



The critical effect of electrodes components mixing on efficiency of anode material for lithium-ion batteries



Fábio R. Bento, Patricia G. Corradini, Lucia H. Mascaro*

Department of Chemistry, Federal University of São Carlos (UFSCar), Rod. Washington Luiz, Km 235, 13565-905, São Carlos -SP, Brazil

ARTICLE INFO

Keywords:

Anode
Lithium ion batteries
SWCNTs
SnO₂
Carbon graphite
Composites

ABSTRACT

An investigation is attempted to highlight the importance of electrode preparation. Graphite carbon (GC), SnO₂ and single wall carbon nanotubes (SWCNT) were used as components of anode catalyst for lithium-ion batteries. For mixing these materials, two common processes were performed: ball milling of GC + SnO₂ + SWCNT and dispersion of SWCNT in GC-SnO₂. The composite electrode prepared from dispersion step presented a superior performance, due the formation of porous and hollow microstructure, which provides more lithium storage sites, shorter Li⁺ diffusion length and sufficient void space.

1. Introduction

Lithium ion batteries (LIB) have achieved great market share since their commercialization by Sony in 1990 [1,2]. Carbon graphite (CG) is currently the commercial anode material, but it presents a low theoretical capacity (372 mA h g⁻¹), encouraging the use of others forms of carbon materials such as graphene, nanofibers, and carbon nanotubes [3–7]. In order to create cooperative effect metal oxides-carbon composites, SnO₂ has been considered a promising candidate for high energy density LIBs [8–12].

However, it is known that in addition to the appropriate materials, it is necessary that the interaction between the components takes place [6,13]. Especially for electrochemical responses such as stability, reversibility and kinetics of Li insertion/extraction process, an attempt is made for further understanding of how component mixing of solid ingredients affects the electrochemical performance of single wall carbon nanotubes (SWCNT) on C-SnO₂ composite electrode. To emphasize the importance of this issue, this letter illustrates how the electrode preparation method can affect the anode electrode performance for LIB.

2. Experimental section

Commercialized SWCNT (Carbon Nanotechnologies Inc., carbon > 95%, lot P0323, specific surface area (SSA): 380 m² g⁻¹), CG (Sigma-Aldrich®) and SnO₂ (Nanostructured & Amorphous Inc., SSA: 5.5 m² g⁻¹) were used as raw material, without further purification to prepare the final products. CG-SnO₂ and CG-SnO₂-SWCNT composites were mixing at the weight ratios 1:1 and 1:1:1, respectively, and were

ball-milled using a planetary ball (Fristcn GmbH) in a stainless-steel vessel under Ar atmosphere at a speed of 140 rpm for 6 h. The ball-to-powder weight ratio was 20/1. The composite was synthesized by a simple two step-process: first, CG-SnO₂ was ball-milled at the ratio 1:1 following the same procedure previously mentioned. Then, CG-SnO₂-SWCNT at a weight ratio of 1:1:1 were sonicated in toluene solution (Aldrich®) for 1 h by a probe sonicator. The previously prepared CG-SnO₂-SWCNT product was then collected by filtration and dried in a vacuum oven at 100 °C for 12 h. The obtained product was denoted as [CG-SnO₂]-dSWCNT.

The electrochemical measurements were conducted by assembly into coin cells. The working electrodes were prepared by mixing the active material, acetylene black and PVDF (Aldrich®) at a weight ratio 80:10:10, respectively, and 0.25 cm² of area. Lithium foil was used as a counter electrode. A polypropylene microporous film was used as separator. LiPF₆ (1 mol L⁻¹) in ethylene carbonate and dimethyl carbonate (1:1, v/v, Merck) was utilized as an electrolyte. Cyclic voltammetry (CV) measurements were conducted on a CHI660A electrochemical analyzer. The cells were cycled at a current density of 10 mA g⁻¹ in a voltage 2.00-0.01 V using a computer-controlled charger system manufactured by Neware Battery Testers. Electrochemical impedance spectroscopy (EIS) was performed by using an Ametek PARSTAT® 2273 electrochemistry workstation, with 10 mV amplitude and in 100 kHz – 10 mHz of frequency range.

3. Results and discussion

Morphologies of the CG-SnO₂-SWCNT and [CG-SnO₂]-dSWCNT are

* Corresponding author.

E-mail address: lmascaro@ufscar.br (L.H. Mascaro).

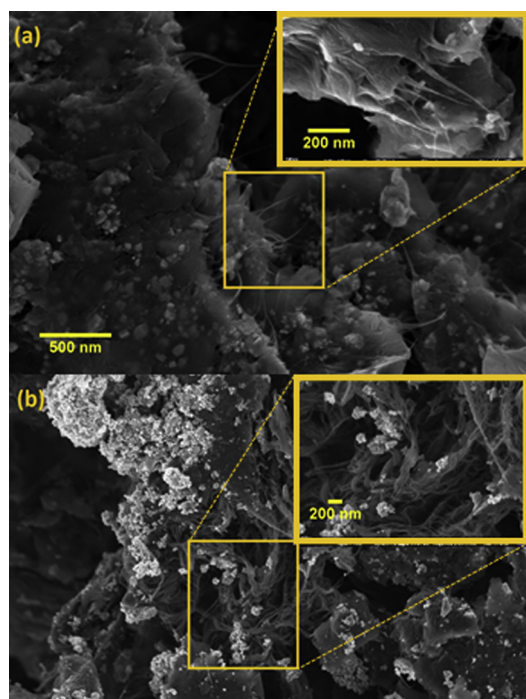


Fig. 1. Scanning electron microscopy images of (a) CG-SnO₂-SWCNT and (b) [CG-SnO₂]-dSWCNT composites.

shown in Fig. 1. Due to the simple mixing of composites, there was no chemical reaction between them. However, CG-SnO₂-SWCNT (Fig. 1 (a)) is an example of the possibility of seeing ball-milled materials as an agglomerate from all materials indicated being composites. On the insert, it is possible to observe only few particles of SnO₂ mixing with the graphite and the SWCNT, indicate a poor iteration between them. On the other hand, Fig. 1 (b) shows a better distribution of oxide particles, and the adherence of SnO₂ on the SWCNT and on CG. Consequently, the structure shows many irregular hollow supporting carbons. The main mechanism of ultrasonic is the cavitation bubbles formation at low pressures [14]. The propagation of ultrasound can result at mechanical, acoustic cavitation, heating and chemical effects. At a heterogeneous solid-liquid reaction, ultrasonic treatment can uniform mixing of reactants, and controls their particle size and distribution [15,16]. It is then expected that [CG-SnO₂]-dSWCNT may be able to promote adsorption of electrolytes into the electrode and enhance the transportation of Li⁺ over the entire electrode.

Fig. 2 (a), (b) and (c) shows cyclic CV curves at scan rate 0.1 mV s⁻¹ for CG-SnO₂, CG-SnO₂-SWCNT and [CG-SnO₂]-dSWCNT, respectively. The first Li⁺ intercalation curve was hardly different from the subsequent ones for both composites. There is no well-defined peak. Moreover, this a multistep electrochemical process, including the formation of a solid electrolyte interphase (SEI) layer on the electrode, irreversible reduction of SnO₂ to metal Sn, reversible formation of Li_xSn alloys (0.0 ≤ x ≤ 4.4) and insertion of Li⁺ in the carbonaceous material [12,17–21]. After the initial cycle, there is a cathodic peak at 0.90 V and it can be assigned to the formation of Li_xSn alloys. During discharge process, anodic peaks are observed at 0.60 and 1.30 V, corresponding to the decomposition of Li_xSn alloys and lithium de-insertion from vacancies in ball-milled graphite, respectively [22].

The charge-discharge profiles of composite electrodes are presented in Fig. 2 (d)-(f). The first charge and discharge capacities are 753 and 392 mA h g⁻¹ for CG-SnO₂, 1009 and 277 mA h g⁻¹ for CG-SnO₂-SWCNT and 2921 and 735 mA h g⁻¹ for [CG-SnO₂]-dSWCNT. The initial efficiencies of these samples are 52%, 27% and 25%, respectively. The results demonstrate that SWCNT contribute to the larger initial irreversible capacity. This behavior is due to reduction of surfaced

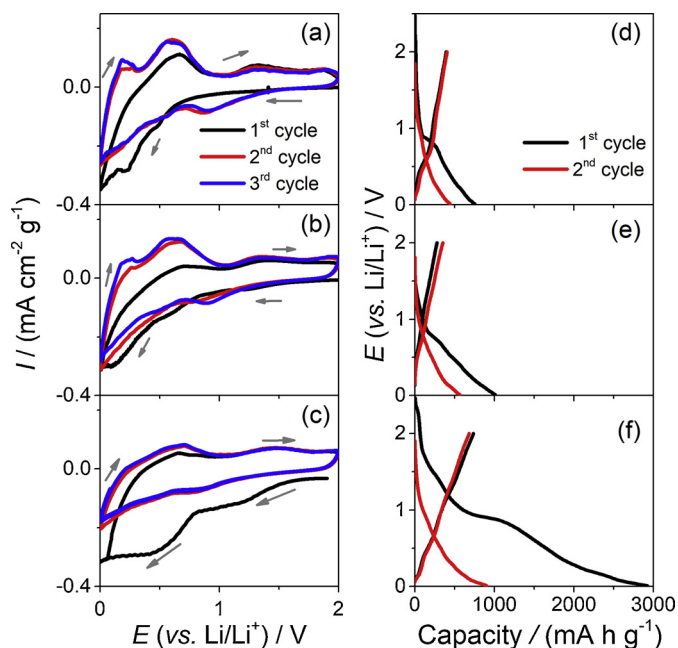


Fig. 2. Cyclic voltammograms at a scan rate of 0.1 mV s⁻¹ and galvanostatic charge-discharge profiles in the 1st and 2nd cycle of C-SnO₂ (a,d), C-SnO₂-SWCNT (b,e) and [C-SnO₂]-dSWCNT electrodes (c,f).

functional groups, formation of SEI and, the large amorphous carbon content [23].

Fig. 3 presents the EIS measurements for the different electrodes. Nyquist plot are shown for the freshly assembled cells (Fig. 3 (a)) and subsequently after cycled 20 times. For both systems, the equivalent circuit was the same, represented at Fig. 3 (c). R_s is described as electrolyte solution resistance. R_F and C_F are associated with Li-ion migration resistance and pseudo-capacitance, respectively [19,24]. R_{CT} and C_{CT} refer to the charge-transfer process, and Z_w is associated the Li-ion diffusion [19]. The simulation results showed at Table 1 illustrated that after 20 cycles the charge transfer resistance (R_{CT}) decreased. Probably the electrolyte accessibility improved by cycling the material [25]. The charge/discharge process leads the composite to balance the stress of the CG-SWCNT-SnO₂ interconnected network and the volumetric expansion of SnO₂ during cycling. The association of the surface area and pores is beneficial to facilitate the rapid diffusion of Li⁺ to access the SnO₂ [26]. However, after 20 cycles the R_{CT} for C-SnO₂-SWCNT and [C-SnO₂]-dSWCNT were smaller compared to the C-SnO₂ sample. This indicates that the electronic conductivity improved due to the good electrical conductivity of SWCNT in the composite materials, where they served as both an active material and a conductor in the anode composite [27].

Fig. 4 (a) compares the cyclic performance of CG-SnO₂, CG-SnO₂-SWCNT and [CG-SnO₂]-dSWCNT electrodes. Comparatively, an obvious improvement can be observed in cyclability with [CG-SnO₂]-dSWCNT electrode, which achieves a reversible capacity of 377 mA h g⁻¹ after 30 cycles, while the reversible capacities of CG-SnO₂, CG-SnO₂-SWCNT electrodes are 191 mA h g⁻¹ and 280 mA h g⁻¹, respectively. The influence of SWCNT considering the effect of components mixed into C-SnO₂ composites are shown in Fig. 4 (b). The calculated SWCNT contribution is obtained from Eq. (1):

$$CC_{\text{SWCNT}} = \frac{C_{\text{C-SnO}_2\text{-SWCNT}} - C_{\text{C-SnO}_2}}{X_{\text{SWCNT}}} \quad (1)$$

where CC_{SWCNT}, C_{C-SnO₂-SWCNT}, C_{C-SnO₂} is the specific capacity of contribution of SWCNT, the specific capacity of CG-SnO₂-SWCNT or [CG-SnO₂]-dSWCNT and CG-SnO₂, is obtained in this work, respectively. X_{SWCNT} weighs a fraction of SWCNT in the CG-SnO₂-SWCNT or [CG-

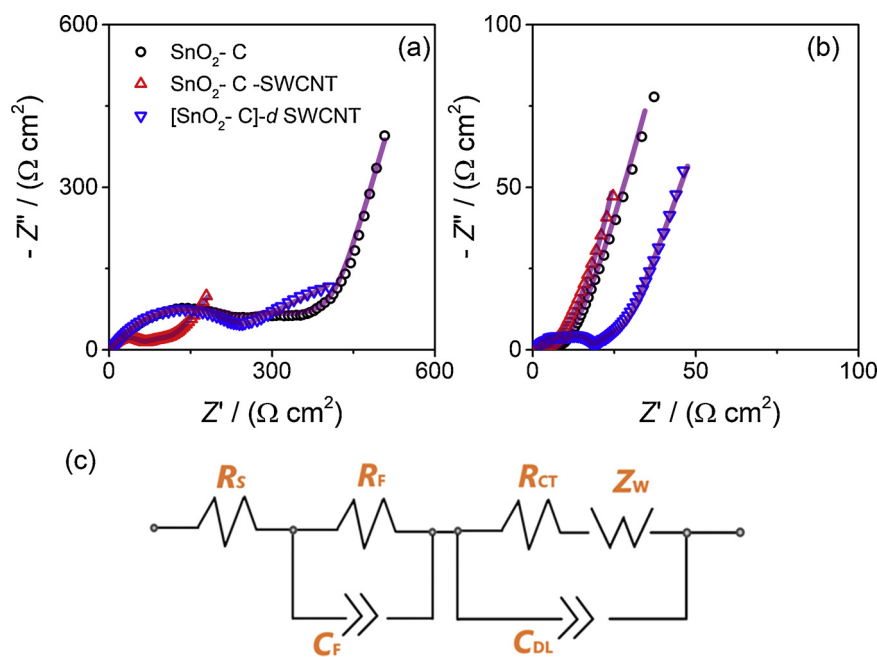


Fig. 3. Nyquist plots of C-SnO₂, C-SnO₂-SWCNT and [C-SnO₂]-dSWCNT electrodes at (a) initial conditions and (b) after 20 cycles. (c) Equivalent circuit model for electrochemical impedance spectroscopy measures.

Table 1

Resistance results of electrochemical impedance spectroscopy analysis of composites electrodes, at initial and after 20 cycles.

| Electrodes | C-SnO ₂ | | C-SnO ₂ -SWCNT | | [C-SnO ₂]-dSWCNT | |
|--------------------------------------|--------------------|-----------------|---------------------------|-----------------|------------------------------|-----------------|
| | Initial | After 20 cycles | Initial | After 20 cycles | Initial | After 20 cycles |
| R _F (Ω cm ²) | 296 | 1.2 | 63 | 0.75 | 193 | 11.8 |
| R _{CT} (Ω cm ²) | 94 | 5.5 | 28 | 2.6 | 388 | 2.3 |

contribution lower than graphite carbon. This data shows that Li_{1.7}C₆ and Li_{0.64}C₆ alloys were formed at the 30th cycle for [CG-SnO₂]-dSWCNT and CG-SnO₂-SWCNT, respectively (Fig. 4 (b)). The higher rate capability of [CG-SnO₂]-dSWCNT than CG-SnO₂-SWCNT can be explained as follows: *i*) ball milling process agglomerated the tubes with CG-SnO₂ reducing the lithium diffusion; *ii*) SWCNT dispersion favored a porous structure, which produces a diminution path Li⁺ [4]. The improved performance for dispersed SWCNT is due to the unique porous structure, as seen at Fig. 1 (b).

4. Conclusion

It was notable that the performance of composite content CG, SnO₂ and SWCNT as anode material for lithium-ion batteries are affected as the products are mixed. The mode of electrode preparation can modify the surface morphology and, consequently, the affinity between the particles and the Li⁺, which is beneficial to improve the cyclic stability of composite electrode. Additionally, the introduction of SWCNT in C-SnO₂ composites facilitate not only possess good cyclability during charge-discharge, which would facilitate the electron transport, but also offers a large surface area which made for enhancing the capacity. When SWCNT are dispersed, the porous structure is responsible for the excellent electrochemical performance. This opens another way to improve the performance of the battery and to work out a series of further study.

Declaration of Competing Interest

None.

Acknowledgments

The authors are grateful to Professor Hua Kun Liu, Professor Jiazha Wang and, Professor Shulei Chou of the University of Wollongong – Institute for Superconducting and Electronic Materials – for their assistance in this work. This work was supported by Conselho Nacional de Pesquisa e Desenvolvimento (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) [Finance Code 001].

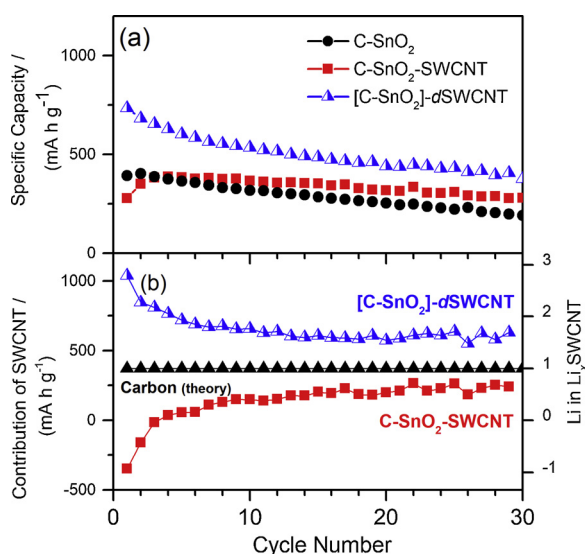


Fig. 4. (a) Reversible capacity of C-SnO₂, C-SnO₂-SWCNT and [C-SnO₂]-dSWCNT. Current density was 10 mA g⁻¹. (b) Calculated contribution of SWCNT at C-SnO₂-SWCNT and [C-SnO₂]-dSWCNT composite electrodes.

SnO₂]-dSWCNT composite materials. It can be seen that the dispersing mode of SWCNT has great influence on the cycle performance of the composite when it is compared with graphite carbon. By contrast, when all components of CG-SnO₂-SWCNT were ball milled, SWCNT lead to

References

- [1] G. Zubi, R. Dufo-Lopez, M. Carvalho, G. Pasaoglu, The lithium-ion battery: state of the art and future perspectives, *Renew. Sustain. Energy Rev.* 89 (2018) 292–308, <https://doi.org/10.1016/j.rser.2018.03.002>.
- [2] Y. Nishi, Lithium ion secondary batteries; past 10 years and the future, *J. Power Sources* 100 (1–2) (2001) 101–106, [https://doi.org/10.1016/S0378-7753\(01\)00887-4](https://doi.org/10.1016/S0378-7753(01)00887-4).
- [3] S. Kumar, M. Nehra, D. Kedia, N. Dilbaghi, K. Tankeshwar, K.H. Kim, Carbon nanotubes: a potential material for energy conversion and storage, *Prog. Energy Combust. Sci.* 64 (2018) 219–253, <https://doi.org/10.1016/j.pecs.2017.10.005>.
- [4] S.J. Kim, A.Y. Lee, H.C. Park, S.Y. Kim, M.C. Kim, J.M. Lee, et al., Carbon nanotube web-based current collectors for high-performance lithium ion batteries, *Mater. Today Commun.* 4 (2015) 149–155, <https://doi.org/10.1016/j.mtcomm.2015.06.010>.
- [5] X.L. Yu, K.Y. Zhang, N. Tian, A.M. Qin, L. Liao, R. Du, et al., Biomass carbon derived from sisal fiber as anode material for lithium-ion batteries, *Mater. Lett.* 142 (2015) 193–196, <https://doi.org/10.1016/j.matlet.2014.11.160>.
- [6] Z.X. Jiang, D.J. Zhang, Y. Li, H. Cheng, M.Q. Wang, X.Q. Wang, et al., One-step, simple, and green synthesis of tin dioxide/graphene nanocomposites and their application to lithium-ion battery anodes, *Appl. Surf. Sci.* 317 (2014) 486–489, <https://doi.org/10.1016/j.apsosc.2014.08.109>.
- [7] Y.X. Gan, C.W. Draper, J.B. Gan, Carbon nanofiber network made by electro-hydrodynamic casting immiscible fluids, *Mater. Today Commun.* 13 (2017) 248–254, <https://doi.org/10.1016/j.mtcomm.2017.10.008>.
- [8] W.W. Xia, Y.W. Wang, Y.F. Luo, J.Y. Li, Y.J. Fang, L. Gu, et al., Facile approach to synthesize SnO₂ nanoparticles@carbon nanofibers as anode materials for lithium-ion battery, *J. Power Sources* 217 (2012) 351–357, <https://doi.org/10.1016/j.jpowsour.2012.05.072>.
- [9] L. Noerochim, J.Z. Wang, S.L. Chou, D. Wexler, H.K. Liu, Free-standing single-walled carbon nanotube/SnO₂ anode paper for flexible lithium-ion batteries, *Carbon* 50 (3) (2012) 1289–1297, <https://doi.org/10.1016/j.carbon.2011.10.049>.
- [10] C.Y. Lin, Y.J. Hu, F.S. Jiang, G.R. Chen, Preparation of ordered mesoporous carbon-SnO₂ composite as electrodes for lithium batteries, *Mater. Lett.* 94 (2013) 83–85, <https://doi.org/10.1016/j.matlet.2012.11.133>.
- [11] A.R. Kamali, D.J. Fray, A possible scalable method for the synthesis of Sn-containing carbon nanostructures, *Mater. Today Commun.* 2 (2015) 38–48, <https://doi.org/10.1016/j.mtcomm.2014.11.001>.
- [12] R. Jia, J.L. Yue, Q.Y. Xia, J. Xu, X.H. Zhu, S. Sun, et al., Carbon shelled porous SnO₂-delta nanosheet arrays as advanced anodes for lithium-ion batteries, *Energy Storage Mater.* 13 (2018) 303–311, <https://doi.org/10.1016/j.ensm.2018.02.009>.
- [13] Y.X. Wang, S.L. Chou, J.H. Kim, H.K. Liu, S.X. Dou, Nanocomposites of silicon and carbon derived from coal tar pitch: cheap anode materials for lithium-ion batteries with long cycle life and enhanced capacity, *Electrochim. Acta* 93 (2013) 213–221, <https://doi.org/10.1016/j.electacta.2013.01.092>.
- [14] M. Marafi, A. Stanislaus, Waste catalyst utilization: extraction of valuable metals from spent hydroprocessing catalysts by ultrasonic-assisted leaching with acids, *Ind. Eng. Chem. Res.* 50 (16) (2011) 9495–9501, <https://doi.org/10.1021/ie200789u>.
- [15] R. Golmohammadzadeh, F. Faraji, F. Rashchi, Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: a review, *Resour. Conserv. Recycl.* 136 (2018) 418–435, <https://doi.org/10.1016/j.resconrec.2018.04.024>.
- [16] G. Hu, X. Xie, Y. Cao, L. Xu, K. Du, W. Wang, et al., Ultrasonic-assisted synthesis of LiFePO₄/C composite for lithium-ion batteries using iron powder as the reactant, *J. Alloys. Compd.* 773 (2019) 1165–1171, <https://doi.org/10.1016/j.jallcom.2018.09.270>.
- [17] W.J. Dong, J.J. Xu, C. Wang, Y. Lu, X.Y. Liu, X. Wang, et al., A robust and conductive black tin oxide nanostructure makes efficient lithium-ion batteries possible, *Adv. Mater.* 29 (24) (2017) 1–9, <https://doi.org/10.1002/adma.201700136>.
- [18] L. Noerochim, J.Z. Wang, S.L. Chou, H.J. Li, H.K. Liu, SnO₂-coated multiwall carbon nanotube composite anode materials for rechargeable lithium-ion batteries, *Electrochim. Acta* 56 (1) (2010) 314–320, <https://doi.org/10.1016/j.electacta.2010.08.078>.
- [19] F.R. Bento, P.G. Corradini, L.H. Mascaro, Inexpensive methodology for obtaining flexible SnO₂-single-walled carbon nanotube composites for lithium-ion battery anodes, *J. Solid State Electrochem.* 23 (6) (2019) 1861–1870, <https://doi.org/10.1007/s10008-019-04283-9>.
- [20] W.J. Dong, J.J. Xu, C. Wang, Y. Lu, X.Y. Liu, X. Wang, et al., A robust and conductive black tin oxide nanostructure makes efficient lithium-ion batteries possible, *Adv. Mater.* 29 (24) (2017), <https://doi.org/10.1002/adma.201700136>.
- [21] C. Liu, Q. Xia, C. Liao, S. Wu, Pseudocapacitance contribution to three-dimensional micro-sized silicon@Fe₃O₄@few-layered graphene for high-rate and long-life lithium ion batteries, *Mater. Today Commun.* 18 (2019) 66–73, <https://doi.org/10.1016/j.mtcomm.2018.11.004>.
- [22] Q. Guo, Z. Zheng, H.L. Gao, J. Ma, X. Qin, SnO₂/graphene composite as highly reversible anode materials for lithium ion batteries, *J. Power Sources* 240 (2013) 149–154, <https://doi.org/10.1016/j.jpowsour.2013.03.116>.
- [23] S.Y. Chew, S.H. Ng, J.Z. Wang, P. Novak, F. Krumeich, S.L. Chou, et al., Flexible free-standing carbon nanotube films for model lithium-ion batteries, *Carbon* 47 (13) (2009) 2976–2983, <https://doi.org/10.1016/j.carbon.2009.06.045>.
- [24] J.J. Kim, C. Ahn, W. Bak, W.C. Yoo, Y.E. Sung, Improved electrochemical performance of a three-dimensionally ordered mesoporous carbon based lithium ion battery using vinylene carbonate, *Mater. Today Commun.* 6 (2016) 69–73, <https://doi.org/10.1016/j.mtcomm.2015.12.003>.
- [25] C.F. Zhang, X. Peng, Z.P. Guo, C.B. Cai, Z.X. Chen, D. Wexler, et al., Carbon-coated SnO₂/graphene nanosheets as highly reversible anode materials for lithium ion batteries, *Carbon* 50 (5) (2012) 1897–1903, <https://doi.org/10.1016/j.carbon.2011.12.040>.
- [26] L. Guo, H. Sun, C. Qin, W. Li, F. Wang, W. Song, et al., Flexible Fe₃O₄ nanoparticles/N-doped carbon nanofibers hybrid film as binder-free anode materials for lithium-ion batteries, *Appl. Surf. Sci.* 459 (2018) 263–270, <https://doi.org/10.1016/j.apsusc.2018.08.001>.
- [27] C.X. Li, Y.H. Chen, B.J. Wei, K.Q. Ding, Y. Zhang, X.M. Shi, et al., A novel composite anode material of Si-SnO₂-graphene prepared in air for lithium ion batteries, *Int. J. Electrochem. Sci.* 12 (12) (2017) 11701–11714, <https://doi.org/10.20964/2017.12.30>.