Research Article
Published: 26 Jan, 2018

SF Journal of Material and Chemical Engineering

Influence of Carbonization Process on the Structures, Morphologies and Electrical Performances of Ag-C Nanofibers Membranes

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Abstract

Ag-C nanofibers membranes were fabricated using electrospinning method by combing with pre-oxidation and carbonization processes, the structures, morphologies and electrical performances were characterized by X-ray diffraction, scanning electron microscopy and four probe instrument. And the influence of carbonization process with different carbonized temperatures on the structures, morphologies and electrical performances of Ag-C nanofibers membranes was investigated. It was found that the sample prepared with the carbonized temperature of 1000°C exhibited a high electrical conductivity of 6.28×10^{-2} S/cm.

Keywords: Ag-C nanofibers membranes; Electrospinning; Carbonization process

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Received Date: 17 Nov 2017
Accepted Date: 15 Jan 2018
Published Date: 26 Jan 2018

Citation: Xia Y, Sun S, Meng L, Zhao Z, Zhu X, Xiao Z, et al. Influence of Carbonization Process on the Structures, Morphologies and Electrical Performances of Ag-C Nanofibers Membranes. SF J Material Chem Eng. 2018; 1(1): 1003.

ISSN 2643-8100

Introduction

Carbon-based nanomaterials (carbon nanotubes and carbon nanofibers, etc.) have captured extensive attention, largely because theirs physic-chemical properties are important for many applications, including solar cells [1,2], capacitors [3,4], lithium batteries [5,6], and electron devices [7,8]. Specially, much effort has been devoted to the study of carbon nanofibers, depending on their unique nanostructures. Carbon nanofibers are fibrous carbon materials formed by multilayer graphite sheets, exhibiting excellent physic-chemical properties [9-12] such as good chemical stability, low density, high electrical conductivity, and high temperature resistance. Furthermore, the achievement of large-scale production lines of carbon nanofibers leads to a high level of carbon nanofibers yields [13-15].

With the development of the study of carbon nanofibers, the metals decorated carbon nanofibers technology has aroused great interest in research. The metals decorated carbon nanofibers technology has combined the advantages of intrinsic characteristics of metals and carbon nanofibers, making the metals decorated carbon nanofibers have some fancy properties that are not available for the only presence of metals or carbon nanofibers. More prominently, much effort has devoted to the exploiting of the metals decorated carbon nanofibers with various nano-synthesized methods, and some achievements have been made [16-20].

It is noted that the metals decorated carbon nanofibers membranes synthesized using electrospinning method by combing with pre-oxidation and carbonization processes have been gradually implemented since electrospinning method has advantages of low cost, simplicity and controllability, etc. Furthermore, the reported literatures have identified that the metals decorated carbon nanofibers membranes synthesized using electrospinning method by combing with pre-oxidation and carbonization processes under some special conditions have superior properties [21,22]. For example, Liu *et al.* [21] obtained the 8% Ni-decorated carbon nanofibers membrane using electrospinning method by combing with pre-oxidation and carbonization processes, which exhibited a relatively high catalytic activity for hydrogen evolution reaction due to its hierarchical nanostructures. Ahn et al. [22] fabricated core-shell-structured carbon/metal hybrid mesh films using electrospinning method by combing with pre-oxidation, carbonization processes and electroplating. Such films displayed superior optoelectrical, mechanical, and thermal properties.

Nevertheless, to the best of our knowledge, the metals decorated carbon nanofibers membranes are currently synthesized using eletrospinning method by combing with pre-oxidation and carbonization processes mainly focusing on the synthetics process or the properties only. The

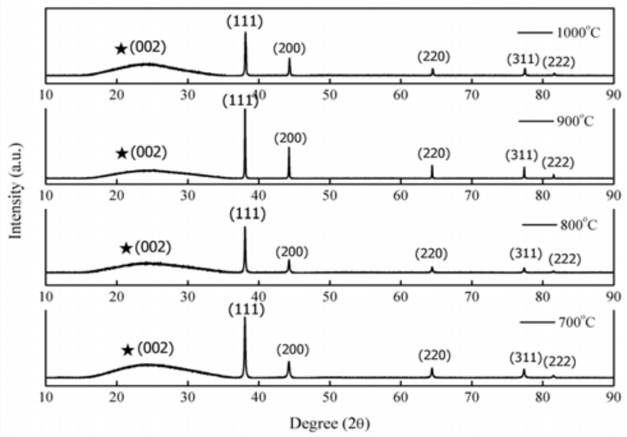

Figure 1: XRD patterns of Ag-C nanofibers membranes samples carbonized at different temperatures in the range of 700°C-1000°C.

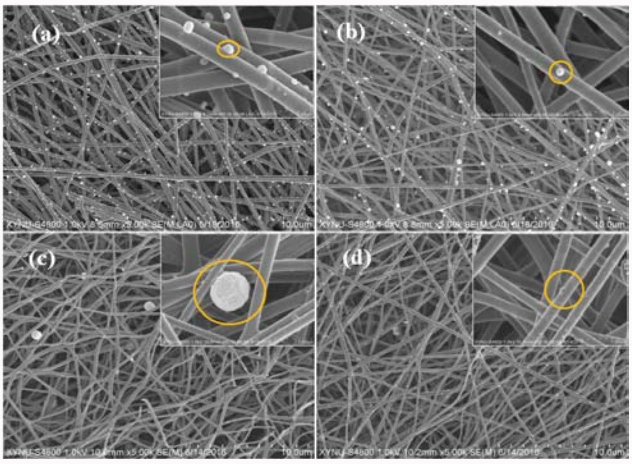

Figure 2: SEM micrographs for Ag-C nanofibers membranes samples carbonized at different temperatures in the range of 700°C-1000°C: (a) 700°C; (b) 800°C; (c) 900°C; (d) 1000°C.

studies relative to the relationship or influence between the synthetics process and the properties for the metals decorated carbon nanofiber membranes synthesized using eletrospinning method by combing with pre-oxidation and carbonization processes have been neglected. Thus, in this work, we fabricated Ag-C nanofibers membranes via electrospinning method by combing with pre-oxidation and carbonization processes. Herein the effect of carbonization process on the structures, morphologies and electrical performances of Ag-C nanofibers membranes was studied.

Experimental

Preparation of Ag^+/PAN solution

2.1g polyacrylonitrile (PAN) was dissolved into 15mL N,N-dimethylformamide (DMF) at 60°C water bath under magnetic stirring for 3h. After dissolving completely, 0.5g $AgNO_3$ was added into this solution slowly. Ag^+/PAN precursor solution was formed after stirring at room temperature for 20h.

Synthesis of Ag-C nanofibers membranes

The as-prepared Ag^+/PAN precursor solution was transferred into a hypodermic syringe and spun under applied voltage of 25kV. The distance between the needle tip and the collector was 14cm. The flow rate of the solution was 0.4mm/min. The as-spun composite fibers were dried at 60°C for 24h. Subsequently, the dried fibers were pre-oxidized at 300°C for 2h and then carbonized at different temperatures (700°C, 800°C, 900°C, and 1000°C) for 2h in N_2. Ag-C nanofibers membranes were obtained.

Figure 3: Diagrammatic sketch of formation procedure of Ag^+/PAN nanofibers membrane.

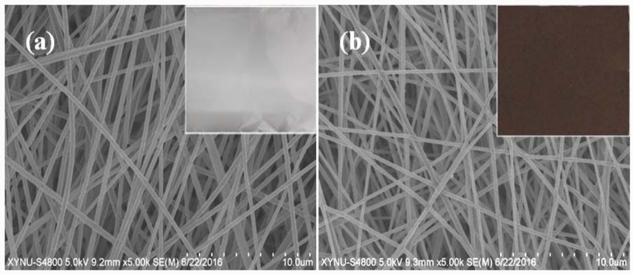

Figure 4: SEM micrographs and pictures of (a): Ag^+/PAN nanofibers, inset of (a): Ag^+/PAN nanofibers membrane and (b): Ag^+/PAN nanofibers, inset of (b): Ag^+/PAN nanofibers membrane after preoxidation process.

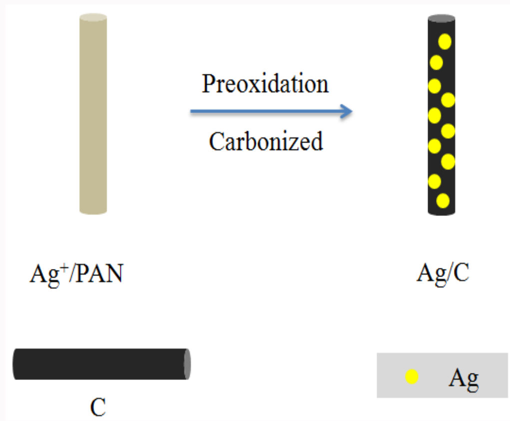

Figure 5: Diagrammatic sketch of formation procedure of Ag/C nanofibers membrane from Ag^+/PAN nanofibers membrane.

Characterization of samples

X-ray diffraction (XRD) patterns were recorded with the D8/Advance (Bruker) equipped with a source of Cu$K\alpha_1$ radiation operating at 40kV and 40mA. Scanning electron microscopy (SEM) images were taken with S-4800I, Hitachi. Electrical conductivity was measured by RTS-9 type four-probe instrument.

Results and Discussion

XRD and SEM analysis

XRD patterns of Ag-C nanofibers membranes samples carbonized at different temperatures in the range of 700°C -1000°C are shown in Figure 1. From Figure 1, it can be seen that all diffraction peaks for Ag-C nanofibers membranes samples can be indexed as either the graphitic phase (crystal plane: ★(002), [23]) or the face-centered

Table 1: The resistivity, conductivity and resistance of Ag/C nanofibers membranes with different carbonized temperatures from 700°C to 1000°C.

Four Probe Test	Ag/C nanofibers membrane 1000°C	Ag/C nanofibers membrane 900°C	Ag/C nanofibers membrane 800°C	Ag/C nanofibers membrane 700°C
resistivity (Ω·cm)	15.925	23.544	147.375	2420
conductivity (S/cm)	$6.28E^{-2}$	$4.34\ E^{-2}$	$7.13E^{-3}$	$4.09E^{-4}$
resistance (Ω)	324.375	531.889	2753.75	48600

cubic Ag (crystal planes: (111), (200), (220), (311), (222), [24]) with no obvious other peaks for impurity, despite of different carbonized temperatures. SEM micrographs for Ag-C nanofibers membranes samples carbonized at different temperatures in the range of 700°C-1000°C are shown in Figure 2a-2d. From the SEM images, it can be observed that the morphologies of Ag-C nanofibers membranes samples are varied due to different carbonization temperatures. At carbonization temperature of 700°C (Figure 2a), the surface of carbon fibers is relatively coarse. Furthermore, Ag nanoparticles are distributed on the surface of carbon fibers and the diameter of carbon fibers is about 350-400 nm. When the carbonization temperature increases to 800°C (Figure 2b), the morphology is almost unchanged besides the surface of carbon fibers becomes smoother than that of 700°C. However, by further increase in temperature, the particle size of Ag nanoparticles at 900°C (Figure 2c) is larger than that of Ag nanoparticles at 700°C or 800°C (Figure 2a and 2b), which could be attributed to higher carbonization temperature, resulting in the growth of Ag naoparticles. Interestingly, when the carbonization temperature increases to 1000°C (Figure 2d), it is found that Ag nanoparticles are not distributed on the surface of carbon fibers, but mainly embedded inside the carbon fibers. The reason may be because this carbonization temperature approaches or exceeds the melting point of Ag, causing Ag nanoparticles to melt and embed inside the carbon fibers. The change of such morphologies is one of the key factors to the different electrical performances of Ag-C nanofibers membranes samples carbonized at different temperatures.

Formation mechanism of Ag-C nanofibers membranes

Diagrammatic sketch of formation procedures of Ag-C nanofibers membranes are depicted in Figure 3 and Figure 5. By electrospinning process, the Ag^+/PAN nanofibers with some residual solvent were obtained. After drying process, the residual solvent was removed and the Ag^+/PAN nanofibers were obtained, as shown in Figure 3. It can be observed that the Ag^+/PAN nanofibers were relatively flat and theirs surfaces are smooth, indicating that these precursor solutions have good spinnability, as shown in Figure 4a. Subsequently, during the preoxidation and carbonized processes, PAN nanofibers were converted into carbon nanofibers, and Ag^+ ions were converted into Ag naoparticles, as shown in Figure 5. On the one hand, after the preoxidation and carbonized processes, the Ag^+/PAN nanofibers were converted into the Ag/C Nanofiber, as shown in Figure 4b and Figure 2a-2d. On the other hand, due to different carbonization temperatures, Ag nanoparticles exist primarily in two ways: one is distributed on the surface of carbon fibers or another is embedded inside the carbon fibers, as shown in Figure 2a-2d. Furthermore, the surface morphology of carbon nanofibers also was different, as shown in Figure 2a-2d. Thus, the carbonization temperatures have a decisive influence on the surface morphology of Ag-C nanofibers membranes and the way in which Ag-C nanofibers membranes are constructed.

Electrical performances

Electrical performances of Ag-C nanofibers membranes samples carbonized at different temperatures in the range of 700°C -1000°C are listed in Table 1. From Table 1, on the one hand, we can observe that the conductivity of Ag-C nanofibers membranes samples increases gradually with an order of magnitude from 700°C to 900°C. On the other hand, by further increasing carbonization temperature to 1000°C, the increase of conductivity of Ag-C nanofibers membranes samples is not with an order of magnitude, but slight relatively. For Ag-C nanofibers membranes samples, such electrical performances changes might be correlated with theirs morphologies mainly (Figure 2a-2d). Firstly, the smoother surfaces of carbon fibers cause Ag-C nanofiber membrane carbonized at 800°C to have higher conductivity than Ag-C nanofiber membrane carbonized at 700°C (Table 1, Figure 2a,2b); secondly, from 800°C to 900°C, the further increasing of conductivity is due to the growth of Ag nanoparticles, which could afford more stable contacts between the carbon fibers and Ag nanoparticles, being favorable for electron transportation (Table 1, Figure 2b,2c). Thus, in the carbonization temperatures of 700°C-900°C, the varieties of carbon fibers surfaces or contacted with Ag nanoparticles have important contribution to the electrical performances changes (Table 1, Figure 2a-2c). While the carbonized temperature goes to 1000°C, the morphology with Ag nanoparticles embedded in carbon fibers leads no significant increase in the conductivity of Ag-C nanofiber membrane, which is a focus of further work to elaborate the mechanism of this phenomenon (Table 1, Figure 2d).

Conclusions

(1) In our paper, using electrospinning method by combing with pre-oxidation and carbonization processes, Ag-C nanofibers membranes have been successfully fabricated. (2) The carbonized temperature plays an important role in subtle differences formation of the nanostructures of Ag-C nanofibers membranes, which is closely linked to the electrical property of Ag-C nanofibers membranes. (3) Within different carbonized temperatures from 700°C to 1000°C, Ag-C nanofiber membrane with carbonized temperature of 1000°C exhibited a high electrical conductivity of 6.28×10^{-2}S/cm.

Acknowledgements

The authors thank the financial supports from Key Technologies R&D program of He'nan province (grant no. 162102210311), Foundation of He'nan Educational Committee (grant no. 16A480004), Nanhu Scholars Program for Young Scholars of XYNU, National Natural Science Foundation of China Nos.51702276, Foundation of He'nan Educational Committee Nos.18A140030 and the analysis and test center of Xinyang Normal University.

References

1. Hossein Nejadasad, Asghar Piri, Hadi Zarei. The effect of carbon nanotubes on the efficiency of dye sensitized solar cells based on TiO_2 nanorods. Optik-International Journal for Light and Electron Optics. 2017; 142: 211-217.

2. Ruiyuan Hu, Liang Chu, Jian Zhang, Xingao Li, Wei Huang. Carbon materials for enhancing charge transport in the advancements of perovskite solar cells. Journal of Power Sources. 2017; 361: 259-275.

3. Xingping He, Bangning Sun, Bo Gao, Anqi Pang, Hui Suo, Chun Zhao. Various micromorphologies and electrochemical properties of polyaniline/carbon cloth composite nanomaterial were induced for super capacitors. Journal of Electroanalytical Chemistry. 2017; 792: 88-94.

4. Jianan Yi, Yan Qing, Chutian Wu, Yinxiang Zeng, Yiqiang Wu, Xihong Lu, et al. Lignocellulose-derived porous phosphorus-doped carbon as advance electrode for supercapacitors. Journal of Power Sources. 2017; 351: 130-137.

5. Changbing Sun, Sihao Chen, Zhen Li. Controllable synthesis of Fe_2O_3-carbon fiber composites via a facile sol-gel route as anode materials for lithium ion batteries. Applied Surface Science. 2018; 427: 476-484.

6. Kei Hasegawa, Suguru Noda. Lithium ion batteries made of electrodes with 99 wt% active materials and 1 wt% cabonnaotubes without binder or metal foils. Journal of Power Sources. 2016; 321: 155-162.

7. Jendai E. Robinson, William R. Heineman, Laura B. Sagle, M. Meyyappan, Jessica E. Koehne. Carbon nanofiber electrode array for the detection of lead. Electrochemistry Communications. 2016; 73: 89-93.

8. Sheng Chi Lin, Yi Ting Lu, Yu An Chien, Jeng An Wang, Ting Hsuan You, Yu Sheng Wang, et al. Asymmetric supercapacitors based on functional electrospun carbon nanofiber/manganese oxide electrodes with high power density and energy density. Journal of Power Sources. 2017; 362: 258-269.

9. Jidong Dong, ChuyuanJia, Mingqiang Wang, Xiaojiao Fang, Huawei Wei, Huaquan Xie, et al. Improved mechanical properties of carbon fiber-reinforced epoxy composites by growing carbon black on carbon fiber surface. Composites Science and Technology.2017; 149: 75-80.

10. Mohammad Andideh, Masoud Esfandeh. Statistical optimization of treatment conditions for the electrochemical oxidation of PAN-based carbon fiber by response surface methodology: Application to carbon fiber/epoxy composite. Composites Science and Technology. 2016; 134: 132-143.

11. Omid Zabihi, Mojtaba Ahmadi, Quanxiang Li, Sajjad Shafei, Mickey G. Huson, Minoo Naebe. Carbon fibre surface modification using functionalized nanoclay: A hierarchical interphase for fibre-reinforced polymer composites. Composites Science and Technology. 2017; 148: 49-58.

12. Nathan Meek, Dayakar Penumadu, Omid Hosseinaei, David Harper, Stephen Young, Timothy Rials. Synthesis and characterization of lignin carbon fiber and composites. Composites Science and Technology. 2016; 137: 60-68.

13. Jasmin Günther, Niels Thevs, Hans JörgGusovus, Ina Sigmund, Torsten Brückner, Volker Beckmann, et al. Carbon and phosphorus footprint of the cotton production in Xingjing, China, in comparison to an alternative fibre (Apocynum) from Central Asia. Journal of Cleaner Production. 2017; 148: 490-497.

14. Mark Holmes. Lowering the cost of carbon fiber. Reinforced Plastics. 2017; 61: 279-283.

15. Son Ich Ngo, Young-II Lim, Moon Heui Hahn, Jaeho Jung, Yun Hyuk Bang. Multi-scale computational fluid dynamics of impregnation die for thermoplastic carbon fiber prepreg production. Computer & Chemical Engineering. 2017; 103: 58-68.

16. Nasser AM Barakat, Mohamed H. EI-Newehy, Ahmed S. Yasin, Zafar Khan Ghouri, Salem S. AI-Deyab. Ni&Mn nanoparticles-decorated carbon nanofibers as effective electrocatalyst for urea oxidation. Applied Catalysis A: General. 2016; 510: 180-188.

17. Ashish Yadav, Agni K. Teja, Nishith Verma. Removal of phenol from water by catalytic wet air oxidation using carbon bead-supported iron nanoparticle-containing carbon nanofibers in an especially configured reactor. Journal of Environmental Chemical Engineering. 2016; 4: 1504-1513.

18. Bhaskar Bhaduri, Nishith Verma. Carbon bead-supported nitrogen-enriched and Cu-doped carbon nanofibers for the abatement of NO emissions by reduction. Journal of Colloid and Interface Science. 2015; 457: 62-71.

19. Prateek Khare, Janakranjan Ramkumar, Nishith Verma. Carbon nanofiber-skinned three dimensional Ni/carbon micropillars: high performance electrodes of a microbial fuel cell. Electrochimica Acta. 2016; 219: 88-98.

20. Guo Lin Cao, Yi Ming Yan, Ting Liu, David Rooney, Yao Fang Guo, Ke Ning Sun. Three-dimensional porous carbon nanofiber networks decorated with cobalt-based nanoparticles: A robust electrocatalyst for efficient water oxidation. Carbon. 2015; 94: 680-686.

21. Qianwei Ding, Mingkai Liu, Yue-E Miao, Yunpeng Huang, Tianxi Liu. Electrospun nickel-decorated carbon nanofiber membranes as efficient electrocatalysts for hydrogen evolution reaction. Electrochimica Acta. 2015; 159: 1-7.

22. Jin Woo Huh, Hwan-Jin Jeon, Chi Won Ahn. Flexible transparent electrodes made of core-shell-structured carbon/metal hybrid nanofiber mesh films fabricated via electrospinning and electroplating. Current Applied Physics. 2017; 17: 1401-1408.

23. Takehiro Kaneko, Yasuhiro Watanuki, Takeshi Toyama, Yoshiyuki Kojima, Nobuyuki Nishimiya. Characterization and hydrogen sorption behaviors of FeNiCr-carbon composites derived from Fe, Ni and Cr-containing polyacrylonitrile fibers prepared by electrospinning method. International Journal of Hydrogen Energy. 2017; 42: 10014-10022.

24. Wenyao Li, Ruoyu Xu, Min Ling, Guanjie He. Ag-Ag2S/reduced graphene oxide hybrids used as long-wave UV radiation emitting nanocomposites. Optical Materials. 2017; 72: 529-532.