

PAPER • OPEN ACCESS

Cr Doping of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by Sol-Gel Method for High Power Lithium-Ion Batteries

To cite this article: Liangliang Chen *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **274** 012064

View the [article online](#) for updates and enhancements.

You may also like

- [Keyword Based System to Enhance the Efficiency of Student's Performance Report in Computer Science Education](#)
Jos Timanta Tarigan, Elvyawati M. Zamzami, Ivan Jaya et al.
- [Mathematical modelling of biology processes based on the table of prime links in the solid torus up to 4 crossings](#)
A A Akimova
- [An Analysis of Haskell Parallel Programming Model in the HalVM](#)
Junseok Cheon, Yeoneo Kim, Taekwang Hur et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Cr Doping of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by Sol-Gel Method for High Power Lithium-Ion Batteries

Liangliang Chen, Chengwei Ma, Xin Li*

School of Chemistry and Chemical Engineering, Beijing Institute of Technology,
100081, Beijing, China

*Corresponding author e-mail: klkxlx@163.com

Abstract. All manuscripts must be in English, also the table and figure texts, otherwise we cannot publish your paper. Please keep a second copy of your manuscript in your office. When receiving the paper, we assume that the corresponding authors grant us the copyright to use the paper for the book or journal in question. Should authors use tables or figures from other Publications, they must ask the corresponding publishers to grant them the right to publish this material in their paper.

1. Introduction

Along with the rapid development of electric vehicles, the demand for lithium-ion batteries with high rate performance is dramatically booming. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has attracted attention on account of its high potential (1.55 V), which provides good stability, and its zero-strain characteristics, which allows high-speed charging and discharging.[1-3] Compared with carbon negative-electrode materials, it can improve the rate capability and cycling life. A main drawback, however, is that its electronic conductivity is very low because of its intrinsically wide band gap of about 2 eV.[4-6]

Various ways have been taken to increase the performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ experimentally and theoretically. High temperature solid-phase method failed to make nanomaterials, but sol-gel did the good job.[7-11] Transition metals, such as chromium, gallium, magnesium, and non-metallic heteroatom, take N, P as examples, could change its electronic properties effectively, which had also been confirmed by the first principle calculations.[12-17] Coating with carbon or graphene to increase the electronic conductivity were also been tried.[18-22] For example, Song et al. modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by doping Cr^{3+} , confirming that stable Cr^{3+} can effectively act as a donor.[23] Sun et al. reported that in situ carbon coating inhibits dimensional expansion and thus nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ could be obtained.[24] Although they have improved the performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ much more, it still can't satisfy the commercial demand for negative-electrode materials. Different chelating agent have been used to control the size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles, different high voltage materials have been tried to combined with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to see any efficient way to obtain superior performance for commercial application.[25-29] Among these research, sol-gel interested us because it can effectively smaller the particle size. Cr^{3+} was been explored mostly because it can be well inserted into the crystal structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. [30-32]

The current paper presents a combined way to obtain modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In this way, sol-gel synthesis and Cr^{3+} doping were used with (EO) 106(PO)70(EO)106 tri-block copolymer (F127) as chelate. This study mainly used it as sol-gel route ligand to form mixed gel under the conditions of



strong acid and the mixed gel was dried at 60 cent degree and calcined in air atmosphere. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to characterize the physical properties, and cyclic voltammetry, charge/discharge test were used to investigate the electrochemical behavior of it. It is found that it shows brilliant rate capacity and cyclability.

2. Experiments

2.1. Synthesis of Cr-Doped LTO

The Cr-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (denoted as LTO as usual) samples were synthesized via a sol-gel route. F127, a kind of nonionic surfactant (EO) 106(PO) 70(EO) 106 tri-block copolymer, was used as chelating agent. 30.0 mL anhydrous ethanol was poured into 2.5 g F127 to dissolve them adequately. 6.0 mL HNO_3 (65 wt%) and 8.8 mL titanate isopropoxide were added in turn with vigorous stirring. Then it is time to prepare another solution. 2.50 g $\text{Li}(\text{AC})_2 \cdot 2\text{H}_2\text{O}$ and 0.36 g $\text{Cr}(\text{AC})_2 \cdot 6\text{H}_2\text{O}$ were added into 20.0 mL anhydrous ethanol to obtain green solution with vigorous stirring. Mixing these two solution and keeping stirring for 5 h to ensure adequate mixing. The final solution was dried for a week at 60°C to form a gel, which was calcined at various temperatures in air gas. The heating rate is set to 1 °C/min and the calcining time is 12 h for every sample. X-ray diffraction (XRD) was used to investigate the lattice structure of the synthesized materials in the range of 10–70 degree. Scanning electron microscopy (SEM) was taken into consideration to examine the morphology of pre-prepared samples, as well as high-resolution transmission electron microscopy (HRTEM).

2.2. Cell fabrication and electrochemical characterizations

The prepared Cr-doped LTO powder, mixed with carbon black and polyvinylidene fluoride (PVDF) to make the negative slurry with several drops of N-methyl pyrrolidinone (NMP). As usual, the weight ratio of them is 8:1:1 and the stirring time is more than 12 h to make sure no more agglomerated particles.[25] This mixed slurry was coated on copper foil using the “doctor blade” technique and then dried at 100°C for more than 12 h under vacuum conditions. The dried film was punched into 12mm round sheets to be the negative electrode for the coin type (CR2025) test cells. 1 M LiPF_6 dissolved in ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate (EC/DMC/EMC, 1:1:1 vol) was used as the electrolyte, porous polypropylene films were used as a separator and Li foil was used as the counter and reference electrodes in the assembled cells. Cyclic voltammetry, electrical impedance spectroscopy (EIS) experiments and constant current charge-discharge measurements at various rates were taken to investigate the electrochemical performance

3. Results and Discussion

Data obtained in previous studies using sol-gel method to synthesize $\text{Li}_4\text{Ti}_5\text{O}_{12}$ indicated that the size can be decreased. According to Sun et al, the grain growth of LTO was effectively restrained by the carbon generated from the carbonization of F127 in the calcination process, and a small particle size of LTO (~20 nm) was successfully obtained.[23] Besides, Song et al. revealed that the Cr^{3+} -ion doping in LTO results in the decreased structural disorder, which lead to both band gap narrowing and the increased ionic diffusivity.[24] In this paper, Cr-doped LTO was obtained using sol-gel method, using F127 as the chelating agent. Figure 1 shows the XRD results.

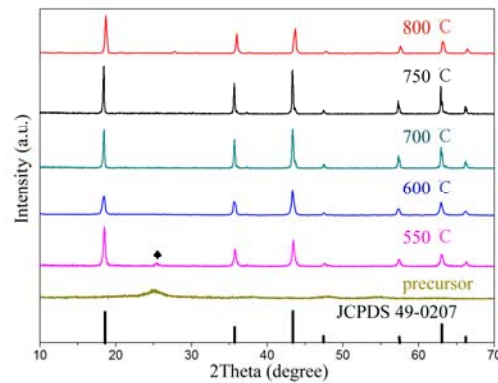


Figure 1. XRD pattern of the Cr-doped LTO calcined at different temperatures.

As can be seen, all peaks of Cr-doped LTO calcined from 600°C to 800°C were perfectly matched with the spinel structure of the $Fd\bar{3}m$ space group without any side peaks, implying that a single-phase spinel structure was prepared. The XRD pattern of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (JCPDS 49-0207) was shown and there is a small difference between 550°C when $2\theta = 25.3^\circ$, which is exactly the typical peak of precursor.[14] This precursor is anatase TiO_2 , which has been pointed out in previous research.[23]

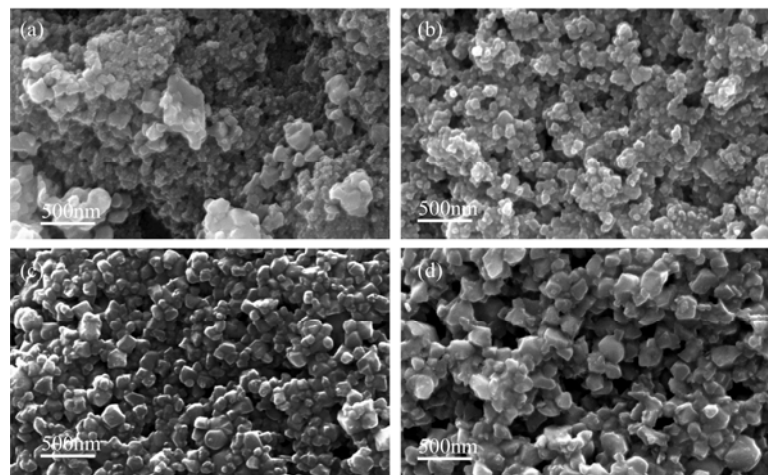


Figure 2. Scanning electronic microscopy images of Cr-doped LTO samples calcined at different temperatures: a) 600°C, b) 700°C, c) 750°C and d) 800°C.

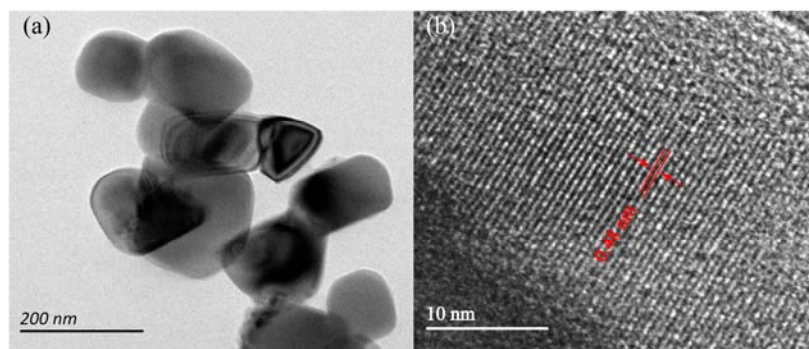


Figure 3. a, b) High-resolution transmission electron microscopy images of Cr-doped LTO

Figure 2 shows SEM images of Cr-doped LTO powders at different temperatures. It is apparent that the cubic morphologies of Cr-doped is familiar with undoped LTO.[23] However, the samples calcined at 750°C showing a quite uniform particle size distribution and the average particle size is about 100 nm. The particles calcined at other temperatures tend to link together rather than form integrated crystal particles. The size of Cr-doped LTO becomes larger along with less dimensional consistency when the calcined temperature is increasing. Transmission electron microscopy (TEM) was examined and the HRTEM images were shown in Figure 3. The uniform particle size distribution is consistent with the SEM images ranging from 80 nm to 200 nm. The average grain diameter is about 100 nm, and the lattice fringe is 0.48 nm, which is consistent with the (111) atomic planes of the spinel structure.

To demonstrate electrochemical performance when the synthesized Cr-doped LTO is used in lithium-ion batteries, electrochemical measurements were applied for the assembled cells with Cr-doped LTO negative electrode, which were shown in Figure 5. The redox peaks were centrosymmetric about the voltage of 1.55 V, which means the intercalation/de-intercalation process is reversible and it is the most important condition for cycling performance. As shown in Figure 4b, the EIS spectra consist of a semicircle and a straight line, which is perfect allied with the fitting curve. They refer to the charge transfer reaction (R_{ct}) and the diffusion of Li^+ in the bulk electrode respectively. By analysing the fitting curve, this R_{ct} is less than 30 Ω and it is smaller than previous research.[14, 25] The first charge/discharge curves and the cycling performance of the as-derived samples at different current rates were shown in Figure 4c and Figure 4d respectively. The specific capacity of first charge/discharge is 255 mAh/g, which is higher than the previous studies for about 50 mAh/g.[23] Additionally, the specific capacity of this synthesized material is 208, 193, 189, 179, 175 and 167 mAh/g at 0.1, 0.5, 1, 5, 10 and 40 C respectively. This quite excellent performance is out of a clear sky, especially for that it can maintain more than 150 mAh/g at 40 C. As shown in Figure 4d, a very stable cyclability is observed for Cr-doped LTO, even at a high current rate of 40 C. at all measured current rates, the capacity loss is less than 0.01% per cycle, which means that the as-derived Cr-doped LTO owns high stability in repeated cycles. From 40 C to 0.1 C, the specific capacity returns 201 mAh/g, indicating superior rate capacity. Moreover, the coulombic efficiency of Cr-doped LTO approaches 100% for each cycle.

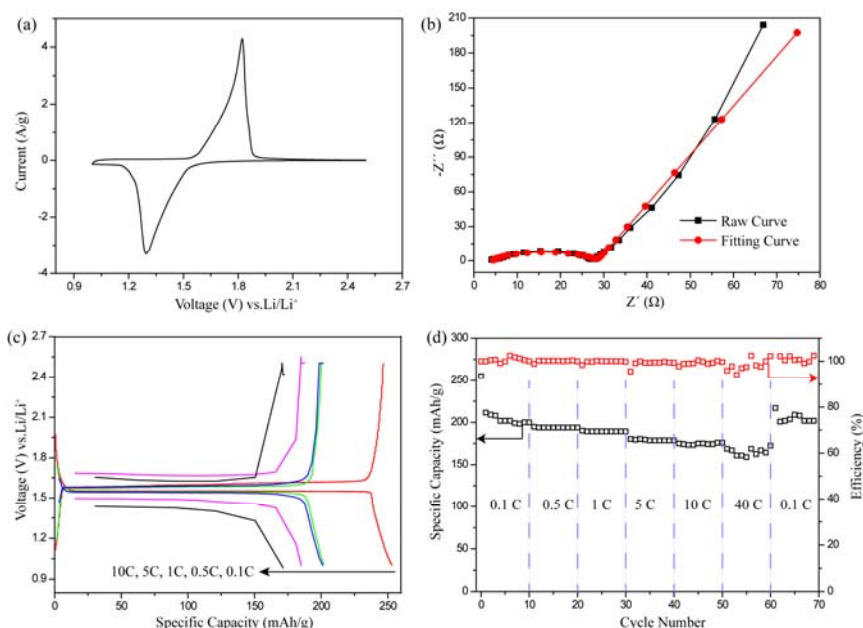


Figure 4. Electrochemical properties of Cr-doped LTO: a) CV curve measuring from 1.0 to 2.5 V, b) EIS curve including the fitting curve at the voltage of 1.55 V, c) charge and discharge curves at different rates and d) cycling performance at various current rates: 1st-10st, 10st-20st, 20st-30st, 30st-40st, 50st-60st and 60st-70st at the rate of 0.1C, 0.5C, 1C, 5C, 10C, 40C and 0.1C respectively.

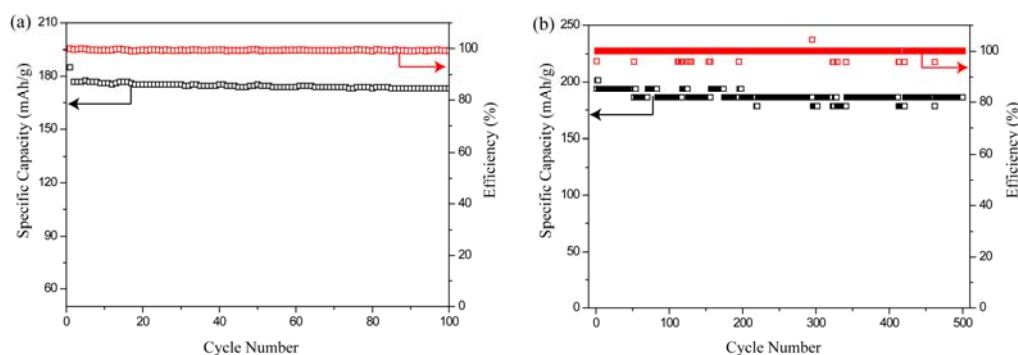


Figure 5. a) Cycling performance at the rate of 1C for 100 cycle numbers, b) at the rate of 5C for 500 cycle numbers.

In order to investigate cycling performance further, a very stable cycling ability was observed for Cr-doped LTO. Cycling for 100 loops at 1C, even cycling for 500 loops at 5C, coulombic efficiency remains at close to 100% and they were shown in Figure 5. These results demonstrated that the Cr-doped LTO has an excellent reversibility and stability.

4. Conclusion

$\text{Li}_{4-x/3}\text{Ti}_{5-2x/3}\text{Cr}_x\text{O}_{12}$ ($x=0.25$) sample was successfully synthesized by sol-gel method in air atmosphere. XRD patterns demonstrated that Cr-doping did not alter the spinel structure or change the fundamental electrochemical reaction mechanism of LTO. The as-prepared samples had an average particle size approximate 100 nm. The electrochemical properties of Cr-doped LTO, especially the rate capability was significantly improved in this work. Experimental results showed that the charge/discharge

specific capacity reached 167 mAh/g at 40C and the coulombic efficiency is almost 100%, showing brilliant high-rate performance for lithium-ion batteries.

Acknowledgments

This work was funded through the National Nature Science Foundation of China (No. 20806008), the National Nature Science Foundation of China (No. 21111120074) and the Beijing Institute of Technology Intercollegiate Cooperation Program (No. 3190012351701).

References

- [1] V. Aravindan, Y.-S. Lee, S. Madhavi, Research progress on negative electrodes for practical lithium-ion batteries: beyond carbonaceous anodes, *Adv. Energy Mater.*, 5 (2015) 1402225.
- [2] S. Chen, Y. Xin, Y. Zhou, Y. Ma, H. Zhou, L. Qi, Self-supported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheet arrays for lithium ion batteries with excellent rate capability and ultralong cycle life, *Energy Environ. Sci.*, 7 (2014) 1975-2044.
- [3] Q. Huang, Z. Yang, J. Mao, Research progress on the low-temperature electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material, *Ionics*, 23 (2017) 803-811.
- [4] D. Liu, C. Ouyang, J. Shu, J. Jiang, Z. Wang, L. Chen, Theoretical study of cation doping effect on the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, *Phys. Stat. Sol. (b)*, 243 (2006) 1835-1841.
- [5] Y. Liu, J. Lian, Z. Sun, M. Zhao, Y. Shi, H. Song, The first-principles study for the novel optical properties of LiTi_2O_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_2\text{Ti}_2\text{O}_4$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$, *Chem. Phys. Lett.*, 677 (2017) 114-119.
- [6] C.Y. Ouyang, Z.Y. Zhong, M.S. Lei, Ab initio studies of structural and electronic properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel, *Electrochem. Commun.*, 9 (2007) 1107-1112.
- [7] S.-L. Chou, J.-Z. Wang, H.-K. Liu, S.-X. Dou, Rapid synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microspheres as anode materials and its binder effect for lithium-ion battery, *J. Phys. Chem. C*, 115 (2011) 16220-16227.
- [8] S.-Y. Li, M. Chen, Y. Xue, J. Wu, X.-G. Zhang, Z.-B. Wang, Electrochemical properties of citric acid-assisted combustion synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ adopting Cr by the solid-state reaction process, *Ionics*, 21 (2015) 1545-1551.
- [9] A.S. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J.M. Tarascon, A.K. Shukla, Solution-combustion synthesized nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as high-rate performance Li-ion battery anode, *Chem. Mater.*, 22 (2010) 2857-2863.
- [10] C. Wang, S. Wang, L. Tang, Y.-B. He, L. Gan, J. Li, H. Du, B. Li, Z. Lin, F. Kang, A robust strategy for crafting monodisperse $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanospheres as superior rate anode for lithium ion batteries, *Nano Energy*, 21 (2016) 133-144.
- [11] L. Yao, Z. Ning, S. Guo, Y. Guo, Y. Sun, C.R. Rambo, T. Yuan, Z. Huang, C. Zhang, D. He, On the sol-gel synthesis mechanism of nanostructured $\text{Li}_{3.95}\text{La}_{0.05}\text{Ti}_{4.95}\text{Ag}_{0.05}\text{O}_{12}$ with enhanced electrochemical performance for lithium ion battery, *Ceram. Int.*, 43 (2017) 3393-3400.
- [12] M. Ganesan, $\text{Li}_4\text{Ti}_2.5\text{Cr}_{2.5}\text{O}_{12}$ as anode material for lithium battery, *Ionics*, 14 (2007) 395-401.
- [13] Y.-J. Hao, Q.-Y. Lai, J.-Z. Lu, X.-Y. Ji, Effects of dopant on the electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials, *Ionics*, 13 (2007) 369-373.
- [14] L. Tang, Y.B. He, C. Wang, S. Wang, M. Wagemaker, B. Li, Q.H. Yang, F. Kang, High-density microporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microbars with superior rate performance for lithium-ion batteries, *Adv. Sci.*, 4 (2017) 1600311.
- [15] N. Wu, Y.-C. Lyu, R.-J. Xiao, X. Yu, Y.-X. Yin, X.-Q. Yang, H. Li, L. Gu, Y.-G. Guo, A highly reversible, low-strain Mg-ion insertion anode material for rechargeable Mg-ion batteries, *NPG Asia Mater.*, 6 (2014) e120.
- [16] Q. Zhang, M.G. Verde, J.K. Seo, X. Li, Y.S. Meng, Structural and electrochemical properties of Gd-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode material with improved rate capability for lithium-ion batteries, *J. Power Sources*, 280 (2015) 355-362.

- [17] L. Zhao, Y.S. Hu, H. Li, Z. Wang, L. Chen, 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 (2011) 1385-1388.
- [18] F. Li, P. Chen, H. Wu, Y. Zhang, Cooperative enhancement of electrochemical properties in double carbon-decorated $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite as anode for Li-ion batteries, *J. Alloy. Compd.*, 633 (2015) 443-447.
- [19] M. Lu, H. Yang, Y. Zhang, G. Wang, S. Zhuang, Novel insights into the charge/discharge characteristics of spherical porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ co-coated with carbon and metal, *J. Power Sources*, 349 (2017) 52-56.
- [20] L. Sun, W. Xiong, H. Mi, Y. Li, H. Zhuo, Q. Zhang, C. He, J. Liu, In situ coating of graphene-like sheets on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles for lithium-ion batteries, *Electrochim. Acta*, 230 (2017) 508-513.
- [21] G. Wang, C. Lu, X. Zhang, B. Wan, H. Liu, M. Xia, H. Gou, G. Xin, J. Lian, Y. Zhang, Toward ultrafast lithium ion capacitors: A novel atomic layer deposition seeded preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene anode, *Nano Energy*, 36 (2017) 46-57.
- [22] H. Xu, J. Chen, D. Wang, L. Xiao, X. Guo, Y. Zhang, Z. Wang, Carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}-\text{TiO}_2$ microspheres as anode materials for lithium ion batteries, *Surf. Eng.*, 33 (2017) 559-566.
- [23] H. Song, S.-W. Yun, H.-H. Chun, M.-G. Kim, K.Y. Chung, H.S. Kim, B.-W. Cho, Y.-T. Kim, Anomalous decrease in structural disorder due to charge redistribution in Cr-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative-electrode materials for high-rate Li-ion batteries, *Energ. Environ. Sci.*, 5 (2012) 9903-9913.
- [24] Z. Liu, N. Zhang, K. Sun, A novel grain restraint strategy to synthesize highly crystallized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (~20 nm) for lithium ion batteries with superior high-rate performance, *J. Mater. Chem.*, 22 (2012) 11688-11693.
- [25] H.G. Jung, M.W. Jang, J. Hassoun, Y.K. Sun, B. Scrosati, A high-rate long-life $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{1.45}]\text{O}_4$ lithium-ion battery, *Nat. Commun.*, 2 (2011) 516.
- [26] K.-W. Kim, H.W. Kim, Y. Kim, J.-K. Kim, Composite gel polymer electrolyte with ceramic particles for $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2-\text{Li}_4\text{Ti}_5\text{O}_{12}$ lithium ion batteries, *Electrochim. Acta*, 236 (2017) 394-398.
- [27] S.R. Li, C.H. Chen, J.R. Dahn, Studies of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a positive electrode for Li-ion batteries: M^{3+} Doping ($\text{M} = \text{Al}, \text{Fe}, \text{Co}$ and Cr), electrolyte salts and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells, *J. Electrochem. Soc.*, 160 (2013) A2166-A2175.
- [28] A. Mahmoud, I. Saadoune, P.-E. Lippens, M. Chamas, R. Hakkou, J.M. Amarilla, The design and study of new Li-ion full cells of $\text{LiCo}_{2/3}\text{Ni}_{1/6}\text{Mn}_{1/6}\text{O}_2$ positive electrode paired with MnSn_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative electrodes, *Solid State Ionics*, 300 (2017) 175-181.
- [29] N. Zhang, Z. Liu, T. Yang, C. Liao, Z. Wang, K. Sun, Facile preparation of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and its high electrochemical performance as anode material for lithium-ion batteries, *Electrochem. Commun.*, 13 (2011) 654-656.
- [30] H. Song, T.G. Jeong, S.W. Yun, E.K. Lee, S.A. Park, Y.T. Kim, An upper limit of Cr-doping level to retain zero-strain characteristics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material for Li-ion batteries, *Sci. Rep.*, 7 (2017) 43335.
- [31] F. Wu, X. Li, Z. Wang, H. Guo, Synthesis of chromium-doped lithium titanate microspheres as high-performance anode material for lithium ion batteries, *Ceram. Int.*, 40 (2014) 13195-13204.
- [32] H.L. Zou, H.F. Xiang, X. Liang, X.Y. Feng, S. Cheng, Y. Jin, C.H. Chen, Electrospun $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers as anode material for high-rate and low-temperature lithium-ion batteries, *J. Alloy. Compd.*, 701 (2017) 99-106.