrode for electrochemical generators. *J Power Sources* 119–121:88–94
- Cheng L, Liu HJ, Zhang JJ, Xiong HM, Xia YY (2006) Nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by molten salt method as an electrode material for hybrid electrochemical supercapacitors. *J Electrochem Soc* 153:A1472–A1477
- Abe Y, Matsui E, Senna M (2007) Preparation of phase pure and well-crystallized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles by precision control of starting mixture and calcining at lowest possible temperatures. *J Phys Chem Solids* 68:681–686
- Yi TF, Shu J, Zhu YR, Zhu XD, Zhu RS, Zhou AN (2010) Advanced electrochemical performance of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ as a reversible anode material down to 0 V. *J Power Sources* 195:285–288
- Capsoni D, Bini M, Massarotti V, Mustarelli P, Chiodelli G, Azzoni CB, Mozzati MC, Linati L, Ferrari S (2008) Cations distribution and valence states in Mn-substituted $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structure. *Chem Mater* 20:4291–4298
- Wolfenstine J, Allen JL (2008) Electrical conductivity and charge compensation in Ta doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$. *J Power Sources* 180:582–585
- Huang SH, Wen ZY, Zhu XJ, Gu ZH (2004) Preparation and electrochemical performance of Ag doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$. *Electrochem Commun* 6:1093–1097
- Kim J, Cho J (2007) Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowires for high-rate Li-ion intercalation electrode. *Electrochem. Solid State Lett.* 10:A81–A84
- Ji S, Zhang J, Wang W, Huang Y, Feng Z, Zhang Z, Tang Z (2010) Preparation and effects of Mg-doping on the electrochemical properties of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode material for lithium ion battery. *Mater Chem Phys* 123:510–518
- Wang J, Liu XM, Yang H, Shen XD (2011) Characterization and electrochemical properties of carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by a citric acid sol–gel method. *J Alloys Compd* 509:712–718
- Wang GJ, Gao J, Fu LJ, Zhao NH, Wu YP, Takamura T (2007) Preparation and characteristic of carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material. *J Power Sources* 174:1109–1112
- Huang JJ, Jiang ZY (2008) The preparation and characterization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon nano-tubes for lithium ion battery. *Electrochim Acta* 53:7756–7759
- Li X, Qu MZ, Yu ZL (2010) One-step synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C anode material with high performance for lithium ion batteries. *Solid State Ionics* 181:635–639
- Lewandowski A, Kurc B, Stepniak I, Swiderska-Mocek A (2011) Properties of Li-graphite and LiFePO_4 electrodes in LiPF₆ 6-sulfolane electrolyte. *Electrochim Acta* 56:5972–5978
- Yuan T, Yu X, Cai R, Zhou YK, Shao ZP (2010) Synthesis of pristine and carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and their low-temperature electrochemical performance. *J Power Sources* 195:4997–5004
- Kurc B (2014) Gel electrolytes based on poly(acrylonitrile)/sulpholane with hybrid $\text{TiO}_2/\text{SiO}_2$ filler for advanced lithium polymer batteries. *Electrochim Acta* 125:415–419

39. Chen JZ, Yang L, Fang SH, Hirano S, Tachibana K (2012) Synthesis of hierarchical mesoporous nest-like $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for high-rate lithium ion batteries. *J Power Sources* 200:59–62
40. Tang YF, Yang L, Fang SH, Qiu Z (2009) *Electrochim Acta* 54: 6244–6247
41. Kurc B, Swiderska-Mocek A (2014) Properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as an anode material in non-flammable electrolytes. *J Appl Electrochem* 44:245–253
42. Woo S, Dokko K, Kanamura K (2007) Preparation and characterization of three dimensionally ordered macroporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for lithium batteries. *Electrochim Acta* 53:79–82
43. Nobili F, Tossici R, Croce F, Scrosati B, Marassi R (2001) An electrochemical ac impedance study of $\text{Li}_x\text{Ni}_{0.75}\text{Co}_{0.25}\text{O}_2$ intercalation electrode. *J Power Sources* 94:238–241
44. Croce F, Nobili F, Deptula A, Lada W, Tossici R, D'Epifanio A, Scrosati B (1999) Marassi an electrochemical impedance spectroscopic study of the transport properties of $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$. *Electrochem Commun* 1:605–607
45. Umeda M, Dokko K, Fujita Y, Mohamedi M, Uchida I, Selman JR (2001) Electrochemical impedance study of Li-ion insertion into mesocarbon microbead single particle electrode: Part I. Graphitized carbon. *Electrochim. Acta* 47:885–888
46. Fey GTK, Yo WH, Chang YC (2002) Electrochemical characterization of $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ electrodes in a 1 M LiPF_6 solution of the ethylene carbonate–diethyl carbonate. *J Power Sources* 105:82–85
47. Edfouf Z, Cuevas F, Latroche M, Georges C, Jordy C, Hezeque T, Caillon G, Jumas JC, Sougrati MT (2011) Nanostructured Si/Sn-Ni/C composite as negative electrode for Li-ion batteries. *J Power Sources* 196:4762–4768
48. Wang C, Appleby AJ, Little FE (2001) Electrochemical impedance study of initial lithium ion intercalation into graphite powders. *Electrochim Acta* 46:1793–1795
49. Nakahara K, Nakajima R, Matsushima T, Majima H (2003) Preparation of particulate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ having excellent characteristics as an electrode active material for power storage cells. *J Power Sources* 117:131–136
50. Schamer S, Weppner PW (1999) *J Electrochem Soc* 146:857–861
51. Xu B, Qian D, Wang Z, Meng YS (2012) *Mater Sci Eng* 73:51–65
52. Chen J (2013) *Materials* 6:156–183
53. Yaroslavtsev AB, Kulova TL, Skundin AM (2015) *Russ Chem Rev* 84:826–852
54. Maier J (2005) *Nat Mater* 4:805–815
55. Maier J (2003) *Solid State Ionics* 157:327–334
56. Yaroslavtsev AB (2012) *Inorg Mater* 48:1193–1209
57. Lewandowski A, Swiderska-Mocek A (2009) Properties of the lithium and graphite-lithium anodes in N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide. *J Power Sources* 194:502–507
58. Lai C, Dou YY, Li X, Gao XP (2010) *J Power Sources* 195:3676–3679
59. Xu D, Wang P, Yang R (2017) *Ceram Int* 43:7600–7606
60. Wang P, Zhang G, Cheng J, You Y, Li Y-K, Ding C, Gu J-J, Zheng X-S, Zhang C-F, Cao FF (2017) *ACS Appl Mater Interfaces* 9: 6138–6143
61. Zhou TP, Feng XY, Guo X, Wu WW, Cheng S, Xiang HF (2015) *Electrochim Acta* 174:369–375
62. Yu L, Wu HB, Lou XWD (2013) *Adv Mater* 25:2296–2300
63. Bai YJ, Gong C, Lun N, Qi YX (2013) *J Mater Chem A* 1:89–96
64. Bai YJ, Gong C, Qi YX, Lun N, Feng J (2012) *J Mater Chem* 22: 19054–19060
65. Kim JG, Park MS, Hwang SM, Heo YU, Liao T, Sun Z, Park JH, Kim KJ, Jeong G, Kim YJ (2014) *ChemSusChem* 7:1451–1457
66. Lin C, Ding B, Xin Y, Cheng F, Lai MO, Lu L, Zhou H (2014) *J Power Sources* 248:1034–1041
67. Yi TF, Xie Y, Wu Q, Liu H, Jiang L, Ye M, Zhu R (2012) High rate cycling performance of lanthanum-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials for lithium ion batteries. *J Power Sources* 214:220–226
68. Zhang Y, Zhang C, Lin Y, Xiong DB, Wang D, Wu X, He D (2014) Influence of Sc 3+ doping in B-site on electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials for lithium-ion battery. *J Power Sources* 250:50–57
69. Yi TF et al (2010) Recent development and application of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anodematerial of lithium ion battery. *J Phys Chem Solids* 71:1236–1242
70. Du G, Sharma N, Peterson VK, Kimpton JA, Jia D, Guo Z (2011) *Adv Funct Mater* 21:3990–3997
71. Feckl JM, Fominykh K, Doblinger M, Fattakhova-Rohlfing D, Bein T (2012) *Angew Chem Int Ed* 51:7459–7463
72. Hao X, Bartlett BM (2013) *Adv Energy Mater* 3:753–761
73. Jung HG, Myung ST, Yoon CS, Son SB, Oh KH, Amine K, Scrosati B, Sun YK (2011) *Energy Environ Sci* 4:1345–1351
74. Kim C, Norberg NS, Alexander CT, Kostecki R, Cabana J (2013) Mechanism of phase propagation during lithiation in carbon-free $\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery electrodes. *Adv Funct Mater* 23:1214–1222
75. Li N, Zhou G, Li F, Wen L, Cheng HM (2013) *Adv Funct Mater* 23: 5429–5435
76. Liu J, Song K, Aken PA, Maier J, Yu Y (2014) *Nano Lett* 14:2597–2603
77. Ma Y, Ding B, Ji G, Lee JY (2013) *ACS Nano* 7:10870–10878
78. Pan H, Zhao L, Hu YS, Li H, Chen L (2012) *Chem Sus Chem* 5: 526–529
79. Park KS, Benayad A, Kang DJ, Doo SG (2008) Nitridation-driven conductive $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for lithium ion batteries. *J Am Chem Soc* 130:14930–14931
80. Shen L, Uchaker E, Zhang X, Cao G (2012) Hydrogenated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowire arrays for high rate lithium ion batteries. *Adv Mater* 24:6502–6506
81. Shen L, Yuan C, Luo H, Zhang X, Xu K, Xia Y (2010) Facile synthesis of hierarchically porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microspheres for high rate lithium ion batteries. *J Mater Chem* 20:6998–7004
82. Shen L, Yuan C, Luo H, Zhang X, Yang S (2011) In situ synthesis of high-loading $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -graphene hybrid nanostructures for high rate lithium ion batteries. *Lu X. Nano* 3:572–574
83. Shen L, Zhang X, Uchaker E, Yuan C, Cao G (2012) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles embedded in a mesoporous carbon matrix as a superior anode material for high rate lithium ion batteries. *Adv nergy Mater* 2:691–698
84. Tang Y, Huang F, Zhao W, Liu Z, Wan D (2012) Synthesis of graphene-supported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets for high rate battery application. *J Mater Chem* 22:11257–11260
85. Yang Y, Qiao B, Yang X, Fang L, Pan C, Song W, Hou H, Ji X (2014) Lithium titanate tailored by cathodically induced graphene for an ultrafast lithium ion battery. *Adv Funct Mater* 24:4349–4356
86. Zhao L, Hu YS, Li H, Wang Z, Chen L (2011) Porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated with N-doped carbon from ionic liquids for Li-Ion batteries. *Adv Mater* 23:1385–1388
87. Li N, Mei T, Zhu Y, Wang L, Liang J, Zhang X, Qian Y, Tang K (2012) Hydrothermal synthesis of layered $\text{Li}_{1.8}\text{Hf}_{0.19}\text{Ti}_{2.05}\text{xH}_2\text{O}$ nanosheets and their transformation to single-crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets as the anode materials for Li-ion batteries. *Cryst Eng Comm* 14:6435–6440
88. Kim JG, Shi D, Park MS, Jeong G, Heo YU, Seo M, Kim YJ, Kim JH, Dou SX (2013) Preparation and characterization of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles anode materials for lithium ion battery. *Nano Res* 6:365–372
89. Krajewski M, Michalska M, Hamankiewicz B, Ziolkowska D, Korona KP, Jasinski JB, Kaminska M, Lipinska L, Czerwinski A (2014) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ modified with Ag nanoparticles as an advanced anode material in lithium-ion batteries. *J Power Sources* 245:764–777
90. Liu Z, Zhang N, Wang Z, Sun K (2012) Highly dispersed Ag nanoparticles (<10 nm) deposited on nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ demonstrating high-rate charge/discharge capability for lithium-ion battery. *J Power Sources* 205:479–482

91. Wang W, Guo Y, Liu L, Wang S, Yang X, Guo H (2014) Gold coating for a high performance $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorod aggregates anode in lithium-ion batteries. *J Power Sources* 245:624–629
92. Li X, Qu MZ, Huai YJ, Yu ZL (2010) Preparation and electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon/carbon nano-tubes for lithium ion battery. *Electrochim Acta* 55:2978–2982
93. Webber A, Blomgren GE (2002) In: van Schalkwijk WA, Scrosati B (eds) *Advances in lithium-ion batteries*. New York, Kluwer
94. Lewandowski A, Swiderska-Mocek A (2009) Ionic liquids as electrolytes for Li-ion batteries - an overview of electrochemical studies. *J Power Sources* 194:601–609