# Supporting Information

## $Sn_{0.1}$-$Li_4Ti_5O_{12}$/C as a promising cathode material with a large capacity and high rate performance for Mg-Li Hybrid Batteries

Wei Lin, Xingwei Zuo, Chao Ma, Xia Peng, Haowei Bian, Guobing Liang, Jianbing Hu, Zhongcheng Song, Wutao Mao*, Keyan Bao*

School of chemistry and chemical engineering, Jiangsu University of Technology, Changzhou 213001, China.

* Corresponding author (email:maowutao@126.com, baokeyan@126.com)

## 1 Experimental Part

### 1.1 Material Synthesis

Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$), lithium acetate dihydrate ($C_2H_3O_2Li \cdot 2H_2O$), butyltinic acid ($C_4H_{10}O_2Sn$) and citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) were added into anhydrous ethanol in turn according to stoichiometric ratio, and stirred at room temperature for 20 minutes. Then the solution was dried at 80℃ for 8 hours. The precursor were then calcined at 800 ℃ for 12 h in $N_2$ to obtain $Li_4Ti_{5-x}Sn_xO_{12}$/C (x=0, 0.05, 0.1, 0.2) materials. The samples were labeled as LTO/C, $Sn_{0.05}$-LTO/C, $Sn_{0.1}$-LTO/C and $Sn_{0.2}$-LTO/C when x=0.05, 0.1, and 0.2, respectively. The preparation methods of $Sn_{0.05}$-LTO，$Sn_{0.1}$-LTO，$Sn_{0.2}$-LTO are similar to that of $Li_4Ti_{5-x}Sn_xO_{12}$/C. The difference is that the calcination atmosphere changes from $N_2$ to air atmosphere.

### 1.2 Electrolyte preparation

The electrolyte preparation was prepared in an argon-filled glove box containing < 1 ppm of $H_2O$ and $O_2$. 1.667g of anhydrous aluminum chloride was added into a 25 mL beaker, and then 12 mL of anhydrous tetrahydrofuran was slowly added under stirring, and then 8mL of phenyl magnesium chloride was added and stirred for 10 h. Finally, 0.1696 g of anhydrous lithium chloride was added into a glass bottle, 10 mL of the above-mentioned solution was added into the glass bottle, and stirred for 12 h to complete the configuration of magnesium lithium double-ion electrolyte.

**1.3 Material characterization**

XRD patterns were measured by D8 ADVANCE ECOX X-ray diffractometer. SEM images were analyzed using a Quanta FEG 250 scanning electron microscope. TEM and HRTEM were analyzed using the JEOL JEM-2010 instrument. Raman spectra were measured by Raman Station 400 spectrometer with 514 nm laser as excitation light source. TGA analysisThe thermal properties of the samples in air at room temperature ~ 900 °C were analyzed by STA25000 synchronous thermal analyzer. The elemental composition of the samples was determined by vario MACRO CN elemental analyzer. The XPS spectra were recorded by a Thermo Ka X-ray photoelectron spectrometer equipped with a monochromatic Al-Ka X-ray source. The crystal structure refinement method is the Rietveld method of full spectrum fitting.

**1.4.1 Lithium-ion Battery Assembly and Testing**

The work electrode was prepared by mixing the following components in N-methyl-2-pyrrolidone (NMP) through ball milling for an hour: 80% active material, 10% acetylene black, and 10% polyvinylidene fluoride binder (PVDF). Conductive agents free electrodes were prepared using a similar method, but without the addition of acetylene black; The mixture contains 90% active material and 10% PVDF. The mixture was then coated onto a copper foil and vacuum-dried for 12 hours at 110 °C before being pressed and cut into 1.13 $cm^2$ sized electrodes with a loading of active material of about 1.0-1.5 $mg/cm^2$. In order to verify the practicality of Sn0.1-LTO, high loading electrodes (5.0-5.5 $mg/cm^2$) was also prepared using a similar method. In an argon-filled glove box with low water and oxygen levels (<0.1 ppm), CR2016 coin cells were assembled comprising of a lithium metal foil counter electrode, Celgard 2400 porous polypropylene separator, and 1 M LiPF6 in EC:DMC:DEC (1:1:1 by volume) as the electrolyte. Constant current charge/discharge tests were carried out on a Land-2001A instrument with a voltage range of 1.5-3.0 V at 25 ℃. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a CHI660E electrochemical workstation at 25 ℃. The CV measurements were taken with a voltage range of 1.5-3.0 V and a scan rate of 0.1 mV/s, while the EIS measurements were carried out over a frequency range of 200 kHz-10 MHz at 25 ℃; Before EIS testing, the cells undergo a discharge-charge activation and is tested in a charged state.

### 1.4.2 Mg-Li Hybrid Batteries Assembly and Testing

To prepare the working electrode, a 50 mL agate spherule tank was used to mix 80% of active material, 10% of acetylene black, and 10% of Polyvinylidene fluoride binder through ball milling for 1 hour. The resulting slurry was then coated onto a graphite foil and vacuum dried at 60℃ for 6 hours. The dried electrode material was then pressed and rolled before finally being cut into a working electrode with an area of 1.13 cm2 and an active material loading level of about 1.0-1.5 mg/cm2. The Magnesium-Lithium hybrid electrolytes were prepared in an argon-filled glove box. Firstly, a molar ratio of 2:1 phenyl magnesium chloride (Ph-MgCl) and aluminium trichloride (AlCl3) was dissolved in tetrahydrofuran. The resulting all-phenyl complex (APC) was then diluted to 0.4 molar and 1.0 mole of lithium chloride (LiCl) was used as an additive. The CR2016-type coin cell was assembled in the glove box, whereby magnesium metal sheet was used as the counter electrode, Celgard 2400 porous polypropylene separator used as the separator, and Magnesium-Lithium hybrid electrolyte used as the electrolyte. A constant current discharge/charge test was then carried out using the Land-2001A device with a voltage range of 0.5-1.3V at 25 ℃. CV tests and electrochemical impedance spectroscopy (EIS) were done using the CHI660E electrochemical workstation, where the former utilized a voltage range of 0.05-1.3 V and a scan speed of 0.1 mV/s, and the latter was taken over a frequency range of 200 kHz to 10 MHz, at 25 ℃; Before EIS testing, the cells undergo a discharge-charge activation and is tested in a charged state.

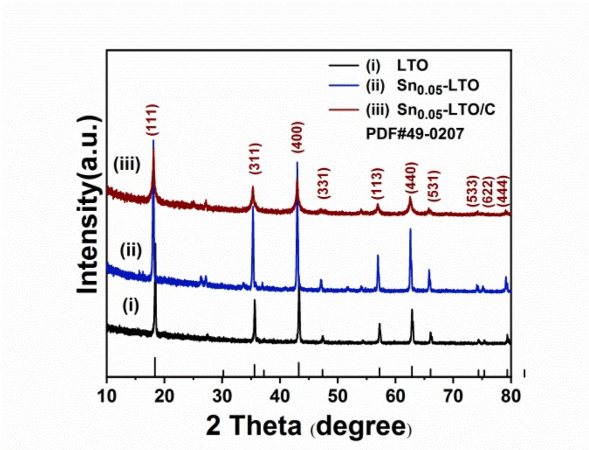


Figure S1 XRD patterns of LTO, $Sn_{0.05}$-LTO, and $Sn_{0.05}$-LTO/C .

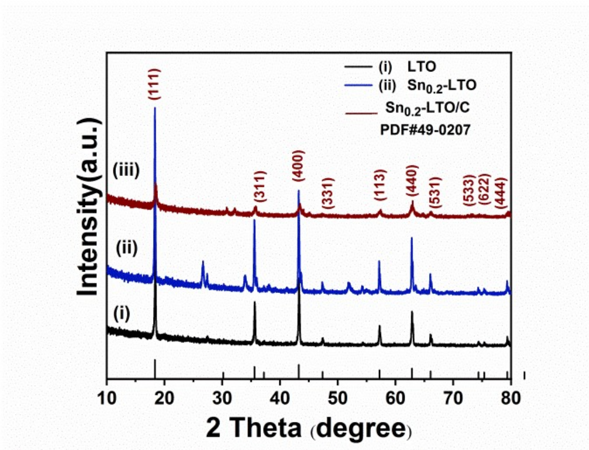


Figure S2 XRD patterns of LTO, $Sn_{0.2}$-LTO, and $Sn_{0.2}$-LTO/C.

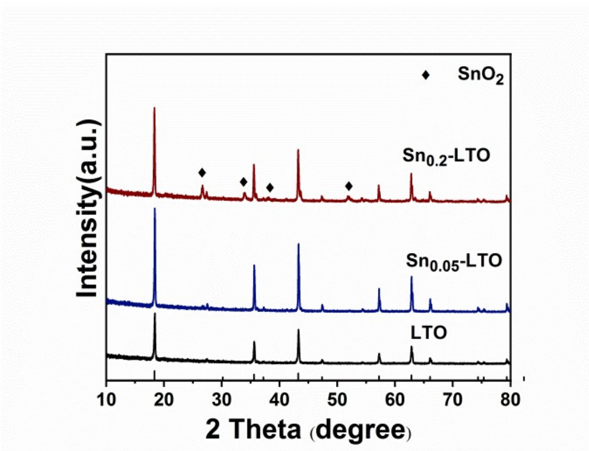


Figure S3 XRD patterns of LTO, $Sn_{0.2}$-LTO, and $Sn_{0.05}$-LTO .

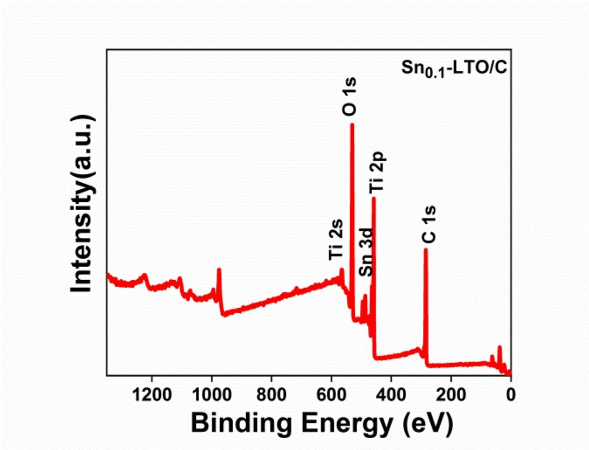


Figure S4 XPS of $Sn_{0.1}$-LTO/C sample.

Table S1 Crystal Structure Refinement Data of LTO/C

**Sample_LTO-Li4Ti5O12**

***(1) Phase analysis***

| Phase name | Formula | Space group | Phase reg. detail |
|---|---|---|---|
| Li4Ti5O12 | Li4Ti5O12 | F d -3 m | / |

***(2) Lattice parameters***

| Phase name | a(Å) | b(Å) | c(Å) | alpha(°) | beta(°) | gama(°) |
|---|---|---|---|---|---|---|
| Li4Ti5O12 | 8.35467 15 | 8.35467 15 | 8.35467 15 | 90 | 90 | 90 |

***(3) Atomic parameters***

| | | | x | y | z | Occ. | B | Site | Sym. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Li | Li1_Li1+ | 0.00000 | 0.00000 | 0.00000 | 1.000 | 1.057 | 8a | -43m |
| 2 | Ti | Ti1_Ti4+ | 0.62500 | 0.62500 | 0.62500 | 0.625 | 1.053 | 16d | .-3m |
| 3 | O | O1_O2- | 0.38900 | 0.38900 | 0.38900 | 0.750 | 1.054 | 32e | .3m |

***(4) Quantitative analysis results***

| Phase name | content(*wt%*) |
|---|---|
| Li4Ti5O12 | 100 |

***(5) R factor***

sig= 1.1769264， Rwp (%) = 13.909026， Rb (%) = 10.477331， Rexp (%) = 11.818093

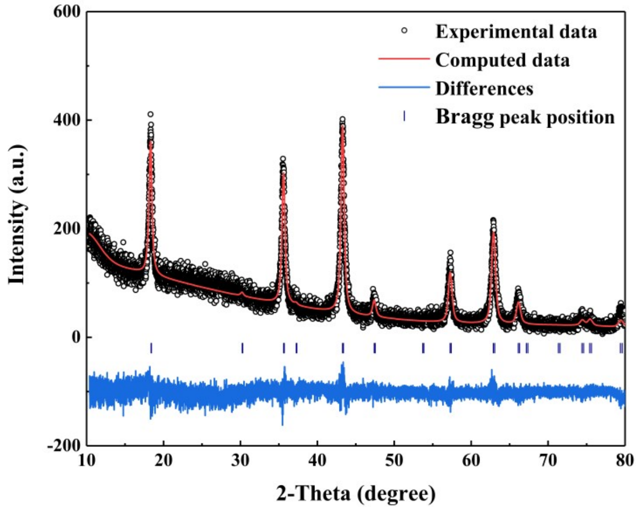


Figure S5 Refined XRD of LTO/C sample

Table S2 Crystal Structure Refinement Data of $Sn_{0.05}$-LTO/C

**Sample_Sn-LTO-1-Li4Ti4.95Sn0.05O12**

***(1) Phase analysis***

| Phase name | Formula | Space group | Phase reg. detail |
|---|---|---|---|
| Li4Ti4.95Sn0.05O12 | Li4Ti4.95Sn0.05O12 | F d -3 m | / |

***(2) Lattice parameters***

| Phase name | a(Å) | b(Å) | c(Å) | alpha(°) | beta(°) | gama(°) |
|---|---|---|---|---|---|---|
| Li4Ti4.95Sn0.05O12 | 8.364617 | 8.364617 | 8.364617 | 90 | 90 | 90 |

***(3) Atomic parameters***

| | | | x | y | z | Occ. | B | Site | Sym. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Li | Li1_Li1+ | 0.00000 | 0.00000 | 0.00000 | 1.000 | 2.700 | 8a | -43m |
| 2 | Ti | Ti1_Ti4+ | 0.62500 | 0.62500 | 0.62500 | 0.594 | 0.930 | 16d | .-3m |
| 3 | Sn | Sn1_Sn4+ | 0.62500 | 0.62500 | 0.62500 | 0.031 | 0.925 | 16d | .-3m |
| 4 | O | O1_O2- | 0.38900 | 0.38900 | 0.38900 | 0.750 | 0.080 | 32e | .3m |

***(4) Quantitative analysis results***

| Phase name | content(*wt%*) |
|---|---|
| Li4Ti4.95Sn0.05O12 | 100 |

***(5) R factor***

sig= 1.1087097, Rwp (%) = 13.581376, Rb (%) = 9.941311, Rexp (%) = 12.249713

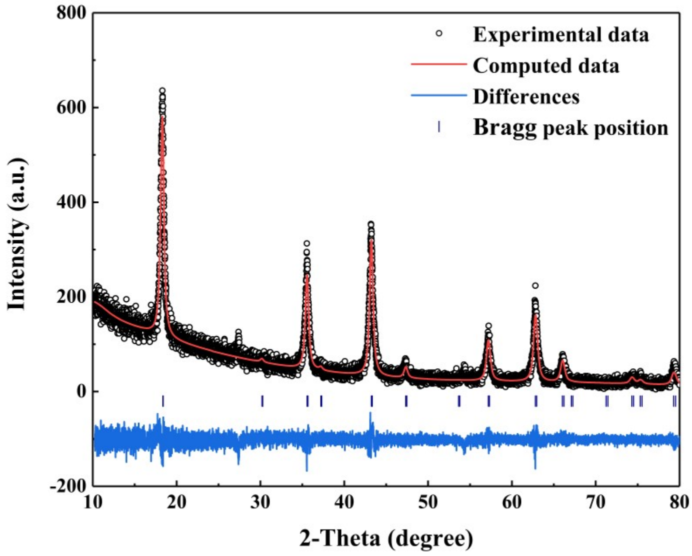


Figure S6 Refined XRD of $Sn_{0.05}$-LTO/C sample

Table S3 Crystal Structure Refinement Data of $Sn_{0.1}$-LTO/C

**Sample_Sn-LTO-2-Li4Ti4.9Sn0.1O12**

***(1) Phase analysis***

| Phase name | Formula | Space group | Phase reg. detail |
|---|---|---|---|
| Li4Ti4.9Sn0.1O12 | Li4Ti4.9Sn0.1O12 | F d -3 m | / |

***(2) Lattice parameters***

| Phase name | a(Å) | b(Å) | c(Å) | alpha(°) | beta(°) | gama(°) |
|---|---|---|---|---|---|---|
| Li4Ti4.9Sn0.1O12 | 8.372889 | 8.372889 | 8.372889 | 90 | 90 | 90 |

***(3) Atomic parameters***

| | | | x | y | z | Occ. | B | Site | Sym. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Li | Li1_Li1+ | 0.00000 | 0.00000 | 0.00000 | 1.000 | 12.000 | 8a | -43m |
| 2 | Ti | Ti1_Ti4+ | 0.62500 | 0.62500 | 0.62500 | 0.563 | 0.967 | 16d | .-3m |
| 3 | Sn | Sn1_Sn4+ | 0.62500 | 0.62500 | 0.62500 | 0.063 | 0.967 | 16d | .-3m |
| 4 | O | O1_O2- | 0.38900 | 0.38900 | 0.38900 | 0.750 | 0.347 | 32e | .3m |

***(4) Quantitative analysis results***

| Phase name | content(*wt%*) |
|---|---|
| Li4Ti4.9Sn0.1O12 | 100 |

***(5) R factor***

sig= 1.1158847， Rwp (%) = 13.614911， Rb (%) = 10.127131， Rexp (%) = 12.201001

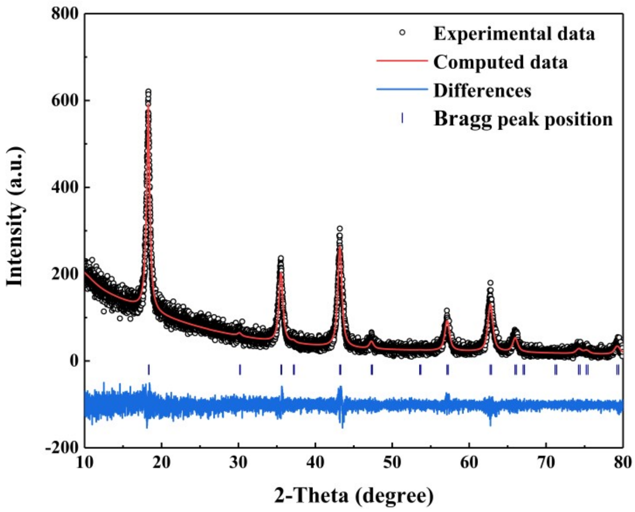


Figure S7 Refined XRD of $Sn_{0.1}$-LTO/C sample

Table S4 Elemental concentration of $Sn_{0.1}$-LTO/C from EDX data

| Elemental | Elemental concentration | Intensity correction | wt% | Atomic % |
|---|---|---|---|---|
| C K | 0.95 | 0.8193 | 7.52 | 13.64 |
| O K | 2.95 | 0.3434 | 46.91 | 65.47 |
| Ti K | 6.99 | 0.8850 | 44.18 | 20.63 |

| Material name | Specific capacity / rate | Initial specific capacity / rate / number of cycles / residual specific capacity after cycle | reference |
|---|---|---|---|
| $Li_4Ti_5O_{12}$/C | 174.3mAh $g^{-1}$ / 0.5C | 174.3mAh $g^{-1}$ / 0.5C / 300 cycles /143.9mAh $g^{-1}$ | 1 |
| Highly porous $Li_4Ti_5O_{12}$/C | 161mAh $g^{-1}$ / 0.5C | 153 mAh $g^{-1}$ / 30C / 300 cycles / 131mAh $g^{-1}$ | 2 |
| Cr doped LTO nanocrystals | 130mAh $g^{-1}$ / 1C | 163 mAh $g^{-1}$ / 20C / 400 cycles / 110mAh $g^{-1}$ | 3 |
| $Li_4Ti_5O_{12}$/reduced graphene oxide | 165mAh $g^{-1}$ / 1C | 165 mAh $g^{-1}$ / 1C / 150 cycles / 150mAh $g^{-1}$ | 4 |
| $Li_4Ti_5O_{12}$/C(5 wt.% G_157M) | 175mAh $g^{-1}$ / 0.1C | 120 mAh $g^{-1}$ / 5C / 100 cycles / 115mAh $g^{-1}$ | 5 |
| $Sn_{0.1}$-$Li_4Ti_5O_{12}$/C | 174.3mAh $g^{-1}$ / 1C | 131.1 mAh $g^{-1}$ / 5C / 1,000 cycles /122.5mAh $g^{-1}$ | |

Table S5 Comparative analysis of electrochemical properties of LTO related materials[1-5]

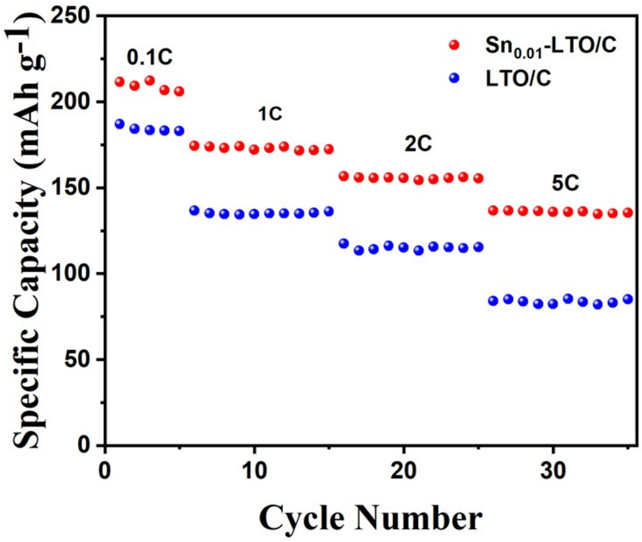


Figure S8 Rate performances at various current densities between 0.1 and 5 C

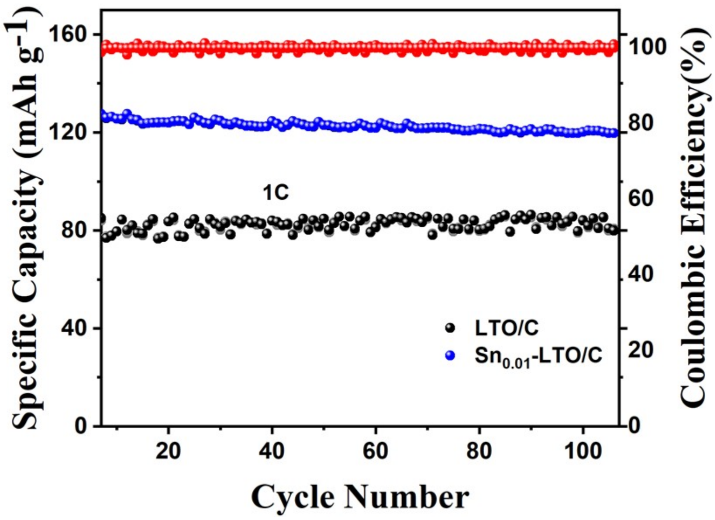


Figure S9 $Sn_{0.01}$-LTO/C and LTO/C were tested for 100 charge-discharge cycles at 1C rate（5mg/cm$^2$）

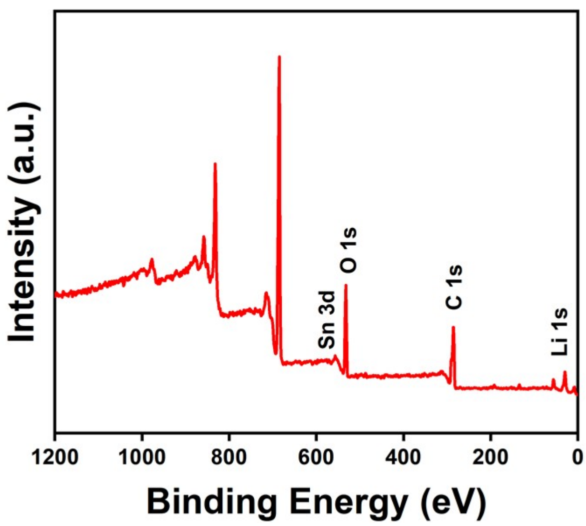


Figure S10 XPS test on the surface of MLIB pole piece charged to 1.3V

## Reference


1. L. Yang and L. Gao, *Journal of Alloys & Compounds*, 2009, **485**, 93-97.
2. H. Xu, X. Hu, Y. Sun, W. Luo, C. Chen, Y. Liu and Y. Huang, *Nano Energy*, 2014, **10**, 163-171.
3. S. H. Gong, J. H. Lee, D. W. Chun, J. H. Bae and H. S. Kim, *Journal of Energy Chemistry*, 2020, **59**.
4. M. U. A, H. C. C. A, R. G. A, K. Z. B and G. P. D. A, *Energy Storage Materials*, 2020, **26**, 560-569.
5. I. Stenina, R. Shaydullin, T. Kulova, A. Kuz'Mina, N. Tabachkova and A. Yaroslavtsev, *Energies*, 2020, **13**.