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Simple solution-combustion synthesis of Fe₂TiO₅ nanomaterials with enhanced lithium storage properties



CERAMICS

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ABSTRACT

The porous Fe_2TiO_5 particles are successfully synthesized through a facile one step solution combustion method. The Fe_2TiO_5 negative materials exhibit remarkable electrochemical performance with discharge capacities of 371.4 mAh g⁻¹ at the 100 th cycle, and display promising rate stability with discharge capacities 76.6 mAh·g⁻¹ at a high current density of 3.2 A g^{-1} . In addition, the mechanism of electrochemistry reaction is illustrated by the CV, raman and EIS measurements, the irreversible capacity mainly causes from the irreversible lithium insertion at 1.8 V. The results indicate that the one step solution combustion synthesis of porous Fe_2TiO_5 is a promising strategy for developing low-cost and high-performance Ti-based negative materials.

1. Introduction

Lithium-ion batteries (LIBs) have developed rapidly and are used widely in portable mobile devices in the past two decades due to the advantages of high voltages, high energy densities, long cycle life and no memory effects [1]. Titanium-based materials are an important class of materials with commercial development value as anode materials in LIB. The most representative Li4Ti5O12 [2] exhibit excellent cycling stability, but low theoretical specific capacity (175 mAh·g⁻¹). TiO₂ [3] is another attractive material with stable structure and promising theoretical capacity (335 mAh·g⁻¹). Unfortunately, its actual capacity is less than half of the theoretical value. The metal oxides (MO) [4], such as CoO [5], SnO $_2$ [6], Fe $_3O_4$ [7] and so on, display high discharge capacities as a negative electrode of lithium ion batteries. However, the conversion reaction occurs in the charge-discharge cycles, which causes the structural instability and the rapid decline of capacities [8]. Therefore, researchers have prepared TiNb₂O₇ [9], MnTiO₃ [10], Zn₂Ti₃O₈ [11], SrTiO₃ [12] and other materials, hoping to couple the advantages of the structural stability of TiO2 with the high capacities of MO

 Fe_2TiO_5 [13] has a low band gap energy (2.1 eV), better conductivity than TiO_2 (band gap of 3.1 eV), and application in the photo degradation of water [14], catalysis [15] and gas sensing [16], but generates less attention as an anode materials of LIB. Yong-Song Luo

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[17] et al. synthesized TiO₂@Fe₂O₃ composites by a hydrothermal method that retained the synergistic effect of TiO₂ and Fe₂O₃. Layered hollow TiO₂@Fe₂O₃ nanostructure composites were prepared by Jing-Shan Luo [18] et al. using atomic layer deposition and sacrificial template hydrolysis. In 2012, Fe₂TiO₅ was first synthesized and explored as the negative materials of LIBs by Kyung-Mi Min et al. [19] utilizing ball milling and hydrothermal method, but the capacity decayed rapidly. Then, Shimei Guo et al. [20]. prepared Fe₂TiO₅@C with a hollow structure by a solvothermal method, which improved the electrochemical properties to some extent. Lately, D.T. Franca et al. [21] reported a ball milling and post annealing method for the preparation of Fe₂TiO₅ nanoparticles, while the electrochemical behavior was not discussed.

In this work, we synthesized porous Fe_2TiO_5 with a three-dimensional porous network structure through a one step facile and quick solution combustion strategy. As a negative electrode, Fe_2TiO_5 exhibits remarkable cycling performance and rate stability. In view of the different initial electrochemical processes, we combined the CV, raman and EIS measurements to explore and tentatively analyse the reasons for the irreversible capacity of the larger first discharge process.



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Fig. 1. XRD patterns of the Fe_2TiO_5 nanomaterial prepared by solution-combustion synthesis at different temperatures for 30 min.

2. Experimental

2.1. Material synthesis

The synthetic steps used to prepare porous Fe_2TiO_5 particles were as follows: (1) Dropwise, dilute ammonia solution was slowly added into tetrabutyltitanate $[Ti(C_4H_9O)_4]$ (6 mmol) in an ice-water bath under magnetic stirring and the TiO(OH)₂ was precipitated. (2) The as-prepared TiO(OH)₂ was then dissolved in nitric acid to obtain the [TiO (NO₃)₂] solution. (3) Subsequently, 4.20 g of Fe(NO₃)₃·6H₂O (12 mmol) and 3.00 g of glycine were mixed with the as-prepared [TiO(NO₃)₂] solution by ultrasound. (4) Finally, the mixed solution were collected in an alumina crucible and placed into a muffle furnace preheated to different temperature (700 °C, 800 °C and 900 °C) and roasted for 30 min, then waited for it to cool naturally in the atmosphere, this cooling was the last step in preparing Fe₂TiO₅ materials.

2.2. Material characterization

The Rigaku MiniFlex600 X'pert with Cu K α radiation was applied to record the X-ray diffraction (XRD) patterns. Field emission scanning electron microcopy (SEM, LEO 1530, HITACHI S-4800) was carried out to observe morphologies observance and high-resolution transmission electron microscopy (HRTEM, TECNAI G2 F30) was employed to determine the microstructural character. The Brunauer-Emmette-Teller (BET) method was introduced to attain the specific surface area of the materials by a porosity analyser (ASAP 2020). Raman spectra were



Fig. 3. Nitrogen adsorption-desorption isotherms of Fe₂TiO₅ at 77 K.

collected by a Jobin Yvon Horiba Raman spectrometer (LabRAM HR800) at the excitation wavelength of 632.8 nm.

2.3. Electrochemical measurements

CR2016 coin-type cells were assembled to evaluate the electrochemical performance of the as-prepared Fe₂TiO₅ particles. The electrodes were prepared by preparing a slurry consisting of 80 wt% of the as-prepared Fe2TiO5 powder, 10 wt% of carbon black, and 10 wt% of poly-vinylidene fluoride (PVDF) as the binder, and then uniformly coating the slurry on a copper current collector foil and during under vacuum at 80 °C for 12 h. Moreover, metallic lithium foil was used as the reference electrode and a micro-porous polyethylene film (Celgard 2400) acted as the separator. The electrolyte was 1.0 M LiPF₆ in a 1:1 mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC). Electrodes had the same efficient work area of 0.785 cm^2 , loading of 5.0 mg/cm $^{-2}$ and thickness of 35 μ m. Subsequently, CR2016 coin-type cells were assembled in an argon-filled glove box. Galvanostatic tests were conducted at room temperature $(25 \pm 1^{\circ}C)$ with different current densities over a voltage range of 0.01–3.0 V using a cell test instrument (LAND-CT2001A). Cyclic voltammetry (CV) curves were recorded at a scan rate of 0.1 mV s^{-1} between 0.01 V and 3.0 V (versus Li/Li⁺) by using an electrochemical workstation (Autolab PGSTAT 101). Electrochemical impedance spectra (EIS) of the as-prepared sample discharged and charged at different voltages were performed using the same electrochemical workstation within the frequency range from 10 mHz to 100 kHz and an AC amplitude of 10 mV. The test conditions were unified such that the batteries were discharged or charged to a certain state, held at constant potential for 30 min, and



Fig. 2. SEM images of Fe₂TiO₅ nanomaterials prepared by solution-combustion synthesis at different temperatures for 30 min (a, d) 700 °C; (b, e) 800 °C; (c, f) 900 °C.



Fig. 4. (a, b) HR-TEM images of Fe_2TiO_5 nanomaterials; (c) the corresponding SAED patterns of (b); and (d) representation of the Fe_2TiO_5 structure with projection along the *b* cell axis [23].



Fig. 5. (a) Cycle performance of Fe_2TiO_5 electrode over 100 cycles at a low capacity rate of 100 mA g⁻¹; (b) Charge-discharge capacities and rate capabilities of Fe_2TiO_5 at different current densities; (c) Chargedischarge profiles of the Fe_2TiO_5 electrode; (d) Cyclic voltammetry curves of the Fe_2TiO_5 electrode over the voltage range of 0.01–3.0 V at a scan rate of 0.1 mV s⁻¹.



Fig. 6. Ex situ raman patterns of the Fe_2TiO_5 electrode at different discharge and charge voltages in the initial cycle.



Fig. 7. Nyquist plots of the Fe_2TiO_5 electrode at a series of potentials in the initial discharge process.

then subjected to the EIS test.

3. Results and discussion

Fig. 1 exhibits the XRD patterns of the as-prepared Fe_2TiO_5 particles at different temperature. It can be observed that the sample synthesized at 700 °C displays some impurities peaks of Fe_2O_3 . Compared with the sample, the other two samples prepared at 800 °C and 900 °C both

Table 1

exhibit a stronger characteristic peak of Fe₂TiO₅, and most diffraction peaks can be assigned to an orthorhombic structure with the main characteristic peaks marked by their indices (JCPDS 41-1432). However, the intensities of the peaks corresponding to Fe₂O₃ (JCPDS 33-0664) are significantly increased when the sintering temperature up to 900 $^{\circ}$ C, indicating that the well crystalline Fe₂TiO₅ can be obtained at 800 $^{\circ}$ C through the solution combustion method.

The SEM images of three Fe₂TiO₅ samples at different temperature are shown in Fig. 2. It is found that the sample prepared at 700 °C mainly displays a bock-shaped structure, while the other two Fe₂TiO₅ simples at higher temperature both exhibit three dimensional network and embedded pores morphology, The surface area is $18.94 \text{ m}^2 \text{ g}^{-1}$, calculated by N₂ isotherms at 77 K for Fe₂TiO₅ nanomaterials in Fig. 3, and the average pore volume obtained from the Barrett-Joyner-Halenda (BJH) method is $2.15 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$. The average particle size is 316.7 nm and meso-pore width is 6 nm for the Fe₂TiO₅ sample, which exhibits a high surface-to-volume ratio and short path length for lithium insertion, which is beneficial to enhance the electrochemical performance. The hysteresis loops in the curve of Fig. 3 result from by the capillary agglomeration caused by the three-dimensional reticular irregularity. This is consistent with the observation from SEM images.

The TEM images in Fig. 4a further demonstrate that the as-prepared Fe_2TiO_5 is bonded by nanoscale primary particles. The high magnification image (Fig. 4b) demonstrates that the lattice fringes of the crystals are complex. The corresponding SAED patterns of Fig. 4c indicate that the as-prepared Fe_2TiO_5 is amorphous. The structure of Fe_2TiO_5 as reported by Guillaume Seitz et al. [24], is shown in Fig. 4d. The two layers of O^{2-} deposited octahedra are connected by with the edge to form M1 (4c) and M2 (8f), while Fe^{3+} and Ti^{4+} are arranged amorphously in these sites. Because the sample prepared at 800 °C has a good crystallinity and minimal impurities, this sample is subjected to a more detailed analysis in subsequent tests.

The Fe₂TiO₅ sample was formed into electrodes, and their cycling performance was tested. In Fig. 5a, the discharge capacity of Fe₂TiO₅ is 1176 mAh·g⁻¹ in the first cycle with a coulombic efficiency of 53.6% at the capacity rate of 0.1 Ag^{-1} . The capacity is markedly reduced in the previous discharge processes, but this is followed by almost no further capacity loss. The discharge capacity remains at 355.1 mAh·g⁻¹ after 100 cycles. Meanwhile, the Fe₂TiO₅ exhibits excellent rate properties. As shown in Fig. 5b, the discharge capacities are 406.2, 318.7, 248.7, 174.4, 117.8 and 76.6 mAh g^{-1} at the current densities of 0.1, 0.2, 0.4, 0.8, 1.6 and 3.2 A g^{-1} , respectively, and it still retains a high capacity of 376.4 mAh g^{-1} when the current density returns back to 0.1 A g^{-1} . The excellent cycling performance and rate stability should be mainly contributed to the two following factors: (1) The as-prepared Fe₂TiO₅ particles exhibit three dimensional network and embedded pores morphology, which facilitates the infiltration of electrolyte; (2) the nano-primary particles with favourable surface-to-volume ratio can increase the diffusion coefficient of lithium ions.

The equivalent circuit paramete	s obtained from a fit of the experimenta	il impedance spectra in the initia	al discharge and charge process.

	OCP	D-1.8V	D-0.9V	D-0.5V	D-0.2V	D-0.01V	C-0.5V	C-1.5V	C-3.0V
$R_s(\Omega)$	2.8	2.8	2.8	5.4	4.6	5.3	2.5	2.9	1.7
CPE1-T	3.4E-05	7.1E-05	2.8E-03	4.3E-05	9.2E-04	3.0E-05	1.3E-05	1.7E-06	7.7E-05
CPE1-P	0.7	0.7	0.8	0.7	0.8	0.7	0.9	0.9	0.7
$R_{f}(\Omega)$	446.8	68.1	45.5	117.7	244.8	54.7	8.8	12.3	108.2
CPE2-T	-	-	2.0E-06	7.8E-04	2.6E-05	9.3E-04	2.9E-05	3.2E-07	-
CPE2-P	-	-	0.9	0.9	0.7	0.8	0.8	0.8	-
R_{ct1} (Ω)	-	-	15.3	67.5	57.7	114.0	51.1	50.7	-
CPE3-T	3.1E-04	1.5E-03	2.1E-05	4.7E-06	1.6E-05	8.8E-05	3.2E-03	2.2E-03	9.0E-04
CPE3-P	0.9	0.8	0.8	0.8	0.9	0.8	0.8	0.8	0.6
R_{ct2} (Ω)	438.7	195.5	57.1	61.3	91.1	41.9	35.5	45.1	257.7
Wo-R	102900.0	7246.0	113.3	176.3	592.3	739.0	76.4	72.4	21265.0
Wo-T	154.7	154.0	18.0	2.2	124.8	250.5	15.0	11.1	65.9
Wo-P	0.9	0.8	0.4	0.4	0.4	0.7	0.3	0.4	0.8

From the charge-discharge profiles of Fe_2TiO_5 electrodes at constant current (Fig. 5c), four platforms at approximately 1.8 V, 0.8 V, 0.5 V and 0.1 V can be observed in the first discharge process. Only a stable platform at approximately 0.9 V remains in the subsequent discharge cycles because of the disappearance of platforms at 1.8 V, 0.5 V and 0.1 V, which is the main reason for the capacity loss in the first cycle.

To characterize the electrochemical behavior of Fe₂TiO₅ electrodes during the charging and discharging processes and to confirm the capacity decrease in the first cycle, the cyclic voltammetry (CV) curves of Fe₂TiO₅ electrodes are measured and displayed in Fig. 5d. Corresponding to the charge-discharge profiles, three cathodic peaks occurs at 1.8 V. 0.8 V and 0.3 V, while two anodic peaks at 0.7 V and 1.5 V simultaneously appear in the first cycle. In the subsequent cycles, the cathodic peaks at 1.8 V and 0.3 V disappear. At the same time, the cathodic peak at 0.9 V migrates to 0.6 V. The literature explains that the cathodic peak at 0.9 V can be attributed to the Fe³⁺ reduction reaction [17,18,20], and that the irreversible cathodic peak below 0.5 V that belongs to the multi-step reduction of Ti⁴⁺ and the formation process of solid electrolyte interface (SEI) film [25]. The cathodic peaks at approximately 0.7 V appearing in the subsequent cycles of 0.7 V can be ascribed to the reduction of Ti⁴⁺, while the peak at 1.5 V occurring in the corresponding anodic progress can be identified as the Ti⁺⁴/Ti⁺³ conversion peak [20,26-28], whose potential increases in a continuous loop during the subsequent cycles due to the polarization of the materials [23,24].

To further understand the electrochemical behavior of the of Fe_2TiO_5 obtained solution combustion method, we carried out the raman and alternating-current impedance test for the Fe_2TiO_5 electrode at different working stages.

The ex situ raman results (Fig. 6) tested at the open circuit potential (OCP) and different discharge states (D-1.8 V, D-0.9 V, D-0.5 V) provide important information for the study of the structural changes and possible reactions of the Fe₂TiO₅ electrode during the initial discharge process. For the OCP state of the Fe₂TiO₅ electrode, the raman peaks at 200 and 224 cm⁻¹ are attributed to the O–Ti–O angular vibrations [29,30]; the peak at 659 cm⁻¹ belongs to the Ti–O bond vibration in the TiO₆ octahedron [31,32]; and the peaks at 293 and 612 cm⁻¹ are attributed to the Eg symmetric vibration of Fe₂O₃ [33].

In the D-1.8 V state, the stretching vibration peak of the Li-O-Ti bond appears at 338 cm⁻¹ [29,34], which indicates that the intercalation reaction of Li⁺ occurs at 1.8 V, as shown in reaction scheme (1). Since the reduction peak at 1.8 V in the CV plot is irreversible, it is shown that the reaction of the Li⁺ embedded Fe₂TiO₅ lattice is irreversible and can cause the crystal structure of Fe₂TiO₅ to be destroyed. From the observed phenomenon that the Eg symmetrical vibration peak of Fe₂O₃ is weakened at D-1.8 V and disappears at D-0.9 V, it can be judged that Li⁺ begins to embed with Fe₂O₃ lattice as reaction scheme (2), and the reduction of Fe^{3+} is complete when this electrode is discharged to 0.9 V. Meanwhile, the vibration peak at 659 cm⁻¹ belonging to TiO_2 is weakened, probably due to the lattice of Li^+ embedded in TiO₂, as shown in reaction scheme 3. When this electrode is discharged to 0.5 V, new peaks appear at 243 and 410 cm^{-1} , which belong to the $A_{1\sigma}$ symmetrical vibration of Fe₂O₃ [35]. The conversion reaction of Li₂(Fe₂O₃) may occur as shown in reaction scheme 4. These presumed results are reasonable because they are consistent with the results reported in papers (the reduction peak at 0.9 V belongs to the reduction reaction of Fe³⁺ and the reduction peak at 0.7 V is attributed to the reduction peak of Ti⁴⁺).

 $Fe_2TiO_5 + xLi^+ + xe^- \rightarrow Li_xFe_2TiO_5$ (1)

$$Fe_2O_3 + 2Li^+ + 2e^- \rightarrow Li_2(Fe_2O_3)$$
⁽²⁾

 $TiO_2 + x Li^+ + x e^- \rightarrow Li_x TiO_2$ (3)

 $Li_2(Fe_2O_3) + 4Li^+ + 4e^- \rightarrow 2Fe + 3Li_2O$ (4)

Fig. 7 displays the ex situ EIS spectra of the Fe₂TiO₅ electrode

discharged and charged at different voltages in the 1st cycle. Table 1 lists the collected results of various components using the equivalent circuit shown in Fig. 7. At OCP, the Nyquist plot of the Fe₂TiO₅ electrode appears as a small semicircle in the high frequency (HF) range, as a large radius of the semicircle in the middle frequency (MF) region and as the approximation of an inclined straight line in the low frequency (LF) range. With discharge to 1.8 V (D-1.8 V), the MF semicircle radius decreases. With further discharge (D-0.9 V), the semicircle of the MF region splits into two semicircles, and the radii of the two semicircles further decrease. According to the literature and monograph reports [36,37], it is generally believed that the HF region resistance is caused by the formation of SEI film on the electrode surface, the resistance of the MF region represents the charge transfer impedance and that of the LF region arises from Li⁺ diffusion in the electrode material. Connected with the CV and raman analysis results that the as-prepared Fe₂TiO₅ undergoes the reduction reaction of Fe^{3+}/Fe^{2+} and the reaction of Li⁺ embedded in the crystal lattice of TiO2 at D-0.9 V state, the two semicircles of the MF region correspond to the impedance of the two reactions. With the continued discharge, the radii of the two semicircle of the MF region increase, indicating that the reduction resistances of Fe²⁺ and Ti⁴⁺ increase with the progress of the reaction until complete discharge (D-0.01 V). During the initial charging process, the two semicircular impedances of the MF region are gradually reduced, and the charge resistances of the reduction reaction of Fe^{2+} and Ti^{3+} decrease. After charging to 3.0 V, the impedance returns to the same state as the OCP state.

4. Conclusion

In summary, we developed a novel and facile one step solution combustion method for the synthesis of porous Fe_2TiO_5 . The as-prepared Fe_2TiO_5 negative materials exhibits promising electrochemical performance with a discharge capacity of 406.2 mAh g⁻¹ at a current density of 0.1 A g⁻¹ in the voltage range of 0.01–3.0 V and displays perfect cyclic performance. From CV, raman and EIS characterization, we can observe that lithium ions are embedded in different lattice planes at different potentials in the initial discharge process, which illustrates that the irreversible reaction in the first cycling comes from the lithium ions insertion in the lattice of the Fe_2TiO_5 . Our results suggest that the use of solution combustion method could provide a convenient and promising strategy for preparing $SrTiO_3$, NbTiO₃, and other Ti-based transition metal oxide electrode materials.

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References

- J.B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries, Chem. Mater. 22 (2010) 587–603.
- [2] W. Meng, Y. Xu, B. Yan, In situ nano-sized spinel Li₄Ti₅O₁₂ powder fabricated by a one-step roasting process in molten salts, J. Alloy. Comp. 732 (2018) 784–791.
- [3] J. Zhang, Y. Li, T. Gao, X. Sun, P. Cao, G. Zhou, Flower-shaped TiO_2/C microspheres embedded with fish-scale-like MoS_2 as anodes for lithium-ion batteries, Ceram. Int. 44 (2018) 8550–8555.
- [4] J. Shao, J. Feng, H. Zhou, A. Yuan, Graphene aerogel encapsulated Fe-Co oxide nanocubes derived from prussian blue analogue as integrated anode with enhanced Li-ion storage properties, Appl. Surf. Sci. 471 (2019) 745–752.
- [5] X. Yue, W. Wang, Q. Wang, J. Meng, Z. Zhang, X. Wu, X. Yang, Y. Zhou, CoO nanofiber decorated nickel foams as lithium dendrite suppressing host skeletons for high energy lithium metal batteries, Energy Storage Mater. 14 (2018) 335–344.
- [6] D. Narsimulu, S. Vinoth, E.S. Srinadhu, N. Satyanarayana, Surfactant-free microwave hydrothermal synthesis of SnO₂ nanosheets as an anode material for lithium battery applications, Ceram. Int. 44 (2018) 201–207.
- [7] R. Ding, J. Zhang, J. Qi, Z. Li, C. Wang, M. Chen, N-doped dual carbon-confined 3D architecture rGO/Fe₃O₄/AC nanocomposite for high-performance lithium-ion

batteries, ACS Appl. Mater. Interfaces 10 (2018) 13470-13478.

- [8] B. Xiao, X. Sun, Surface and subsurface reactions of lithium transition metal oxide cathode materials: an overview of the fundamental origins and remedying approaches, Adv. Energy. Mater. 8 (2018) 1802057.
- [9] G. Liu, X. Liu, Y. Zhao, X. Ji, J. Guo, Synthesis of Ag-coated TiNb₂O₇ composites with excellent electrochemical properties for lithium-ion battery, Mater. Lett. 197 (2017) 38–40.
- [10] X. Li, X. He, Y. Xu, L. Huang, J. Li, S. Sun, J. Zhao, Superiority of the bi-phasic mixture of a tin-based alloy nanocomposite as the anode for lithium ion batteries, J. Mater. Chem. A 3 (2015) 3794–3800.
- [11] L. Wang, Z. Meng, H. Wang, X. Li, G. Zhang, Effects of TiO₂ starting materials on the synthesis of Li₂ZnTi₃O₈ for lithium ion battery anode, Ceram. Int. 42 (2016) 16872–16881.
- [12] Z. Li, S. Yasui, S. Takeuchi, A. Creuziger, S. Maruyama, A.A. Herzing, I. Takeuchi, L.A. Bendersky, Structural study of epitaxial LiCoO₂ films grown by pulsed laser deposition on single crystal SrTiO₃ substrates, Thin Solid Films 612 (2016) 472–482.
- [13] Q. Liu, J. He, T. Yao, Z. Sun, W. Cheng, S. He, Y. Xie, Y. Peng, H. Cheng, Y. Sun, Y. Jiang, F. Hu, Z. Xie, W. Yan, Z. Pan, Z. Wu, S. Wei, Aligned Fe₂TiO₅-containing nanotube arrays with low onset potential for visible-light water oxidation, Nat. Commun. 5 (2014) 5122–5126.
- [14] J. Deng, X. Lv, K. Nie, X. Lv, X. Sun, J. Zhong, Lowering the onset potential of Fe₂TiO₅/Fe₂O₃ photoanodes by interface structures: F and Rh based treatments, ACS Catal. 7 (2017) 4062–4069.
- [15] S. Sathasivam, D. Bhachu, Y. Lu, S. Bawaked, A. Obaid, S. thabaiti, S. Basahel, C. Carmalt, I. Parkin, Highly photocatalytically active iron(III) titanium oxide thin films via aerosol-assisted CVD, Chem. Vap. Depos. 21 (2015) 21–25.
- [16] C. Zhu, H. Yu, Y. Zhang, T. Wang, Q. Ouyang, L. Qi, Y. Chen, X. Xue, Fe₂O₃/TiO₂ Tube-like nanostructures: synthesis, structural transformation and the enhanced sensing properties, ACS Appl. Mater. Interfaces 4 (2012) 665–671.
- [17] Y. Luo, D. Kong, J. Luo, Y. Wang, D. Zhang, K. Qiu, C. Cheng, C. Li, T. Yu, Seedassisted synthesis of highly ordered TiO₂@α-Fe₂O₃ core/shell arrays on carbon textiles for lithium-ion battery applications, Energy Environ. Sci. 5 (2012) 6559.
- [18] J. Luo, X. Xia, Y. Luo, C. Guan, J. Liu, X. Qi, C. Ng, T. Yu, H. Zhang, H. Fan, Rationally designed hierarchical TiO₂@Fe₂O₃ hollow nanostructures for improved lithium ion storage, Adv. Energy Mater. 3 (2013) 737–743.
- [19] K. Min, K. Park, A. Lim, J. Kim, D. Kim, Synthesis of pseudobrookite-type Fe₂TiO₅ nanoparticles and their Li-ion electroactivity, Ceram. Int. 38 (2012) 6009–6013.
- [21] D.T. Franca, B.F. Amorim, A.M. de Morais Araujo, M.A. Morales, F. Bohn, S.N. de Medeiros, Structural and magnetic properties of Fe_2TiO_5 nanopowders prepared by ball-milling and post annealing, Mater. Lett. 236 (2018) 526–529.
- [23] X. Li, Q. Xiao, B. Liu, H. Lin, J. Zhao, One-step solution-combustion synthesis of

complex spinel titanate flake particles with enhanced lithium-storage properties, J. Power Sources 273 (2015) 128–135.

- [25] A.S. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J.M. Tarascon, A.K. Shukla, Solution-combustion synthesized nanocrystalline Li₄Ti₅O₁₂ as high-rate performance Li-ion battery anode, Chem. Mater. 22 (2010) 2857–2863.
- [26] C. Qiu, Z. Yuan, L. Liu, S. Cheng, J. Liu, Sol-gel synthesis and electrochemical performance of Li_{4-x}Mg_xTi_{5-x}Zr_xO₁₂ anode material for lithium-ion batteries, Chin. J. Chem. 31 (2013) 819–825.
- [27] D. Dambournet, I. Belharouak, K. Amine, MLi₂Ti₆O₁₄ (M = Sr, Ba, 2Na) lithium insertion titanate materials: a comparative study, Inorg. Chem. 49 (2010) 2822–2826.
- [28] N. Jovic, M. Vucinic-Vasic, A. Kremenovic, B. Antic, C. Jovalekic, P. Vulic, V. Kahlenberg, R. Kaindl, HEBM synthesis of nanocrystalline LiZn_{0.5}Ti_{1.5}O₄ spinel and thermally induced order-disorder phase transition (P4₃32→Fd3m), Mater. Chem. Phys. 116 (2009) 542–549.
- [29] S. Panero, V. Gentili, S. Brutti, L. Hardwick, A. Armstrong, P. Bruce, Lithium insertion into anatase nanotubes, Chem. Mater. 24 (2012) 4468–4476.
- [30] X. Li, J. Zhao, S. Sun, L. Huang, Z. Qiu, P. Dong, Y. Zhang, The application of plasma treatment for Ti³⁺ modified TiO₂ nanowires film electrode with enhanced lithiumstorage properties, Electrochim. Acta 211 (2016) 395–403.
- [31] H. Chiu, X. Lu, S. Elouatik, K. Zaghib, G. Demopoulos, Formation of lithium titanate hydrate nanosheets: insight into a two-dimension growth mechanism by in situ Raman, Cryst. Growth Des. 16 (2016) 3898–3904.
- [32] B. Laskova, L. Kavan, M. Zukalova, K. Mocek, O. Frank, In situ Raman spectroelectrochemistry as a useful tool for detection of TiO₂ (anatase) impurities in TiO₂ (B) and TiO₂ (rutile), Monatsh. Chem. 147 (2016) 951–959.
- [33] Y. Gao, D. Wu, T. Wang, D. Jia, W. Xia, Y. Lv, Y. Cao, Y. Tan, P. Liu, One-step solvothermal synthesis of quasi-hexagonal Fe₂O₃ nanoplates/graphene composite as high performance electrode material for supercapacitor, Electrochim. Acta 191 (2016) 275–283.
- [34] L. Hardwick, M. Holzapfel, P. Novak, L. Dupont, E. Baudrin, Electrochemical lithium insertion into anatase-type TiO₂: an in situ Raman microscopy investigation, Electrochim. Acta 52 (2007) 5357–5367.
- [35] M. Balogun, Z. Wu, Y. Luo, W. Qiu, X. Fan, B. Long, M. Huang, P. Liu, Y. Tong, High power density nitridated hematite (α-Fe₂O₃) nanorods as anode for high-performance flexible lithium ion batteries, J. Power Sources 308 (2016) 7–17.
- [36] K. Wu, J. Yang, X. Qiu, J. Xu, Q. Zhang, J. Jin, Q. Zhuang, Study of spinel Li₄Ti₅O₁₂ electrode reaction mechanism by electrochemical impedance spectroscopy, Electrochim. Acta 108 (2013) 841–851.
- [37] Q. Zhuang, S. Xu, X. Qiu, Y. Cui, L. Fang, S. Sun, Diagnosis of electrochemical impedance spectroscopy in lithium ion batteries, Prog. Chem. 22 (2010) 1044–1057.