Synthesis of Carbon Nanotube/Graphene Composites on Ni Foam without Additional Catalysts by CVD and their Nitrogen-Plasma Treatment for Anode Materials in Lithium-ion Batteries

Chuen-Chang LIN* and Ping-Lin CHANG

Department of Chemical & Materials Engineering, National Yunlin University of Science and Technology, 123 University Road Sec. 3, Douliu, Yunlin 64002, Taiwan

* Corresponding author: linchuen@yuntech.edu.tw

ABSTRACT
To simultaneously synthesize carbon nanotubes and graphene on nickel foam without additional catalysts, one-step ambient pressure chemical vapor deposition (CVD) is used to grow them at different temperatures. Next, adding nitrogen-doped defects to the surface of the carbon nanotube/graphene composites, the carbon nanotube/graphene composites are modified by RF (radio frequency) nitrogen-plasma treatment at different power levels and time periods. Carbon nanotubes and graphene are simultaneously synthesized by CVD at 800°C. Furthermore, the specific capacity (618 mAh g⁻¹) reaches a maximum at the nitrogen-plasma treatment conditions (power = 100 W and time = 15 min). Moreover, it also shows the nearly double improvement of the specific capacity and higher electrochemical stability after carbon nanotube/graphene composites are treated by nitrogen-plasma.

Keywords : Carbon Nanotube/Graphene Composites, Chemical Vapor Deposition, Nitrogen-Doped, Lithium-ion Batteries

1. Introduction
The applications of lithium-ion batteries include portable electronic devices, electric vehicles, and hybrid electric vehicles. Compared to other batteries (such as Ni-Cd, Lead-Acid, and Ni-MH), lithium-ion batteries possess higher energy densities (100–150 Wh kg⁻¹), higher voltage, and lower maintenance.¹ The energy density and performance of lithium-ion batteries mainly depend on the properties of anode and cathode materials. In this research, we focused on anode materials of lithium-ion batteries.

Carbon nanotubes (CNTs) have nanometer size, hollow structure, low ratio of micropores, high accessible surface area, low resistance, and high stability.² Graphene has larger accessible specific surface area in comparison with CNTs as well as activated carbon and higher electronic conductivity in comparison with activated carbon as well as CNTs.³⁻⁵ These properties make them potentially suitable for anode materials of lithium-ion batteries.

Thicker graphene results from higher growth temperature.⁶ The thickness of graphene films can be synthesized under control by chemical vapor deposition (CVD) on polycrystalline copper; the number of layers of graphene increases as temperature increases.⁷ The layer spacing between the graphene nanosheets controlled through interacting functional nanocarbons such as CNTs might be crucial for enhancement of the storage capacity.⁸ The CNTs can act as the spacer in fabricating a three-dimensional hierarchical structure with graphene sheets, thus enhancing its effective surface area and capacitance performance.⁹ The multiwalled carbon nanotubes in the graphene/multiwalled carbon nanotube film can efficiently increase the basal spacing and bridge the defects for electron transfer between graphene sheets, thus increasing electrolyte/electrode contact area and facilitating transportation of electrolyte ion as well as electron into the inner region of electrode.¹⁰ Three-dimensional CNTs/graphene sandwich structures with CNTs pillars grown in between the graphene layers were prepared by CVD; the unique structure possessed the high-rate transportation of electrolyte ions and electrons throughout the electrode matrix since the introduction of CNTs can provide diffusion path for electrolyte ions on the surface of graphene and the interconnection of CNTs with graphene can form a conductive network for the transport of electrons.¹¹

Vertically aligned CNTs were directly grown by CVD (60 sccm C₂H₂, 120 sccm H₂, 200 sccm Ar, 750°C) on graphene paper coated with Fe and Al₂O₃; a higher and more stable discharge capacity in comparison with graphene paper and CNTs was achieved.¹² Hybrid CNTs and graphene nanostructures applied in lithium ion batteries were directly grown by ambient pressure CVD; methane was introduced to form graphene on copper foils at 950°C, then Fe catalysts were deposited on graphene/copper foils by e-beam evaporation, and ethylene was next introduced to grow pillar CNTs on graphene/copper foil at 750°C.¹³ The CNTs-graphene hybrid materials were synthesized on an oxygen-plasma treated copper film coated with Fe catalysts by e-beam evaporation through a one-step CVD process using a mixture of acetylene and hydrogen at 650 torr for 10 to 20 min.¹⁴ Vertically grown multiwalled CNTs on a single layer graphene floor were synthesized by a one-step acetylene-CVD process on copper foil (catalysts for graphene growth) coated with Fe (catalysts for multiwalled CNTs growth) by e-beam evaporation.¹⁵ To increase the accessible specific surface area and the stability as well as conductivity between the carbon nanotube bundles as well as the nickel foam, three dimensional few layer graphene/multi-walled carbon nanotube architectures were fabricated on oxygen-plasma treated nickel foam coated with Fe catalysts by e-beam evaporation through a one-step ambient pressure CVD process using a mixture of acetylene and hydrogen.¹⁶ The CNTs-graphene hybrid materials were grown by simple one-step ambient pressure CVD on copper foil spin-coated with silicon nanoparticles using ethanol as precursor at different temperatures and the density of CNTs can be controlled by the CVD growth temperature.¹⁷ N-doped graphene sheets with the nitrogen-doping level as high as 7.04% synthesized by thermal annealing pristine graphene sheets with low-cost industrial material melamine exhibited higher initial reversible capacity (1123 mAh g⁻¹) at 50 mA/g than that (848 mAh g⁻¹) for pristine graphene sheets due to the topological
defects and the existence of pyridinic nitrogen atoms on the graphene sheets. N-doped graphene materials prepared by CVD technique using acetonitrile as liquid precursor and then under an ammonia atmosphere exhibited nearly double reversible discharge capacity in comparison with pristine graphene because of the large amount of surface defects induced by N-doping. N-doped multiwall carbon nanotubes prepared by a plasma enhanced CVD process contain wall defects through which lithium ions can diffuse so as to occupy a large portion of the interwall space as storage regions and then improve the Li storage capability. N-doped graphene nanosheets prepared by heat treatment (800°C and 2 h) of graphite oxide under an ammonia atmosphere exhibited a high reversible capacity due to N-doping inducing a large number of defects on the graphene layer as well as then forming a disordered carbon structure (further enhancing Li intercalation properties) and enhanced cycling stability, which demonstrated the N-doped graphene nanosheets to be a promising candidate for anode materials of lithium ion batteries. The effects of the electron-deficiency (making the defect graphene sheets have an electron-accepting tendency) of N-doped (pyridinic, pyrrolic, and graphitic) graphene sheets on their application in lithium ion batteries were investigated and the pyridinic graphene possessed the best as anode materials of lithium ion batteries, while graphitic graphene would be the weakest of the three defect structures.

The main aim of this research was to simultaneously synthesize carbon nanotubes as well as graphene on nickel foam without additional catalysts by CVD at different temperatures and then add nitrogen-doped defects to the surface of carbon nanotube/graphene composites by RF nitrogen-plasma treatment at different power levels and periods of time.

2. Experiment

Nickel foam with three dimensional conductive network structure working as template for the growth of graphene facilitated easy access of electrolyte ions to the electrode surface. The use of Ni foam is known to increase the active material utilization of the electrode, and thus the specific capacitance of the electrode with the Ni foam current collector was higher than that with the Ti mesh current collector. The Nickel foam (1 mm thick) was used as a current collector for rechargeable lithium ion batteries, while graphitic graphene would be the weakest of the three defect structures.

The main aim of this research was to simultaneously synthesize carbon nanotubes as well as graphene on nickel foam without additional catalysts by CVD at different temperatures and then add nitrogen-doped defects to the surface of carbon nanotube/graphene composites by RF nitrogen-plasma treatment at different power levels and periods of time.

First, the pretreated nickel foam substrate was heated at 1000°C in H₂ (100 sccm) and Ar (250 sccm) for 10 min to reduce the surface oxide layer. Next, to simultaneously synthesize carbon nanotubes and graphene on nickel foam without additional catalysts, one-step ambient pressure CVD was used to grow them on the annealed nickel foam with a gas mixture of C₂H₂ (15 sccm), H₂ (100 sccm), as well as Ar (250 sccm) for 10 min at different temperatures (700, 800, and 900°C) and then cooling to ambient temperatures in Ar with the same volume flow rate as carbon nanotube/graphene composites grown. Finally, the carbon nanotube/graphene composites were weighed.

The carbon nanotube/graphene composites were placed in the reaction chamber (85 cm²) of the apparatus for RF plasma treatment (frequency: 13.56 MHz and maximum power: 1000 W). Then, the chamber was vacated to 10⁻⁷–10⁻⁴ mbar. Next, 20 sccm of nitrogen gas and 10 sccm of argon gas were introduced to the chamber to maintain its pressure at 0.174 mbar. Finally, adding nitrogen-doped defects to the surface of the carbon nanotube/graphene composites, the carbon nanotube/graphene composites were modified by nitrogen-plasma at different power levels (50, 100, and 150 W) and periods of time (5, 15, and 30 min), and then weighed.

A solution of 1 M LiPF₆ dissolved in 1:1 (v/v) ethylene carbonate (EC)-ethyl methyl carbonate (EMC)-dimethyl carbonate (DMC) from Ubiq Technology was used as the electrolyte. The anode electrode (Li metal: 99.9%, 0.3 mm thick, Ubiq Technology) was assembled with the cathode electrode (carbon nanotube/graphene composites or carbon nanotube/graphene composites treated by nitrogen-plasma) into a coin cell by using a coin cell manual crimping machine (CR2032, Taiwan) in an Ar-filled glovebox. The electrochemical cycling tests were performed with a voltage range of 0.01–3 V using a cycler (PFX 2011, Kikusui, Japan). The current density is about 41.5–61.8 mA g⁻¹ (0.1 C) and the measurement temperature is ambient temperature.

The micrographs of CNTs grown at 700°C, carbon nanotube/graphene composites synthesized at 800°C, and graphene grown at 900°C were conducted by field emission scanning electron microscope (FE-SEM: JEOL JSM-6700F, Japan). Furthermore, the D peak intensity, the G peak intensity, as well as the 2D peak intensity of CNTs grown at 700°C, carbon nanotube/graphene composites synthesized at 800°C, as well as graphene grown at 900°C and the I_D/I_G of carbon nanotube/graphene composites without nitrogen-plasma as well as with nitrogen-plasma (power = 100 W and time = 15 min) were investigated by microscopic Raman spectrometer (inVia, Renishaw, England). Moreover, functional groups (pyridinic-N, pyrrolic-N and graphitic-N) of carbon nanotube/graphene composites modified by nitrogen-plasma at different power levels and periods of time were explored by XPS (Fison VG ESCA210, England). Finally, impedance measurement was performed using an electrochemical analyzer (CH Instruments CHI 608B, USA) at 5 mA AC amplitude with a frequency range between 100 kHz and 0.01 Hz to measure the charge transfer resistance for carbon nanotube/graphene composites before cycling and obtain the charge transfer resistance as well as the solid electrolyte interface (SEI) film resistance using the supposed equivalent circuit to fit EIS data by an EC-Lab demo (EC-LAB Electrochemistry, Bio-Logic Science Instruments, French) for carbon nanotube/graphene composites after the third cycle due to requiring first three cycles to get proper SEI film on the active mass. Cyclic voltammetry tests for carbon nanotube/graphene composites without nitrogen-plasma and with nitrogen-plasma (power = 100 W and time = 15 min) were performed using an electrochemical analyzer (CH Instruments CHI 608B, USA) at a scan rate of 0.1 mV s⁻¹ over a potential range of 0.01 to 3.0 V (vs. Li⁺/Li⁻).

3. Results and Discussion

CNTs were grown at 700°C, CNTs as well as graphene sheets were simultaneously synthesized at 800°C, and graphene sheets were grown at 900°C (See Fig. 1). Furthermore, the higher the I_D/I_G (See Figs. 2(a) and 2(b)), the higher the content of defects, which can be attributed to CNTs (See Figs. 1(a) and 1(b)). The presence of the G peak as well as the 2D peak and the I_D/I_G (See Figs. 2(b) and 2(c)) indicate the typical Raman characteristics for few-layer graphene sheets (See Figs. 1(b) and 1(c)).

Figure 3 shows the effects of nitrogen-plasma power and time on the specific capacity at the second cycle of carbon nanotube/graphene composites. The specific capacity (618 mA h g⁻¹) reached a maximum at the nitrogen-plasma treatment conditions (power = 100 W and time = 15 min) which possessed the highest atomic percentage of N (See Table 1). The higher the percentage of the pyridinic-N, the higher the specific capacity (See Figs. 3 and 4) since the pyridinic-N results in the improvement of the capacity, the pyridinic defect structure is the most suitable for Li storage with a high storage capacity and the binding energy with ion for the pyridinic-N is the largest. Therefore, the specific capacity is proportional to the natural logarithm of the pyridinic-N% (R² = 0.9963, See Fig. 5). For the functional groups of carbon nanotube/graphene composites modified by nitrogen-plasma, the binding energy values for pyridinic-N, pyrrolic-N and graphitic-N are 398.5, 400.1, and 401.5 eV, respectively. Furthermore, the 2nd discharge
profiles of carbon nanotube/graphene composites treated by nitrogen-plasma at different periods of time (power levels = 100 W) and different power levels (periods of time = 15 min) are shown in Figs. 6(a) and 6(b), respectively. All discharge curves are similar except differently specific capacity which is shown in Fig. 3. Moreover, the 1st coulombic efficiency (specific capacity of 2nd charge divided by specific capacity of 1st discharge) for carbon nanotube/graphene composites is about 75.33%. However, the 1st coulombic efficiency (See Fig. 7) for carbon nanotube/graphene composites being treated by nitrogen-plasma decreases in comparison with that for carbon nanotube/graphene composites. The reason behind this behavior may be explained as follows. After carbon nanotube/graphene composites being treated by nitrogen-plasma, N-doping can induce a large number of topological defects, and then enhance the surface area of carbon nanotube/graphene composites, which leads to increasing the irreversible capacity since a large surface area probably also increases electrolyte decomposition and then forms a SEI film on the surface of electrodes. The higher the atomic percentage of N, the lower the 1st coulombic efficiency (See Table 1 and Fig. 7).

Figure 1. The FESEM images of (a): CNTs grown at 700°C, (b): CNTs and graphene sheets simultaneously synthesized at 800°C, and (c): graphene sheets grown at 900°C.

Figure 2. Raman spectra of (a): CNTs, (b): CNTs and graphene sheets, and (c): graphene sheets.

Figure 3. The effects of nitrogen-plasma power and time on the specific capacity at the second cycle of carbon nanotube/graphene composites (the average values and deviations were obtained from three samples prepared by exactly the same procedures).

The discharge/charge profiles of carbon nanotube/graphene composites and carbon nanotube/graphene composites treated by nitrogen-plasma (power = 100 W and time = 15 min) are shown in Figs. 8(a) and 8(b). Since the crystallinity of carbon nanotube/graphene composites is probably poor, their potential plateaus in the first discharge curves in Figs. 8(a) and 8(b) are not distinct, which...
also is observed for porous carbon. For carbon nanotube/graphene composites treated by nitrogen-plasma, its discharge specific capacity (618 mAh g\(^{-1}\)) at the 2nd cycle is much higher than that (338 mAh g\(^{-1}\)) of carbon nanotube/graphene composites \[\text{See Figs. 8(a) and 8(b)}\]. If discharge specific capacity (200 mAh g\(^{-1}\)) at the 2nd cycle is same, it occurs at higher potential (about 0.4 V) for carbon nanotube/graphene composites treated by nitrogen-plasma and at lower potential (about 0.1 V) for carbon nanotube/graphene composites \[\text{See Figs. 8(a) and 8(b)}\]. The discharge curves at the 2nd cycle and the 10th cycle in Figs. 8(a) and 8(b) are almost overlapped. Therefore, the difference of discharge capacity between the 2nd cycle and the 10th cycle in Fig. 11 is very small since possibly irreversible lithium loss (the side reaction of electrolyte decomposition and then formation of a SEI film)\(^{28}\) is also very small in comparison with the 1st cycle. Furthermore, the anode electrode (Li metal) was assembled with the cathode electrode (carbon nanotube/graphene composites or carbon nanotube/graphene composites treated by nitrogen-plasma) into a coin cell and their charge processes almost occurred at lower voltage (below 0.5–1.0 V) \[\text{See Figs. 8(a) and 8(b)}\] in this research. Therefore, if carbon nanotube/graphene composites or carbon nanotube/graphene composites treated by nitrogen-plasma was as an anode electrode for lithium-ion batteries, their discharge processes should almost occur at higher voltage for the benefit of merchantable lithium-ion batteries.

### Table 1. The effects of nitrogen-plasma power and time on the atomic percentage of C, N, and O.

| Power/W | Time/min | C/ at\%  | N/ at\%  | O/ at\%  |
|---------|----------|----------|----------|----------|
| 50 W    | 5        | 83.78    | 2.6      | 13.62    |
|         | 15       | 82.79    | 3.64     | 13.57    |
|         | 30       | 86.84    | 2.97     | 10.19    |
| 100 W   | 5        | 85.97    | 3.5      | 10.54    |
|         | 15       | 84.71    | 6.33     | 8.96     |
|         | 30       | 87       | 4.64     | 8.36     |
| 150 W   | 5        | 83.08    | 3.15     | 13.78    |
|         | 15       | 85.09    | 5.16     | 9.75     |
|         | 30       | 83.12    | 3.97     | 12.91    |

**Figure 4.** The effects of nitrogen-plasma power and time on the percentage of the pyridinic-N of carbon nanotube/graphene composites.

**Figure 5.** The correlation between the specific capacity and the natural logarithm of the pyridinic-N%.

**Figure 6.** The 2nd discharge profiles of carbon nanotube/graphene composites treated by nitrogen-plasma at (a) different periods of time (power levels = 100 W) and (b) different power levels (periods of time = 15 min).

**Figure 7.** The effects of nitrogen-plasma power and time on the 1st coulombic efficiency of carbon nanotube/graphene composites.
(5 Hz – 1 kHz, charge-transfer resistance) were separated. The detail characterizations were further analyzed by fitting the measured impedance data [See Fig. 9(b)] using the supposed equivalent circuit [See Fig. 9(c)]. Then the charge transfer resistance (about 6.7 ohm) and the SEI film resistance (about 3.2 ohm) were obtained after the third cycle (See Table 3). After cycling, the wetting of the electrode by the electrolyte could be improved due to aging as well as continuous electrochemical interaction and then led to lower charge transfer resistance, so the charge transfer resistance before cycling is higher than the charge transfer resistance after the third cycle (See Tables 2 and 3). Finally, the reactions for the anode electrode (Li metal) and the cathode electrode (carbon nanotube/graphene composites and carbon nanotube/graphene composites treated by nitrogen-plasma) are same and shown in the following:

Cathode: 6C + xLi⁺ + xe⁻ ↔ C₆Liₓ
Anode: xLi ↔ xLi⁺ + xe⁻

Overall reaction: 6C + xLi ↔ C₆Liₓ

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Overall reaction: 6C + xLi ↔ C₆Liₓ

Since both carbon nanotube/graphene composites and carbon nanotube/graphene composites treated by nitrogen-plasma exhibit similar behaviors [See Figs. 10(a) and 10(b)], which also are observed for graphene and nitrogen-doped graphene. The board peaks [i.e. the potential plateaus in the first discharge curves of

Table 2. Parameter values observed from Fig. 9(a) for carbon nanotube/graphene composites before charge-discharge test.

| Parameter | Value |
|-----------|-------|
| Rₛ/Ω      | 3.9   |
| R_SEI/Ω   | 0.0   |
| R_ct/Ω    | 13.6  |

Table 3. Component values of the supposed equivalent circuit used to fit EIS data for carbon nanotube/graphene composites after the third cycle.

| Component | Fitted value |
|-----------|--------------|
| Rₛ/Ω      | 4.2 ± 0.08   |
| R_SEI/Ω   | 3.2 ± 0.04   |
| CPE₁/F    | (9.1 ± 0.096) × 10⁻⁶ |
| R_ct/Ω    | 6.7 ± 0.02   |
| CPE₂/F    | (35.1 ± 0.07) × 10⁻⁶ |
| Z_w/Ohm s¹⁰² | 2.2 ± 0.06    |

Figs. 8(a) and 8(b) are not distinct] for carbon nanotube/graphene composites and carbon nanotube/graphene composites treated by nitrogen-plasma nearly occur at the same potential (about 0.5 V) during the first discharge scan [See Figs. 10(a) and 10(b)] due to formation of a SEI film and disappear in the following cycles. The peaks for carbon nanotube/graphene composites and carbon nanotube/graphene composites treated by nitrogen-plasma nearly locate at the same potential [close to 0 V, i.e. the potential plateaus in the
discharge curves of Figs. 6(a), 6(b), 8(a) and 8(b)] that can result from the Li$^+$ intercalation into the carbon composites [See Figs. 10(a) and 10(b)]. The peaks for carbon nanotube/graphene composites and carbon nanotube/graphene composites treated by nitrogen-plasma nearly occur at the same potential [about 0.3 V, i.e. the potential plateaus in the charge curves of Figs. 8(a) and 8(b)] that can be attributed to the Li$^+$ de-intercalation from the carbon composites [See Figs. 10(a) and 10(b)]. Those are similar to the peaks for carbon nanotubes.32

Figure 11 shows the effects of carbon nanotube/graphene composites without nitrogen-plasma as well as with nitrogen-plasma (power = 100 W and time = 15 min) and different charge-discharge cycles on the specific capacity. The specific capacity of carbon nanotube/graphene composites treated by nitrogen-plasma was higher than the specific capacity of carbon nanotube/graphene composites. The reason behind this behavior may be explained as follows. The I_D/I_G (1.01) of carbon nanotube/graphene composites treated by nitrogen-plasma is larger than the I_D/I_G (0.62) of carbon nanotube/graphene composites (See Fig. 12). After N-doping, the I_D/I_G increases which demonstrates some disordered carbon in carbon materials (i.e. introduces more defect sites).32 Thus the larger I_D/I_G, the more the defect of carbon nanotube/graphene composites,33 and then the higher the surface area of carbon nanotube/graphene composites, which leads to increasing the specific capacity. The carbon nanotube/graphene composites treated by nitrogen-plasma also contain wall defects through which lithium ions can diffuse so as to occupy a large portion of the interwall space as storage regions and then improve the Li storage capability.20 After carbon nanotube/graphene composites being treated by nitrogen-plasma, N-doping can induce a large number of topological defects and then form a disordered carbon structure that further enhances Li intercalation properties.21 The extra capacity over the theoretical capacity (372 mAh g$^{-1}$) is considered to come from the contribution of cavities or defects.34,35 Therefore, the x in the cathode reaction (6C + xLi$^+$ + xe$^-$ ↔ C$_x$Li$_x$) for carbon nanotube/graphene composites treated by nitrogen-plasma is larger than one, then its specific capacity is higher than the theoretical capacity (372 mAh g$^{-1}$ correspond to x = 1 in C$_x$Li$_x$).20 Furthermore, it also shows the nearly double improvement of the specific capacity and higher electrochemical stability (specific capacity only decreased 5% from the 2nd cycle to the 20th cycle) after carbon nanotube/graphene composites being treated by nitrogen-plasma in comparison with carbon nanotube/graphene composites (specific capacity decreased 10% from the 2nd cycle to the 20th cycle) (See Fig. 11).

4. Conclusions

A higher percentage of the pyridinic-N led to higher specific capacity due to the pyridinic defect structure being the most suitable for Li storage with a high storage capacity; then the specific capacity is proportional to the natural logarithm of the pyridinic-N%. Furthermore, the specific capacity of carbon nanotube/graphene composites treated by nitrogen-plasma was higher than the specific capacity of carbon nanotube/graphene composites. Moreover, discharge processes of carbon nanotube/graphene composites or carbon nanotube/graphene composites modified by nitrogen-plasma as an anode electrode of lithium-ion batteries should almost occur at lower potential for the benefit of merchandising.

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References

1. D. Miranda, C. M. Costa, and S. Lanceros-Mendez, J. Electroanal. Chem., 739, 97 (2015).
2. J. H. Chen, W. Z. Li, D. Z. Wang, S. X. Yang, J. G. Wen, and Z. F. Ren, Carbon, 40, 193 (2002).
3. P. Simon and V. Gogotsi, Acc. Chem. Res., 46, 1094 (2013).
4. S. J. Chae, F. Günes, K. K. Kim, E. S. Kim, G. H. Han, S. M. Kim, H. J. Shin, S. M. Yoon, J. Y. Choi, M. H. Park, C. W. Yang, S. M. Yoon, J. Y. Choi, M. H. Park, C. W. Yang, and P. Richard, Carbon, 73, 252 (2014).
5. N. R. Franklin, Q. Wang, T. W. Tombler, A. Javey, M. Shim, and H. Dai, Appl. Phys. Lett., 81, 913 (2002).
6. W. Liu, C. H. Chung, C. Q. Miao, V. J. Wang, B. Y. Li, L. Y. Ruan, K. Patel, Y. J. Park, J. Woo, and Y. H. Xie, Thin Solid Films, 518, S128 (2010).
7. Z. Tu, Z. Liu, Y. Li, F. Yang, L. Zhang, Z. Zhao, C. Xu, S. Wu, H. Liu, H. Yang, and P. Richard, Carbon, 73, 252 (2014).
8. E. Yoo, J. Kim, E. Hosono, H. S. Zhou, T. Kudo, and I. Honma, Nano Lett., 8, 2277 (2008).
9. Y. Wang, Y. Wu, Y. Huang, F. Zhang, X. Yang, Y. Ma, and Y. Chen, J. Phys. Chem. C, 115, 23192 (2011).
10. X. Lu, H. Hou, B. Gao, C. Yuan, S. Yang, L. Hao, L. Shen, and X. Zhang, Electrochim. Acta, 56, 5115 (2011).
11. Z. Fan, J. Yan, L. Zhi, Z. Zhang, T. Wei, J. Feng, M. Zhang, W. Qian, and F. Wei, Adv. Mater., 22, 3723 (2010).
12. S. Li, Y. Luo, W. Yu, S. Wu, P. Hou, Q. Yang, Q. Meng, C. Liu, and H. M. Cheng, Adv. Energy Mater., 1, 486 (2011).
13. W. Wang, I. Ruiz, S. Guo, Z. Favors, H. H. Bay, M. Ozkan, and C. S. Ozkan, Nano Energy, 3, 113 (2014).
14. M. Ghazinejad, S. Guo, R. K. Paul, A. S. George, M. Penchov, M. Ozkan, and C. S. Ozkan, Mater. Res. Soc. Proc., 1344, mrsx11-1344-x91-07 (2011).
15. Rajesh, R. K. Paul, and A. Mulchandani, J. Power Sources, 223, 23 (2013).
16. W. Wang, S. Guo, M. Penchov, I. Ruiz, K. N. Bozhilov, D. Yan, M. Ozkan, and C. S. Ozkan, Nano Energy, 2, 294 (2013).
17. X. Dong, B. Li, A. Wei, X. Cao, M. B. Chan-Park, H. Zhang, L. J. Li, W. Huang, and P. Chen, Carbon, 49, 2944 (2011).
18. D. Cai, S. Wang, P. Lian, X. Zhu, D. Li, W. Yang, and H. Wang, Electrochim. Acta, 90, 492 (2013).
19. A. L. M. Reddy, A. Srivastava, S. R. Gowda, H. Gullapalli, M. Dubey, and P. M. Ajayam, ACS Nano, 4, 6337 (2010).
20. W. H. Shin, H. M. Jeong, B. G. Kim, J. K. Kang, and J. W. Choi, Nano Lett., 12, 2283 (2012).
21. H. Wang, C. Zhang, Z. Liu, L. Wang, P. Han, H. Xu, K. Zhang, S. Dong, J. Yao, and G. Cui, J. Mater. Chem., 21, 5430 (2011).
22. C. Ma, X. Shao, and D. Cao, J. Mater. Chem., 22, 9011 (2012).
23. T. Xiao, X. Hu, B. Heng, X. Chen, W. Huang, W. Tao, H. Wang, Y. Tang, X. Tan, and X. Huang, J. Alloys Compd., 549, 147 (2013).
24. Y. Wang, A. Yuan, and X. Wang, J. Solid State Electrochem., 12, 1101 (2008).
25. S. Li, Y. Luo, W. Yu, S. Wu, P. Hou, Q. Yang, Q. Meng, C. Liu, and H. M. Cheng, Adv. Energy Mater., 1, 486 (2011).
26. H. Wang, T. Maiyalagan, and X. Wang, ACS Catal., 2, 781 (2012).
27. W. Fan, Y. E. Miao, Y. Huang, W. W. Tjiu, and T. Liu, RSC Adv., 5, 9228 (2015).
28. X. M. Liu, Z. D. Huang, S. W. Oh, B. Zhang, P. C. Ma, M. M. F. Yuen, and J. K. Kim, Compos. Sci. Technol., 72, 121 (2012).
29. Y. Han, L. Dong, J. Feng, D. Li, X. Li, and S. Liu, Electrochim. Acta, 167, 246 (2015).
30. P. Lv, H. Zhao, C. Gao, T. Zhang, and X. Liu, Electrochim. Acta, 152, 345 (2015).
31. X. Li, D. Geng, Y. Zhang, X. Meng, R. Li, and X. Sun, Electrochem. Commun., 13, 822 (2011).
32. W. Ren, D. Li, H. Liu, R. Mi, Y. Zhang, and L. Dong, Electrochim. Acta, 105, 75 (2013).
33. A. Umair and H. Raza, Nanoscale Res. Lett., 7, 437 (2012).
34. H. Fujimoto, A. Mahushi, K. Tokumitsu, and T. Kasuh, J. Power Sources, 54, 440 (1995).
35. E. Peled, C. Menachem, D. Bar-Tow, and A. Melman, J. Electrochem. Soc., 143, L4 (1996).
36. Y. Liu, J. S. Xue, T. Zheng, and J. R. Dahn, Carbon, 34, 193 (1996).