Mini Review

Recent Development of Graphene-Based Materials for Cathode Application in Lithium Batteries: A Review and Outlook

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Graphene composites have great potential in the field of lithium ion batteries due to their high specific surface area, high specific capacity, excellent electrical conductivity and remarkable chemical stability. In cathode materials, graphene can not only form a conductive network to improve the conductivity of composite materials but also buffer the volume effect that occurs during charging and discharging processes, improving the rate performance and cycle life of the material. In addition, it can theoretically be used to design large capacity and high stability lithium-ion batteries. Therefore, the preparation of graphene composites with different compositions and structures is a very important subject. Researchers have prepared graphene composites with different compositions and structures by various methods in recent years, and the results of these studies are summarized in this review.

1. INTRODUCTION

As high-tech electronic devices, such as smart phones and smart wearing devices, and electric vehicles, such as those manufactured by Tesla, have increased in popularity in recent years, higher battery requirements are necessary to supply sufficient energy [1-3]. Traditional lead-acid batteries and manganese-zinc batteries are neither suitable for lightweight devices nor high-power applications because their capacity is limited and their cycle efficiency is low [4-7]. Lithium-ion batteries, which were first introduced into the market by Sony in 1991, are the most widely used high-energy batteries in the world. Researchers are still improving their capacity, energy density and cycle performance through

continuous improvement to the materials and processes to achieve the long-term operation necessary for electrical devices [8-10].

On the other hand, graphene materials, which were first reported in Science in 2004, have developed rapidly in recent years. Tens of thousands of papers related to graphene materials have been published each year, and graphene has shown outstanding potential for practical production and application. Andre Gaim and Constantine Novosholov were awarded the 2010 Nobel Prize in Physics for their discovery of graphene. Graphene is a two-dimensional molecule with a honeycomb-like planar structure and sp^2 hybridized carbon atoms. Graphene has been widely used in energy collection and storage applications due to its excellent physical and chemical properties [11-14], including high load factor mobility, super high theoretical surface area and wide electrochemical window. Specifically, graphene is widely used in solar cells, fuel cells, supercapacitors and lithium batteries [15-19].
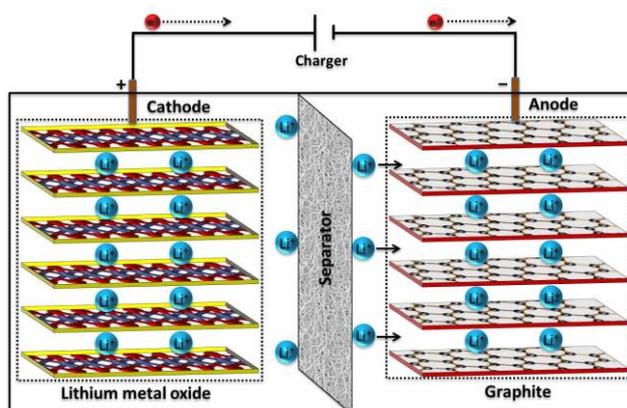
A common structure of graphite-lithium cobalt oxide batteries is shown in Figure 1. The cathode is a copper current collector with a graphite coating, which is separated from copper by a porous insulating diaphragm material [20,21], and the anode is an aluminium current collector coated with $LiCoO_2$. The anode, cathode and diaphragm are all simultaneously immersed in the electrolyte. During the discharge process [22], the electrons in the external circuit of the battery migrate from the anode to the cathode, while the lithium ions in the battery detach from the graphite layer that exists between the negative electrodes and then penetrate the crystal structure of the anode material via the conduction of the electrolyte through the diaphragm. The chemical reactions related to this process are as follows:

$$Li_xC - xLi^- - xe^- = C$$

$$Li_{1-x}CoO_2 + xLi - + xe^- = LiCoO_2$$
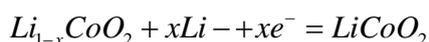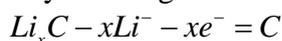
The charging reaction is the inverse of the abovementioned reaction. A lithium ion is removed from the $LiCoO_2$ cathode material and embedded in the graphite layer.

$$C + xLi^- + xe^- = Li_xC$$

$$LiCoO_2 - xLi^- - xe^- = Li_{1-x}CoO_2$$
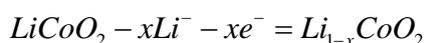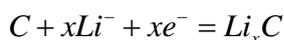
It can also be seen from the abovementioned reaction equation that the capacity and performance of lithium batteries depend on the total amount and intercalation rate of lithium ions that are recycled out of the anode and cathode materials [23].

Figure 1. Schematic of the charge and discharge structure of a graphite-lithium cobalt oxide battery.

Graphite is the main cathode material currently used for lithium batteries. Because lithium ions are stored between the graphite sheets, the theoretical specific capacity of lithium batteries is 372 mAh/g, which was calculated using the chemical formula of LiC_6. To further improve the specific capacity of cathode materials, researchers have started to develop a new generation of high-capacity cathode materials, including metal lithium and lithium-silicon. Graphene is an ideal matrix material because of its good chemical stability and excellent electrical conductivity.

Lithium metal can be used as a cathode material because it has a very high theoretical specific capacity of 3860 mAh/g, but lithium dendrites are easily produced during the charging process. The diaphragm is easily pierced, which results in a short circuit due to the contact of the cathode with the anode; this can cause significant heating and even combustion of the battery, which may lead to safety problems. On the other hand, during the charging and discharging cycles, lithium dendrites fall off easily, leading to the loss of active substances and reduction of the battery cycle life. Therefore, determining how to inhibit the formation of lithium dendrites is a key issue to improve the safety and recyclability of lithium batteries. Researchers have found that the formation of lithium dendrites can be significantly hindered by using three-dimensional nanostructured graphene sheets or nitrogen-doped graphene as conductive substrates for lithium deposition.

In addition, because silicon can form an alloy with lithium, it has a high theoretical specific capacity of 4200 mAh/g, which makes it a potential cathode material. However, during the intercalation and removal of lithium, which occur during the charging and discharging of the battery, the volume of intercalated lithium and removed lithium changes dramatically, which leads to brittleness and even fracture of the materials. Therefore, batteries made from lithium metal can have serious safety issues due to the intercalation and removal of lithium. Because graphene is chemically stable and compact and has a high conductivity, a nano-material slurry composed of a graphene-coated lithium-silicon alloy was prepared by a mixed solid-melting method, and a metal-free cathode material was obtained by coating and rolling.

In this review, we focus on summarizing the preparation and specific applications of graphene materials for their use in the cathodes of lithium batteries.

2. PREPARATION OF GRAPHENE

So far, graphene has been prepared by many different methods, including mechanical peeling, epitaxial crystal growth, SiC thermal decomposition, chemical vapour deposition, graphite intercalation, graphite oxide reduction, and, the latest, microwave and electrostatic deposition.

The mechanical stripping method is used to strip graphene from the surface of pyrolytic graphite by mechanical forces [24-27]. First, ion etching is carried out on the surface of highly oriented pyrolytic graphite by an ion beam. A microgroove is etched into the pyrolytic graphite surface, and then, a photoresist is adhered and baked on the pyrolytic graphite surface. Excess highly oriented graphite is removed by adhering transparent tape to the surface and repeatedly removing the tape. Then, the graphite sheet was washed in an acetone solution, and finally, the graphite was dispersed in propanol for ultrasonic treatment to obtain monolayer graphene. An advantage to using this method is that the

obtained product has a perfect crystal structure with minimal defects. A disadvantage is the low efficiency of the process.

Silicon carbide epitaxial growth is a method used to remove oxides from SiC wafers treated by either oxidation or H_2 etching by electron bombardment heating [28-32]. Graphene can be grown on the surface of a SiC single crystal by evaporating Si atoms and reconstructing the remaining carbon atoms on the surface layer at a high temperature. The sample was heated to 1250~1450 °C and then held at a constant temperature for 1~20 min, resulting in a very thin layer of graphene. This method can be used to obtain an ideal graphene material with a single or few layers. However, disadvantages of this process are poor controllability and difficultly to control the formation of defects. It is difficult to prepare single layers of graphene with large surface areas.

Chemical vapour deposition (CVD) is an effective and controlled method used to prepare graphene [33-38]. Specifically, a planar substrate is placed in a high-temperature atmosphere with decomposed precursors and then annealed at a high temperature to deposit carbon atoms on the substrate surface, and this process results in the formation of a single graphene sheet. The greatest advantage to using this method is that large surface areas of graphene can be prepared. However, it still has some shortcomings. Some properties of the graphene prepared by this method are comparable to those of the graphene prepared by mechanical stripping, but other graphene properties obtained by mechanical stripping are not present in the graphene prepared by CVD. The electronic properties of the graphene prepared by CVD are greatly affected by the substrate.

The thermal expansion and reduction of a graphite oxide are the most promising methods for the large-scale preparation of graphene [39-42]. Graphite oxide was obtained from flake graphite by a series of oxidation reactions, and graphene was obtained by the reduction of graphite oxide. Large quantities of cheap graphene materials can be prepared by this method because graphite reacts with strong oxidants to increase the spacing between the graphite layers, resulting in the formation of graphite oxide. This method is simple and cost-effective and can produce a large amount of graphene. However, the disadvantage to using this method is that graphite oxidized by a strong oxidizer cannot be completely reduced, which causes a significant reduction in the conductivity.

Graphene prepared at a low temperature can be directly used as a cathode material for lithium ion batteries. Its first discharge specific capacity can reach 650 mAh/g [43-45]. However, the first charge-discharge efficiency and cycle efficiency are low, and thus, the graphene structure needs to be modified. Multilayer graphene should have a better consolidation rate because of its lithium storage capacity and the short diffusion path for lithium ions.

3. APPLICATION OF GRAPHENE IN CATHODE MATERIALS

The graphene materials used in some of the first lithium-ion batteries was prepared by a redox method. Pan et al. [46] found that highly disordered graphite sheets have a higher reversible capacity and more stable cycling characteristics, and this kind of material has great potential for applications as the cathode materials used in lithium-ion batteries. The increase in the capacity of these materials is

mainly attributed to an increase in the number of lithium ion binding sites in graphene materials, due to their highly disordered structures [47].

Quantum capacitance is an important feature for graphene cathodes used in lithium ion capacitors. However, the origin of quantum capacitance electrons in the graphene cathode will affect the electrochemical reaction that occurs at the electrode/electrolyte interface. Su et al. used DFT calculations to investigate the quality control problems experienced by various graphene cathodes [48]. This study found that the source of the quality control issues mainly depends on the defects that occur in graphene and the presence of foreign atoms. Graphene that has pentagon defects has fewer quality control issues than the original graphene, due to the contribution of the electronic state of the carbon pentagon (Figure 2).
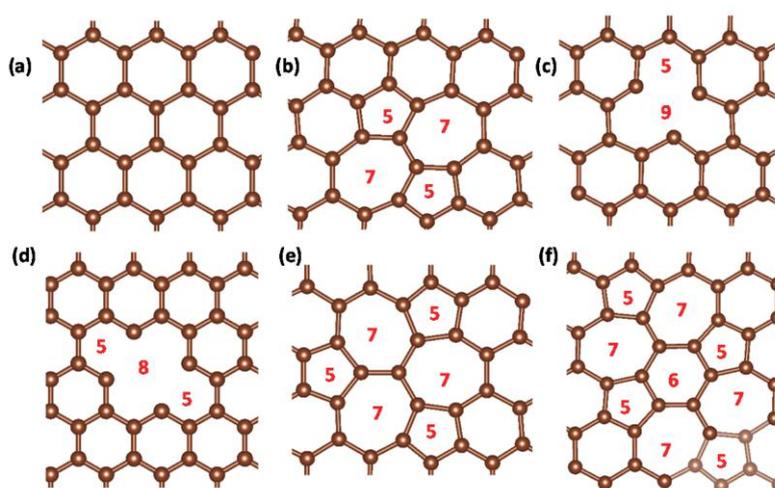
Figure 2. Geometric structure of pristine and defect-containing graphene. Copyright obtained from MDPI [48].

Shanmugharaj et al. [49] reported that a graphite material with a layered structure was prepared by the oxidation and rapid expansion of graphite by microwave heat treatment. The reversible discharge capacity of the layered graphite structure was 580 mAh/g, and its specific capacity was 420 mAh/g after 50 cycles. This occurs because the charge transfer resistance of the composites decreases with an increase in the cycle times. The graphene nanosheets prepared by microwave treatments have many micropores and voids, which can be used as storage sites for lithium ions, thus increasing the storage capacity of lithium ions and the cycle stability of batteries. Tong et al. [50] prepared graphene with controllable layers by an oxidation process. The electrochemical test showed that the graphene prepared with many layers can result in a cathode that has a low first irreversible specific capacity; the first specific capacity decreased from 1175 mAh/g for a cathode containing single layer graphene to 845 mAh/g for a cathode containing five layer graphene, which also lowered the cycle stability. However, a reduction in the number of layers will lead to voltage lag, which is a topic requiring further exploration and improvement in future work. GO was dispersed in a DMF solution and reduced by a solvothermal method at 180 °C [51]. The reduced GO was used as a cathode material for lithium ion batteries. An

electrochemical performance test showed that GO had a reversible capacity that reached 600 mAh/g for the first time at a 0.1C current density and had a good cycling performance. This occurred because the reduced graphene oxide prepared by this process has a better conductivity and better dispersibility in the DMF solution. Moreover, a sulfur/activated carbon/graphene aerogel cathode structure was used to prepare lithium/sulfur battery electrodes with a high specific capacity and good cycle durability [52]. The composites had clear interconnection conductive networks and were prepared by reduction-induced self-assembly, and dense porous structures were obtained. In this process, reduced graphene oxide was formed (Figure 3). Oxygen-containing functional groups existed on the surface of graphene oxide, which not only improved the conductivity of the cathode but also effectively inhibited the dissolution and shuttle of polysulfides. The introduction of activated carbon into the cathode results in the formation of horizontal and vertical connections between the individual graphene plates, which results in the formation of a stable three-dimensional interconnected graphene framework.
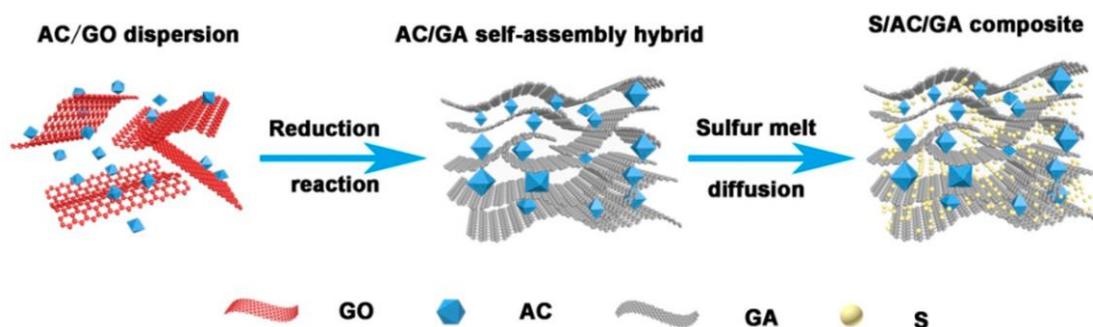
Figure 3. Schematic of the fabrication of a sulfur/activated carbon/graphene aerogel cathode. Copyright obtained from MDPI [52].

In general, doping with non-metallic elements can improve the storage capacity of graphene electrode materials [53]. For example, phosphorus-doped graphene sandwich composites were synthesized by Wang et al. [54]. The graphene composites exhibit excellent cycling performance, thus making them promising cathode materials for lithium-ion batteries. The first charge capacity reaches 1876 mAh/g, and the reversible capacity remains at 990 mAh/g after 50 cycles.

The electrochemical properties of graphene are closely related to the structure of graphene. The edges and defects present in the graphene layers provide enough space to store lithium ions. Graphene has an excellent ability to store lithium and an excellent rate performance because of its good electrical conductivity. Although graphene and its derivatives exhibit excellent electrochemical properties, we still face enormous challenges. Currently, the cost to produce graphene is very high. In addition, graphene has a large irreversible capacity, and voltage lag occurs in the first charge process. Additionally, the morphology changes because agglomeration occurs easily in the cycle process, and the formation of an SEI film will affect the electrochemical performance of the lithium ion batteries, thus limiting their potential for application as electrode materials. Future research should focus on optimizing the properties of graphene mainly by developing multi-component composites. Low-cost and large-scale production technology also deserves attention.

4. METAL SULFIDE-GRAPHENE HYBRID CATHODE MATERIALS

To obtain cathode materials for lithium-ion batteries with excellent performance and the ability to satisfy consumer and industry demands, many studies have been carried out [55,56]. The results show that metal sulfides have excellent electrochemical properties [57-62]. Metal sulfides have excellent electrochemical properties, especially when they are used as cathode materials for lithium-ion batteries. Metal sulfides have unique capacities and stabilities compared with other materials, but the volume changes that occur during lithium deintercalation are comparable. Currently, the most effective mitigation method is to combine transition metal sulfides with a graphene matrix. Graphene is considered to be the most ideal matrix material because of its high mechanical strength, electrical conductivity, large specific surface area and porosity.

Chang et al. [63-65] prepared a series of MoS_2/graphene composites for use as lithium ion cathode materials. The composite materials have high storage capacities. The storage capacity remains between 1100 and 1290 mAh/g after repeated cycles at current densities from 0.1 A/g to 1 A/g. The excellent electrochemical performance of the MoS_2/graphene composites when used as cathode materials for lithium ion batteries can be attributed to the synergy of their layered structures.

SnS_2/graphene composites were synthesized by loading SnS_2 nanorods on the surface of the graphene layer [66]. The reversible capacity of the SnS_2/graphene composites was 504 mAh/g after 200 cycles at a 0.5C current density. The reversible capacity of cathodes containing pure SnS_2 measured after 200 cycles is only 168 mAh/g. Zhang et al. reported the preparation of hexagonal SnS_2 nanoparticle/reduced graphene oxide nanosheet composites by a one-step hydrothermal method [67]. The electrochemical cycling performance was evaluated; the test showed that the storage capacity of the SnS_2 nanoparticles was 1005 mAh/g after 200 cycles at a current density of 100 mA/g, and its reversible capacity was still 612 mAh/g at a current density of 2000 mA/g. Similarly, Lin et al. reported the preparation of a high energy density $NiOOH/Ni_3S_2$/3D graphene composite cathode [68]. Lyu et al. demonstrated the use of a hybrid composed of CoS_2 nanoparticles and graphene for use as a cathode [69]. The hybrid composed of CoS_2 nanoparticles and graphene has the largest discharge rates, which proves that graphene can improve the rate capability of cathode materials [2,70,71]. The combination of both graphene and carbon seems to provide the best results for cathodes composed of metal sulfides, suggesting that less crystalline carbon species interrupt the stacking of the graphene layers [72-74].

The stability and capacity of lithium ion batteries have been significantly improved when graphene sulfide composite materials are used as cathode materials, which can be attributed to the synergistic effect between the materials. However, many problems must be solved in this field and include the following: the environmental impact of sulfide electrode materials should be improved, the lithium storage mechanism of composite materials needs to be further explored, the electrochemical properties of composite materials with different structures need to be studied, and the synergistic mechanism observed in composites of multiple metal sulfides and graphene needs to be explored.

5. TRANSITION METAL OXIDE-GRAPHENE COMPOSITES CATHODE MATERIALS

Transition metal oxides have a high theoretical lithium storage, which is generally between 600 and 1100 mAh/g and is 2 to 3 times the theoretical lithium storage of graphite-carbon materials. Transition metal oxides are promising cathode materials because of their low voltage and low cost, and they are environmentally friendly and naturally abundant. The use of two-dimensional flake graphene as buffer and conductive materials has attracted the attention of researchers. The results show that the introduction of graphene into transition metal oxide materials solves the problems related to the volume expansion and poor conductivity. The good elasticity between the graphene layers can buffer the volume changes of the oxide materials, inhibit the agglomeration between the oxides and the powdered electrode materials, and obviously improve the cycling performance of the electrode materials. The EIS results suggest that graphene decreases the charge transfer resistance more effectively than conventional carbon additives [75-77].

Based on a model, a series of composite materials were synthesized and found to have good electrochemical properties, making them promising for use as lithium ion cathode materials. Co_3O_4 nanoparticles with uniform sizes were synthesized from cobalt salts [78]. Then, the nanoparticles were evenly dispersed on the surface of graphene to form graphene/Co_3O_4 composites. The initial reversible lithium storage capacity was 722 mAh/g, and the capacity was maintained at 631 mAh/g after 50 cycles. Yang et al. [79] prepared a GO-Co_3O_4-GO sandwich composite by using mesoporous silicon wafers as templates. The electrochemical performance tests showed that the first discharge capacity of a lithium ion battery composed of a GO-Co_3O_4-GO sandwich composite cathode was 915 mAh/g, and the remaining capacity of the battery was 85% after 30 cycles. The results show that these composite materials with unique structures remarkably improve the stability of electrode materials. These results also indicate that these composite materials have excellent rate capability, thus challenging the use of graphene additives as a method for improving the electrochemical properties of cathodes [5,80-83].

This improvement in the performance of metal oxide/graphene composites is mainly due to the individual properties of each composite component and the peculiar synergies produced by the different structures formed by each component. The unique structure of the composite material was found to greatly improve the storage capacity of lithium ions and the cycle stability of the battery. However, due to the complicated chemical reactions and interfacial interactions, the ability to optimize the composite structures for use as cathode materials remains to be studied. Determining how to choose cost-effective synthetic materials and simple synthesis methods to design and control metal oxides in graphene, how to enhance the interface reaction to form a product with a controllable morphology and superior performance, and how to further reveal the relationship between the structure and the performance are all challenges that must still be overcome.

6. CONCLUSION AND OUTLOOK

The use of graphene and its composites as cathodes in lithium ion batteries in recent years is summarized in this review. The electrochemical properties of graphene composites are closely related to their structures. The edges and defects present in graphene layers provide enough space for storing

lithium ions. The excellent conductivity of graphene provides its composites with excellent lithium storage capacities and rate performances. The storage capacity, rate performance and cycling performance of composite materials used as cathodes in lithium ion batteries are improved compared with pure graphene and pure metal oxides and sulfides. The improved performance is mainly due to the unique synergistic effect that occurs between components. The electrochemical properties of composites are significantly improved by the presence of unique structures. However, the synergistic effects occurring between the two materials and the different methods used to produce these composites have not sufficiently been explored.

In future work, researchers should pay attention to the following issues:

Large-scale production of high-performance graphene materials;

Reduction of storage during the first charge-discharge process;

In-depth exploration of the lithium storage mechanism of graphene and its composites;

Investigation of the effects of the structure and morphology of graphene and its composites on their electrochemical properties;

Investigation of the effects of graphene and its composites on their electrochemical properties;

Investigation of the synergy that occurs between the components of composite materials.

References

1. J. He, Y. Chen, W. Lv, K. Wen, P. Li, F. Qi, Z. Wang, W. Zhang, Y. Li, W. Qin, *J. Power Sources,* 327 (2016) 474.
2. L. Kavan, P. Liska, S.M. Zakeeruddin, M. Grätzel, *Electrochim. Acta,* 195 (2016) 34.
3. W. Cai, W. Liu, J. Han, A. Wang, *Biosens. Bioelectron.,* 80 (2016) 118.
4. L. Fu, A. Wang, W. Su, Y. Zheng, Z. Liu, *Ionics,* 24 (2018) 2821.
5. F. Fathollahi, M. Javanbakht, H. Omidvar, M. Ghaemi, *J. Alloys Compd.,* 627 (2015) 146.
6. C. Shu, B. Li, B. Zhang, D. Su, *ChemSusChem,* 8 (2015) 3973.
7. H. Jin, M. Liu, E. Uchaker, J. Dong, Q. Zhang, S. Hou, J. Li, G. Cao, *CrystEngComm,* 19 (2017) 4287.
8. Y. Lu, *Energy & Fuels,* 31 (2017) 7290.
9. Y. Lu, S. Shi, F. Yang, T. Zhang, H. Niu, T. Wang, *J. Alloys Compd.,* 767 (2018) 23.
10. L. Fu, Y. Zheng, P. Zhang, H. Zhang, W. Zhuang, H. Zhang, A. Wang, W. Su, J. Yu, C. Lin, *Biosens. Bioelectron.,* 120 (2018) 102.
11. Y. Lu, S. Shi, H. Wang, Z. Tian, Q. Ye, H. Niu, *Int. J. Heat Mass Transfer,* 131 (2019) 594.
12. F. Liu, J. Liang, C. Zhang, L. Yu, J. Zhao, C. Liu, Q. Lan, S. Chen, Y. Cao, G. Zheng, *Results Phys.,* 7 (2017) 250.
13. Y.Z. Wang, X.Y. Shan, D.W. Wang, C.M. Chen, F. Li, H.M. Cheng, *Asia-Pac. J. Chem. Eng.,* 11 (2016) 407.
14. L. Yao, L. Li, L. Qin, Y. Ma, W. Wang, H. Meng, W. Jin, Y. Wang, W. Xu, G. Ran, *Nanotechnology,* 28 (2017) 105201.
15. Y. Li, Y. Cai, Z. Cai, J. Xu, J. Sonamuthu, G. Zhu, J. Militky, W. Jin, J. Yao, *Electrochim. Acta,*

285 (2018) 317.

16. A. Ghosh, S. Shukla, G.S. Khosla, B. Lochab, S. Mitra, *Sci. Rep.,* 6 (2016) 25207.
17. S. Jiao, H. Lei, J. Tu, J. Zhu, J. Wang, X. Mao, *Carbon,* 109 (2016) 276.
18. B. Campbell, J. Bell, H.H. Bay, Z. Favors, R. Ionescu, C.S. Ozkan, M. Ozkan, *Nanoscale,* 7 (2015) 7051.
19. J. Feng, X. Qin, Z. Ma, J. Yang, W. Yang, G. Shao, *Electrochim. Acta,* 190 (2016) 426.
20. Y. Lu, M. Pang, S. Shi, Q. Ye, Z. Tian, T. Wang, *Sci. Rep.,* 8 (2018) 2981.
21. Y. Lu, T. Wang, Z. Tian, Q. Ye, *Int. J. Electrochem. Sci.,* 12 (2017) 3941.
22. Y. Lu, T. Wang, Z. Tian, Q. Ye, *Int. J. Electrochem. Sci.,* 12 (2017) 8944.
23. L. Fu, Y. Huang, W. Cai, H. Zhang, J. Yang, D. Wu, W. Su, *Ceram. Int.,* 44 (2018) 19926.
24. C. Wu, X. Huang, X. Wu, R. Qian, P. Jiang, *Adv. Mater.,* 25 (2013) 5658.
25. J.P. Rourke, P.A. Pandey, J.J. Moore, M. Bates, I.A. Kinloch, R.J. Young, N.R. Wilson, *Angew. Chem.,* 123 (2011) 3231.
26. J. Wang, F. Ma, M. Sun, *RSC Advances,* 7 (2017) 16801.
27. L. Fu, Y. Zheng, P. Zhang, J. Zhu, H. Zhang, L. Zhang, W. Su, *Electrochem. Commun.,* 92 (2018) 39.
28. K. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. Kellogg, L. Ley, J. McChesney, T. Ohta, S. Reshanov, J. Röhrl, *Nat. Mater.,* 8 (2009) 203.
29. S. Kim, J. Ihm, H.J. Choi, Y. Son, *Phys. Rev. Lett.,* 100 (2008) 176802.
30. Y. Lin, C. Dimitrakopoulos, K. Jenkins, D. Farmer, H. Chiu, A. Grill, P. Avouris, *Science,* 327 (2010) 662.
31. W. De Heer, C. Berger, M. Ruan, M. Sprinkle, X. Li, Y. Hu, B. Zhang, J. Hankinson, E. Conrad, *P. Natl. Acad. Sci.,* 108 (2011) 16900.
32. L. Fu, A. Wang, F. Lyu, G. Lai, J. Yu, C. Lin, Z. Liu, A. Yu, W. Su, *Sensors Actuators B: Chem.,* 262 (2018) 326.
33. Y. Wang, Y. Zheng, X. Xu, E. Dubuisson, Q. Bao, J. Lu, K.P. Loh, *ACS nano,* 5 (2011) 9927.
34. Z. Jin, T. McNicholas, C. Shih, Q.H. Wang, G. Paulus, A. Hilmer, S. Shimizu, M. Strano, *Chem. Mater.,* 23 (2011) 3362.
35. S. O'Hern, C. Stewart, M. Boutilier, J. Idrobo, S. Bhaviripudi, S. Das, J. Kong, T. Laoui, M. Atieh, R. Karnik, *ACS nano,* 6 (2012) 10130.
36. G. Deokar, J. Avila, I. Razado-Colambo, J. Codron, C. Boyaval, E. Galopin, M. Asensio, D. Vignaud, *Carbon,* 89 (2015) 82.
37. D. Voiry, J. Yang, J. Kupferberg, R. Fullon, C. Lee, H. Jeong, H. Shin, M. Chhowalla, *Science,* 353 (2016) 1413.
38. L. Fu, A. Wang, F. Lyv, G. Lai, H. Zhang, J. Yu, C. Lin, A. Yu, W. Su, *Bioelectrochemistry,* 121 (2018) 7.
39. J. Jiang, B. Wang, J. Wang, H. Park, *J. Phys.: Condens. Matter,* 27 (2015) 083001.
40. X. Ge, K. Yao, J. Lü, *Phys. Rev. B,* 94 (2016) 165433.
41. S. Linas, Y. Magnin, B. Poinsot, O. Boisron, G. Förster, V. Martinez, R. Fulcrand, F. Tournus, V. Dupuis, F. Rabilloud, *Phys. Rev. B,* 91 (2015) 075426.
42. L. Fu, Z. Liu, Y. Huang, G. Lai, H. Zhang, W. Su, J. Yu, A. Wang, C. Lin, A. Yu, *J. Electroanal. Chem.,* 817 (2018) 128.
43. J. Wang, J. Ball, E. Barea, A. Abate, J. Alexander-Webber, J. Huang, M. Saliba, I. Mora-Sero, J. Bisquert, H.J. Snaith, *Nano Lett.,* 14 (2013) 724.
44. H. Feng, R. Cheng, X. Zhao, X. Duan, J. Li, *Nat. Commun.,* 4 (2013) 1539.
45. H. Chang, G. Wang, A. Yang, X. Tao, X. Liu, Y. Shen, Z. Zheng, *Adv. Funct. Mater.,* 20 (2010) 2893.
46. D. Pan, S. Wang, B. Zhao, M. Wu, H. Zhang, Y. Wang, Z. Jiao, *Chem. Mater.,* 21 (2009) 3136.
47. L. Fu, A. Wang, G. Lai, W. Su, F. Malherbe, J. Yu, C. Lin, A. Yu, *Talanta,* 180 (2018) 248.
48. F. Su, L. Huo, Q. Kong, L. Xie, C. Chen, *Catalysts,* 8 (2018) 444.

49. A. Shanmugharaj, W. Choi, C. Lee, S.H. Ryu, *J. Power Sources,* 196 (2011) 10249.
50. X. Tong, H. Wang, G. Wang, L. Wan, Z. Ren, J. Bai, J. Bai, *J. Solid State Chem.,* 184 (2011) 982.
51. X. Lu, X. Jin, J. Sun, *Science China Technological Sciences,* 58 (2015) 1829.
52. H. Li, L. Sun, Z. Wang, Y. Zhang, T. Tan, G. Wang, Z. Bakenov, *Nanomaterials,* 8 (2018) 69.
53. L. Fu, A. Wang, G. Lai, C. Lin, J. Yu, A. Yu, Z. Liu, K. Xie, W. Su, *Microchimi. Acta,* 185 (2018) 87.
54. L. Wang, H. Guo, W. Wang, K. Teng, Z. Xu, C. Chen, C. Li, C. Yang, C. Hu, *Electrochim. Acta,* 211 (2016) 499.
55. L. Fu, K. Xie, Y. Zheng, L. Zhang, W. Su, *Electronics,* 7 (2018) 15.
56. L. Fu, K. Xie, H. Zhang, Y. Zheng, W. Su, Z. Liu, *Coatings,* 7 (2017) 232.
57. H. Han, K.M. Kim, H. Choi, G. Ali, K.Y. Chung, Y. Hong, J. Choi, J. Kwon, S. Lee, J. Lee, *ACS Catalysis,* 8 (2018) 4091.
58. Q. Pang, D. Kundu, L. Nazar, *Mater. Horiz.,* 3 (2016) 130.
59. W. Liu, H. Niu, J. Yang, K. Cheng, K. Ye, K. Zhu, G. Wang, D. Cao, J. Yan, *Chem. Mater.,* 30 (2018) 1055.
60. G. Zhou, E. Paek, G. Hwang, A. Manthiram, *Adv. Energy Mater.,* 6 (2016) 1501355.
61. H. Peng, Q. Zhang, *Angew. Chem. Int. Ed.,* 54 (2015) 11018.
62. G. Zhou, H. Tian, Y. Jin, X. Tao, B. Liu, R. Zhang, Z.W. Seh, D. Zhuo, Y. Liu, J. Sun, *P. Natl. Acad. Sci.,* 114 (2017) 840.
63. K. Chang, W. Chen, *ACS nano,* 5 (2011) 4720.
64. K. Chang, W. Chen, *Chem. Commun.,* 47 (2011) 4252.
65. Q. Xiang, J. Yu, M. Jaroniec, *J. Am. Chem. Soc.,* 134 (2012) 6575.
66. Z. Jiang, C. Wang, G. Du, Y. Zhong, J. Jiang, *J. Mater. Chem.,* 22 (2012) 9494.
67. Q. Zhang, R. Li, M. Zhang, B. Zhang, X. Gou, *Electrochim. Acta,* 115 (2014) 425.
68. T. Lin, C. Dai, K. Hung, *Sci. Rep.,* 4 (2014) 7274.
69. Z. Lyu, J. Zhang, L. Wang, K. Yuan, Y. Luan, P. Xiao, W. Chen, *RSC Advances,* 6 (2016) 31739.
70. L. Chen, H. Yu, J. Zhong, L. Song, J. Wu, W. Su, *Mat. Sci. Eng. B,* 220 (2017) 44.
71. E. Singh, H. Nalwa, *J. Nanosci. Nanotechno.,* 15 (2015) 6237.
72. E. Singh, H. Nalwa, *Sci. Adv. Mater.,* 7 (2015) 1863.
73. B. Yan, X. Li, Z. Bai, X. Song, D. Xiong, M. Zhao, D. Li, S. Lu, *J. Power Sources,* 338 (2017) 34.
74. J. Ni, L. Zhang, S. Fu, S. Savilov, S. Aldoshin, L. Lu, *Carbon,* 92 (2015) 15.
75. Q. Cheng, W. He, X. Zhang, M. Li, L. Wang, *J. Mater. Chem. A,* 5 (2017) 10772.
76. A. Manzano-Ramírez, E.J. López-Naranjo, W. Soboyejo, Y. Meas-Vong, B. Vilquin, *J. Nanomater.,* 2015 (2015) 3.
77. N. Ye, T. Yan, Z. Jiang, W. Wu, T. Fang, *Ceram. Int.,* 44 (2018) 4521.
78. B. Wang, Y. Wang, J. Park, H. Ahn, G. Wang, *J. Alloys Compd.,* 509 (2011) 7778.
79. S. Yang, X. Feng, L. Wang, K. Tang, J. Maier, K. Müllen, *Angew. Chem. Int. Ed.,* 49 (2010) 4795.
80. J.G. Kim, Y. Kim, Y. Noh, W.B. Kim, *ChemSusChem,* 8 (2015) 1752.
81. X. Ji, Y. Xu, W. Zhang, L. Cui, J. Liu, *Compos. Part A,* 87 (2016) 29.
82. W. Kang, N. Deng, J. Ju, Q. Li, D. Wu, X. Ma, L. Li, M. Naebe, B. Cheng, *Nanoscale,* 8 (2016) 16541.
83. J. Paredes, S. Villar-Rodil, *Nanoscale,* 8 (2016) 15389.