

# Synthesis of composite $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorods/Sn-AC as anode material for lithium-ion battery

Anne Zulfia<sup>1,\*</sup>, Aisha Betalia<sup>1</sup>, Bambang Priyono<sup>1</sup>, and Achmad Subhan<sup>2</sup>

<sup>1</sup>Department of Metallurgy and Materials, Faculty of Engineering, Universitas Indonesia, Depok, Indonesia

<sup>2</sup>Center for Research of Physics, LIPI, Puspitek Serpong, Indonesia

**Abstract.** LTO or  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (lithium titanate) is a compound that is used as an anode component in a lithium-ion battery. LTO anode is used because it has zero-strain properties and doesn't produce SEI (solid electrolyte interphase) which cause low battery performance. However, LTO also has a problem, which is its low capacity. To overcome this problem, the LTO needs to be combined with other materials that have high capacity, which, in this case, are active carbon (AC) and Sn. Making the LTO to be nano-sized can also improve the performance of the battery, thus we tried to synthesize LTO in nanorods form. LTO nanorods are synthesized by hydrothermal in NaOH 4 M solution. The LTO nanorods are mixed with various Sn (5wt%, 10wt%, and 15wt%) and 5wt% activated carbon. LTO nanorods/Sn-AC composite was characterized using XRD, SEM-EDS, and BET and the battery performance was analyzed by EIS, CV, and CD. The results showed that the highest capacity was obtained at LTO nanorods-AC/15wt% Sn with 127.24 mAh/g. This result shows that LTO nanorods-AC/15wt% Sn could be used as an alternative for anode component.

## 1 Introduction

With the development of electric vehicle in the automotive industry, the need for a large-scale power source with high energy density and good cycle capabilities increased. The conventional battery used in electric vehicle is a lithium-ion battery with graphite as the anode material, but the use of graphite as an anode component has several disadvantages such as formation of SEI (solid electrolyte interface) which will lower the battery performance, and also formation of dendritic structure which results in low safety factor [1].

Because of the problems mentioned above, another material for anode was developed.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) demonstrates a great potential because of its advantages such as great safety performance, no formation of SEI, and long cycle life. However, the theoretical capacity of LTO is almost half of graphite. Another downside of LTO is its low conductivity ( $10^{-13}$  S/cm) and low diffusion rate of Li-ion ( $10^{-9}$ - $10^{-13}$  cm<sup>2</sup>/s) [2]. To overcome the weaknesses of LTO, adding elements such as Sn can improve the battery performance because of its high theoretical capacity [3]. LTO can also be mixed with activated carbon using carbon surface templating method. Adding activated carbon could improve electrical conductivity and faster Li-ion diffusion [4]. Another way to improve the performance of LTO is to synthesize it in nanorods form to widen the electrode/electrolyte contact area and to shorten the path length for  $\text{Li}^+$  and electronic transport that can make

charge-discharge rates higher [5]. In this paper, we tried to mix LTO nanorods with 5wt% activated carbon (AC) and various Sn (5wt%, 10wt%, and 15 wt%). The performance of composite LTO nanorods/Sn-AC as an anode material is expected to improve compared to the performance of LTO alone as an anode material.

## 2 Experimental Procedures

### 2.1. Carbon activation

The process of carbon activation starts by grinding the carbon and using a sieve to obtain fine carbon powder. The carbon powder was then heated inside a furnace with the temperature of 500°C for 2 hours and with 25 minutes of rising time. Afterwards, the carbon was mixed with NaOH pellet into 10 ml of water with the ratio of carbon to NaOH is 1:3. The mixing process was done with a magnetic stirrer for 2 hours. The mixture was then heated for 4 hours with the temperature of 130°C.

The next process was using a combustion boat to heat the carbon mixture inside a tube furnace with nitrogen gas at a temperature of 700°C with 20°C/minute rising time and 90 minutes holding time. The process results in powder carbon which will then be washed in HCl 0.1 M solvent until the pH turns to 7. After the carbon was filtered, it was then heated again at a temperature of

\* Corresponding author: [anne@metal.ui.ac.id](mailto:anne@metal.ui.ac.id)

110°C for 24 hours. The result of this process is an activated carbon powder.

### 2.2 Synthesis of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanorods

The first step to synthesize LTO nanorods is to synthesize TiO<sub>2</sub> xerogel using a sol-gel method. The xerogel was made by stirring primary and secondary solution until the mixture turns to gel form. The primary solution is a mixture of pH 3 Ethanol and Titanium tetrabutoxide (Ti(OBu)<sub>4</sub>) and the second solution is a mixture of pH 3 Ethanol and water. The gel was then dried for 5 days until it turns to crystal form, and then it was ground to obtain a TiO<sub>2</sub> powder. The TiO<sub>2</sub> powder was then calcined in a tube furnace in the temperature of 300°C with 4°C/minute rising time and 45 minutes holding time.

The next step is hydrothermal. First, the calcined TiO<sub>2</sub> powder was mixed with 4 M NaOH solvent using a magnetic stirrer for 30 minutes and the mixture was poured into an autoclave. The autoclave and the mixture inside it were then heated for 24 hours in the temperature of 180°C. This hydrothermal process results in TiO<sub>2</sub> nanorods. After that, the TiO<sub>2</sub> nanorods was washed with 0.1 M HCl solvent until the pH turns to 7, and then it was filtered and dried until it became powder form. To synthesize LTO nanorod, the TiO<sub>2</sub> nanorods powder was mixed with LiOH powder using a ball mill for 30 minutes. The mixture was then sintered in the temperature of 750°C with 2 hours and 30 minutes rising time, and 1 hour holding time.

### 2.3 Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanorods/Sn-AC composites anode coin cell

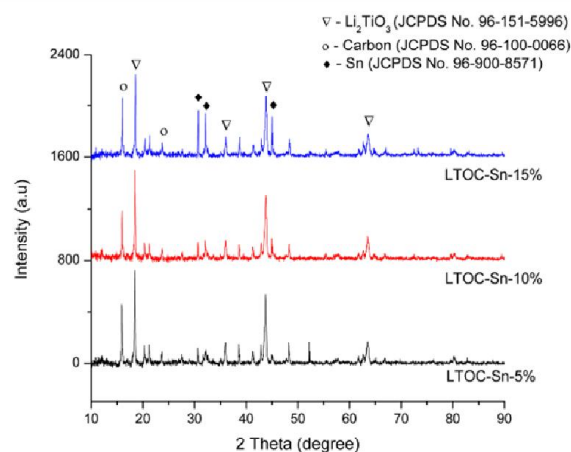
To make LTO nanorods/Sn-AC, we mixed LTO nanorod, micro-sized Sn, and activated carbon using a grinding method. In each sample, the Sn content varies from 5 wt%, 10 wt%, and 15 wt%. The comparison of each sample can be seen in Table 1. The next step is slurry making. The ratio used for active material, acetylene black and PVDF was 8:1:1. Five grams of DMAC was also added to the mixture as a solvent. After the stirring process was done, we used a doctor blade to coat it onto Cu foil and dry the sample for 30 minutes. The samples then subjected to XRD, SEM-EDS, BET, and electrochemical performance studies which are CV, CD, and EIS.

**Table 1.** Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanorods/Sn-AC composite composition.

	Active Material Sample Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> nanorods/Sn-AC (gr)		
	5 wt% Sn	10 wt% Sn	15 wt% Sn
<b>Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanorods</b>	1.805	1.71	1.615
<b>Activated Carbon</b>	0.095	0.09	0.085
<b>Sn</b>	0.1	0.2	0.3

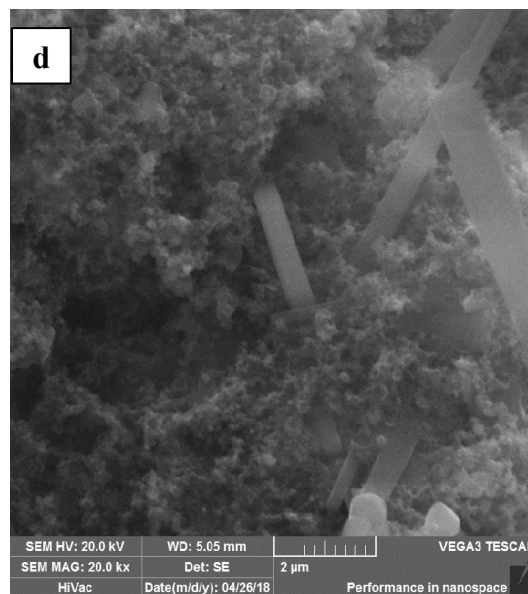
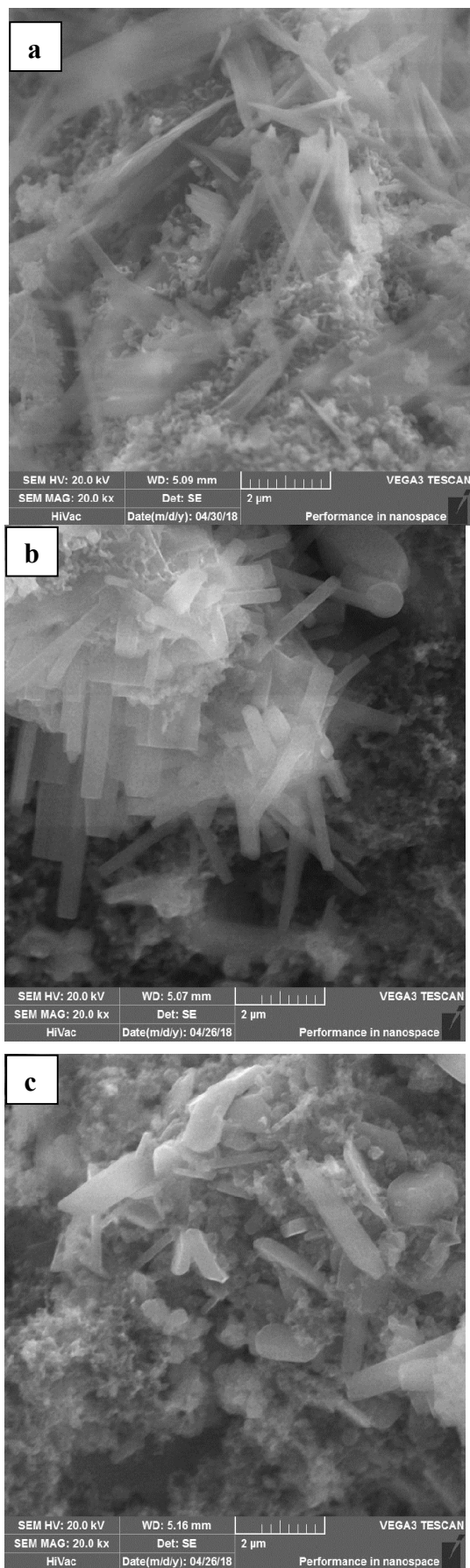
## 3 Results and Discussion

XRD (X-Ray Diffraction) test was performed to samples to determine the phase formed. The XRD results were processed using X'pert High Score Plus program and the graph was processed using Origin program. In Fig. 1, it shows 3 phases formed from LTO nanorods/Sn-AC which are Li<sub>2</sub>TiO<sub>3</sub>, Carbon, and Sn. This indicates that the synthesis of LTO nanorods was unsuccessful because of the absence of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> phase in the samples that were tested. The presence of Li<sub>2</sub>TiO<sub>3</sub> phase was because TiO<sub>2</sub> anatase failed to react with the Li<sup>+</sup> ion source to form Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> during sintering. The other reason is because of the mixing process failed to produce homogeneous mixture [6].

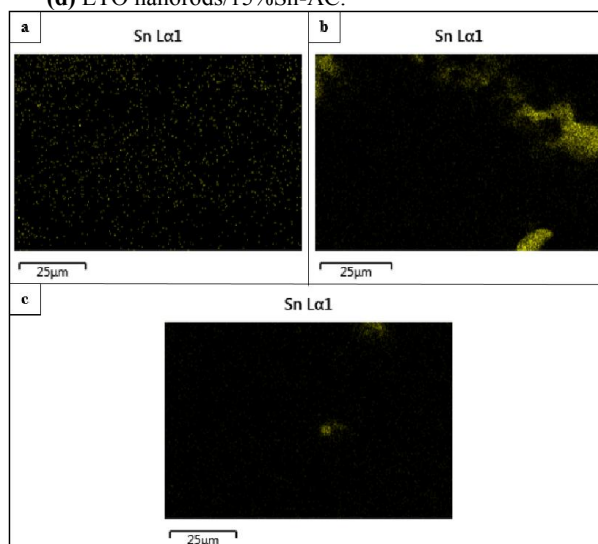


**Fig. 1.** XRD sample test Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanorods/Sn-AC.

To observe the morphology of the sample and to identify the major inorganic elements along with its distribution, the samples are tested using SEM-EDS (Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy) method. The SEM results of three samples of LTO nanorods/Sn-AC with different wt% of Sn didn't show any significant difference. We also did the same test for LTO nanorods powder that we've to synthesize and the result confirms the XRD test that there were no Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanorods formed in the sample. Fig. 2a shows the SEM result of synthesized LTO nanorods. The result shows needle-like forms which are Li<sub>2</sub>TiO<sub>3</sub>, while the agglomerated particles between them are TiO<sub>2</sub> which failed to react with Li<sup>+</sup> ion source.



**Fig. 2.** SEM result of (a) LTO nanorods, (b) LTO nanorods/5%Sn-AC, (c) LTO nanorods/10%Sn-AC, and (d) LTO nanorods/15%Sn-AC.



**Fig. 3.** EDS results shows Sn distribution of sample (a) LTO nanorods/5%Sn-AC, (b) LTO nanorod/10%Sn-AC, and (c) LTO nanorods/15%Sn-AC.

The EDS result of LTO nanorods/Sn-AC samples shows an uneven distribution of Sn as shown in Fig. 3. This is because of the size of the Sn particle is large, so the amount of it in each sample is very small. The mixing process that didn't go well also contributes to the poor distribution of Sn. In every sample that had been tested, there's no Li element detected as shown in Table 2. This is due to the low-energy radiation characteristic of Li so it's making it hard to be detected by EDS method. The EDS testing also shows that there are Na and Cl elements in every sample. Those elements came from the synthesis process. Before the hydrothermal process, the calcined TiO<sub>2</sub> powder was mixed with NaOH, and after the hydrothermal is done, the sample pH was adjusted to pH 7 using HCl solvent. This process results in the formation of NaCl in the TiO<sub>2</sub> sample. The



high presence of NaCl may lead to the disruption of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  formation.

Another test conducted to the LTO nanorods/Sn-AC samples is BET (Brunauer-Emmett-Teller) testing. The result showed the specific surface area for each sample. For LTO nanorods/5%Sn-AC, LTO nanorods/10%Sn-AC, and LTO nanorods/15%Sn-AC, the specific surface area is 518.524  $\text{m}^2/\text{g}$ , 58.510  $\text{m}^2/\text{g}$ , and 64.094  $\text{m}^2/\text{g}$  respectively. LTO nanorods/5%Sn-AC has a surface area that is a lot bigger than the other two samples. This is because the sample weight used for testing LTO

nanorod/5%Sn-AC sample differs significantly from other samples. The sample weight recorded shows a very small number from LTO nanorods/5%Sn-AC sample which is 0.0048 g, while the other samples weighed 0.0445 g and 0.0379 g for LTO nanorods/10%Sn-AC and LTO nanorods/15%Sn-AC respectively.

Data obtained from the EIS test shows the values of Re and Rct for each sample. The lower the Rct value, the better the conductivity. Table 3 shows that the sample who has the lowest Rct value is LTO nanorods/15%Sn-AC with 42  $\Omega$ . The test results show that the higher the

**Table 2.** EDS results of all samples.

Sample	Wt%							
	O	Ti	Na	C	Cl	F	Cu	Sn
<b>LTO nanorods</b>	52.8	24.0	15.7	7.1	0.3	-	-	-
<b>LTO nanorods/5%Sn-AC</b>	24.7	23.1	4.2	36.2	0.4	11.1	0.3	0.1
<b>LTO nanorods/10%Sn-AC</b>	26.7	19.2	5.1	32.7	0.3	10.2	0.3	5.5
<b>LTO nanorods/15%Sn-AC</b>	27.2	23.5	3.4	32.2	0.2	12.0	0.3	0.7

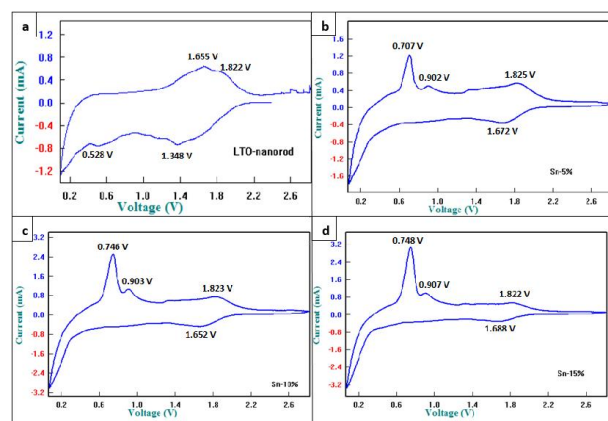
Sn content, the lower the Rct value. This is because Sn has a high conductivity value [7], so its addition to the sample will increase the conductivity. The Re value reflects electric conductivity of the electrolyte, separator, and electrodes, and it also indicates diffusion velocity of  $\text{Li}^+$  ions [8]. The data in Table 3 shows that LTO nanorods/15%Sn-AC, has the best lithium ion diffusion amongst other samples because of its low Re value which is 3  $\Omega$ .

**Table 3.** Parameter impedance of all samples.

Sample	Re ( $\Omega$ )	Rct ( $\Omega$ )
<b>LTO nanorods</b>	7	44
<b>LTO nanorods/5%Sn-AC</b>	19	64
<b>LTO nanorods/10%Sn-AC</b>	14	57
<b>LTO nanorods/15%Sn-AC</b>	3	42

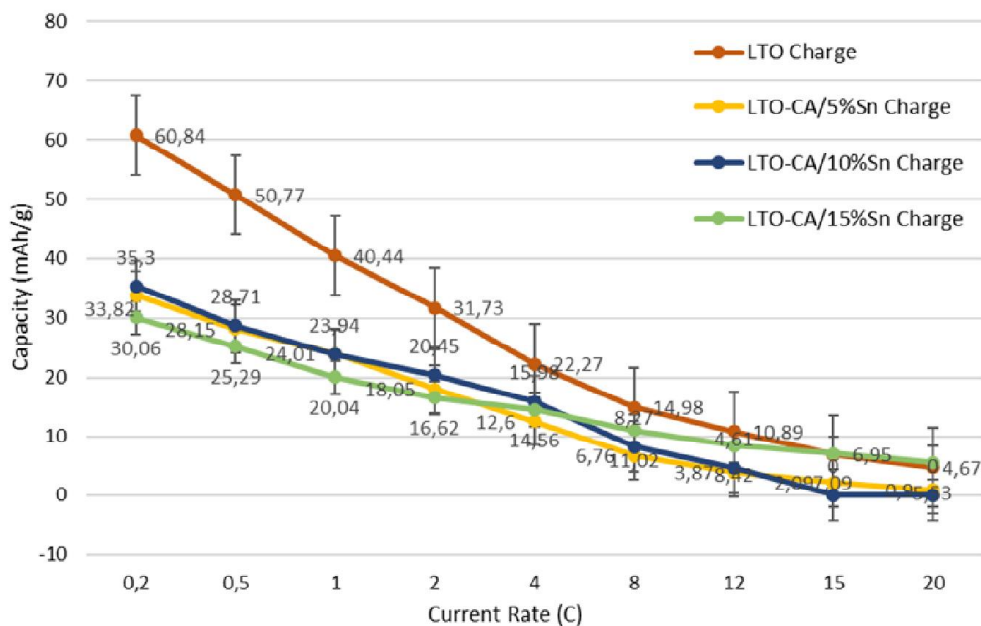
To measure the working potential of every sample, CV (Cyclic Voltammetry) tests was performed. From Fig. 4b-d, the highest peak is around 0.7 V. This is the working voltage of Sn which is around 0.6 to 0.8 V [9]. The working voltage for  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is ~1.5 V [10] and the peak is not present in all samples. This shows that the XRD and SEM-EDS test results are right about LTO failed to form during synthesis. The CV testing also shows the specific capacity of each samples. The specific capacity of LTO nanorods, LTO nanorods/5%Sn-AC, LTO nanorods/10%Sn-AC, and LTO nanorods/15%Sn-AC is 139.9 mAh/g, 97.5 mAh/g, 105.1 mAh/g, and 127.24 mAh/g respectively.

The highest capacity amongst the LTO nanorods/Sn-CA samples is the one with the highest Sn content, but the number is still lower than the capacity of LTO nanorods. This happened due to the unwanted phases and impurities in the samples that lowers the specific capacity.



**Fig. 4.** Cyclic voltammetry curve for (a) LTO nanorods (b) LTO nanorods/5%Sn-AC (c) LTO nanorods/10%Sn-AC, and (d) LTO nanorods/15%Sn-AC.

With the charge-discharge test, the capacities of the battery on certain C-rate are obtained. In CD testing, the higher the C-rate used, the lower the capacity. Fig. 5 shows capacity relationships in the charging process of all samples. This data shows that the highest charging capacity in all C rate is the LTO nanorods sample.



**Fig. 5.** Charge specific capacity from CD testing.

The LTO nanorods/Sn-AC samples look almost identical in the graph except for LTO nanorods/15%Sn-AC in higher C rate where it has higher capacity than the LTO nanorods/5%Sn-AC and LTO nanorods/10%Sn-AC samples. This is due to the higher Sn content in LTO nanorods/15% Sn-AC so the capacity increased [11].

#### 4 Conclusion

The synthesis of LTO nanorods/Sn-AC has been conducted. The LTO nanorod formation was under expectation, therefore, the battery performance was not as good as expectation. However, the addition of Sn element shows that increasing the level of it in the sample will also increase its battery performance. This indicates that the addition of Sn can be used to develop anode material further.

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#### References

1. B. Zhao, R. Ran, M. Liu, Z. Shao, *Mater. Sci. Eng. R* **98**, 1–71 (2015)
2. T. Zeng, X. Hu, P. Ji, Q. Peng, B. Shang, S. Gong, *Electrochim. Acta* **217**, 299–309 (2016)
3. A. Zulfia, F. Aldy, B. Priyono, A. Subhan, *IOP Conf. Ser.: Earth Environ. Sci.* **105**, 012114 (2018)
4. E. C. S. Transactions, T. E. Society **58(14)**, 79–88 (2014)
5. T.-F. Yi, S.-Y. Yang, Y. Xie, *J. Mater. Chem. A* **3(11)**, 5750–77 (2015)

6. B. Priyono, A. Z. Syahrial, A. H. Yuwono, E. Kartini, M. Martelly, W. M. F. Rahmatullah, *Int. J. Technol.* **6(4)**, 555–64 (2015)
7. D. Deng, M. G. Kim, J. Y. Lee, J. Cho, *Energy Environ. Sci.* **2(8)**, 818 (2009)
8. T. F. Yi, S. Y. Yang, Y. R. Zhu, M. F. Ye, Y. Xie, R. S. Zhu, *Ceram. Int.* **40(7)**, PART A, 9853–58 (2014)
9. T. Zeng, X. Hu, P. Ji, B. Shang, Q. Peng, *J. Alloys Compd.* **712**, 311–19 (2017)
10. N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **18(5)**, 252–64 (2015)
11. A. Sivashanmugam, S. Gopukumar, R. Thirunakaran, C. Nithya, S. Prema, *Mater. Res. Bull.* **46(4)**, 492–500 (2011)