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# Chemical reaction and phase transformation mechanism of electrospun iron (III) acetylacetonate-polyacrylonitrile fibers during pre-oxidation process

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<i>Keywords:</i> Electrospinning Iron (III) acetylacetonate Polyacrylonitrile Pre-oxidation process	Low-temperature pre-oxidation of electrospun metal-compound-incorporated carbon fibers can involve phas transitions and chemical reactions. However, their mechanics remain unclear. In this work, a mixture of poly acrylonitrile (PAN) and iron acetylacetonate is subjected to electrospinning followed by a pre-oxidation proces at 230 °C, producing PAN fibers loaded with iron compounds. Our detailed investigations shed light on th mechanisms of phase transitions and associated chemical reactions during the pre-oxidation process. Our find ings reveal that PAN undergoes cyclization during pre-oxidation, and that crystalline iron acetylacetonate withi PAN fibers transforms into amorphous FeO and Fe <sub>2</sub> O <sub>2</sub> .

# 1. Introduction

Metal-compound-decorated carbon fibers [1–3] exhibit enhanced performance in applications such as electrocatalysis and photocatalysis, which is primarily attributed to the synergistic effect between metal compounds and carbon fibers [4–6]. Among the diverse metal compounds investigated, iron compounds have garnered significant interest owing to their exceptional ability to enhance the physical and chemical properties of carbon fibers. [7].

Electrospinning is a versatile and widely utilized technique for the fabrication of metal-compound-incorporated carbon fibers, offering a high surface area to volume ratio and unique physical properties. There are typically three distinct processes [8–10] in the preparation of electrospun iron compounds/carbon fibers: electrospinning, pre-oxidation, and annealing. Most research efforts have focused on examining the physical and chemical properties of iron compounds/carbon fibers after the annealing process. Great progress has been made in improving the performance of iron compound/PAN carbon fiber in practical applications. [11–13] Although there have been some investigations of iron compound/PAN-based carbon fibers after pre-oxidation [14], reports of chemical and structural evolution during the pre-oxidation process are scarce. Up to now, only Zhang *et al.* [15] have investigated the evolution of iron (III) acetylacetonate [Fe(acac)<sub>3</sub>] in PAN fiber during the pre-

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oxidation process, and suggest that Fe(acac)<sub>3</sub> is converted first to free state iron and then to Fe<sub>2</sub>O<sub>3</sub>. More evidence is needed to confirm this evolution. A comprehensive investigation of chemical reactions and phase transformations in Fe(acac)<sub>3</sub>-PAN fibers during pre-oxidation is urgently required.

In this work, Fe(acac)<sub>3</sub>-PAN fibers were synthesized at room temperature (25 °C) using electrospinning followed by pre-oxidation in air at 230 °C. Various characterization techniques were employed to investigate the composition and microstructure of Fe(acac)<sub>3</sub>-PAN fibers before and after pre-oxidation. It was found that after the pre-oxidation process, PAN within the Fe(acac)<sub>3</sub>-PAN fibers underwent cyclization, while the Fe(acac)<sub>3</sub> transformed into amorphous FeO and Fe<sub>2</sub>O<sub>3</sub>.

# 2. Experimental section

#### 2.1. Preparation of the nanofiber membrane

Polyacrylonitrile (PAN, 11 wt%) and iron acetylacetonate [Fe  $(acac)_3$ , 8.5 wt%] were dissolved into N, N-dimethylformamide (DMF) to obtain a viscous mixture. Subsequently, the mixture was spun into nanofiber membranes by electrospinning under a positive voltage of 20 kV. During the electrospinning process, the injection rate was set to 0.4 mL/h by a syringe pump, and the collecting roll speed was set to 600

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Fig. 1. FE-SEM images and statistical diameter distribution histograms from 100 fibers in F-P 25 (a and b) and F-P 230 (c and d).

rpm. The distance between the collecting roll surface and the syringe needle was 16 cm. The as-spun nanofiber membranes were dried at 25 °C for 2 h in air. Afterwards, some membranes were additionally preoxidized in air at 230 °C for 2 h to attain improved thermal stability. Samples produced at 25 °C and 230 °C are denoted as F-P 25 and F-P 230, respectively.

#### 2.2. Materials characterization

The morphologies of the resulting composites were examined using a field-emission scanning electron microscope (FE-SEM, Sigma 500) operated at 20 kV. Crystal structures were analyzed with X-ray diffraction (XRD) using a Bruker D8 Advance with Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha + with an Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV).

Specimens for transmission electron microscopy (TEM) examinations were prepared by grinding the as-prepared membranes, dispersing the powder in ethanol through ultrasonic treatment, and drop-casting onto a Cu TEM grid with a holey carbon support film. Bright-field (BF) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM2100F transmission electron microscope. High-resolution high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging and energy-dispersive Xray spectroscopy (EDS) elemental mapping were performed using a Thermo Fisher Titan STEM (G2 80–200) equipped with a C<sub>s</sub> probe corrector (CEOS), a ChemiSTEM Super-X EDX detector, and a HAADF detector operating with an inner angle of 55 mrad at 200 kV. Electron energy-loss spectra (EELS) were collected in STEM mode. The incident electron beam convergence angle was 21 mrad.

Fourier transform infrared spectroscopy (FT-IR) data were acquired using an FT-IR spectrometer (Thermo Scientific Nicolet 50, Thermo Fisher) equipped with a Polaris long-life infrared light source and a built-in medium/far infrared diamond attenuated total reflection (ATR) module in reflectance mode. The spectral range was 4000–400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. All spectra were collected at room temperature under atmospheric pressure, with an average of 60 scans for



Fig. 2. XRD patterns of (a) F 25, P 25 and F-P 25; (b) F 230, P 230 and F-P 230.



Fig. 3. FT-IR spectra of (a) the P 25 and P 230, (b) the F-P 25 and F-P 230. (c) Structural formula of PAN before and after cyclization. (d) Structural formula for Fe(acac)<sub>3</sub>.

background and ATR correction.

#### 3. Results and discussion

We used FE-SEM to study the morphology of our nanofibers. Fig. 1(a) and 1(c) show typical FE-SEM images of F-P 25 and F-P 230, respectively. It can be seen from both images that the fibers are randomlyoriented and intertwined, which is ascribed to the bending and whipping movement of the electrospinning jet. Fig. 1(b) and 1(d) present diameter histograms for F-P 25 and F-P 230, obtained by measuring the diameters of 100 fibers in each membrane. As can be seen, the average diameter of the fibers shrinks from  $\sim$  712 nm to  $\sim$  546 nm, suggesting that fiber diameter tends to decrease after pre-oxidation. Pyrolysis can cause shrinkage of the PAN fiber volume due to weight loss. [16].

Fig. 2(a) shows XRD patterns of pure Fe(acac)<sub>3</sub> powder at 25 °C (F 25), PAN nanofiber membranes at 25 °C (P 25) and F-P 25. For pure Fe (acac)<sub>3</sub> powder, all diffraction peaks can be indexed to those of orthorhombic Fe(acac)<sub>3</sub> (JCPDS no.: 30–1763) [17,18]. The peaks at 16.8° and 25.4° in P 25 are attributed to pure PAN [13]. For F-P 25, the peaks at 10.6° and 13.1° correspond to the (020) and (002) planes of Fe (acac)<sub>3</sub>, respectively. Moreover, the peak at 16.8° is ascribed to the overlapping of diffraction peaks from Fe(acac)<sub>3</sub> and PAN [15,19].

In the range of  $20.0^{\circ}$ - $30.0^{\circ}$ , the diffusive broad peak of F-P 25 is consistent with the overlap of the weak peak from Fe(acac)<sub>3</sub> and the diffusive broad peak from PAN. The XRD pattern of F-P 25 confirms the co-existence of Fe(acac)<sub>3</sub> and PAN. Fig. **2(b)** presents the XRD patterns of pure Fe(acac)<sub>3</sub> powder at 230 °C (F 230), PAN nanofiber membranes at 230 °C (P 230), and F-P 230. In the XRD pattern of F 230, all diffraction peaks are attributed to cubic Fe<sub>2</sub>O<sub>3</sub> (JCPDS no.: 39–1346) [19,20], indicating that Fe(acac)<sub>3</sub> transforms into Fe<sub>2</sub>O<sub>3</sub> at 230 °C in air. In the case of F-P 230, the profile and position of diffraction peaks are similar to those of P 230. This means that PAN fibers in both F-P and pure PAN undergo similar chemical reactions at 230 °C. In addition, the amorphous diffraction peak intensity of F-P 230 (25.4°) is higher than that of P 230, indicating that Fe(acac)\_3 in F-P reacts with PAN at 230  $^\circ C$ , and an amorphous product is formed.

FT-IR spectroscopy was used to further elucidate the chemical reaction of Fe(acac)<sub>3</sub>/PAN during pre-oxidation. Fig. **3(a)** compares the FT-IR spectra of P 25 and P 230. In the FT-IR spectrum of P 25, the absorption peak at 2931 cm<sup>-1</sup> originates from the stretching vibration peak of C-H. The typical peaks for PAN at 2242 and 1450 cm<sup>-1</sup> are caused by the stretching vibrations of nitrile groups (C $\equiv$ N, labeled as functional group 1') and bending vibrations of methylene groups (CH<sub>2</sub>), respectively [19]. In addition, the prominent peak at about 1735 cm<sup>-1</sup> is associated with the stretching vibrations of carbonyl groups (C $\equiv$ O) from residual DMF solvent [19].

The FT-IR spectrum of P 230 shows two new absorption peaks at 1600 cm<sup>-1</sup> and 1373 cm<sup>-1</sup>, which are assigned to the stretching vibration peak of C=N (labeled as functional group 2') and the bending vibration peak of C=C (labeled as functional group 3'). Compared with the FT-IR spectrum of P 25, the absorption peak at 1735 cm<sup>-1</sup> disappears, indicating that the residual DMF solvent is completely volatilized at 230 °C in air. In addition, the intensity of the peak at 2242 cm<sup>-1</sup> decreases significantly because the C=N in PAN converts to C=N at 230 °C. This indicates that the cyclization reaction of PAN occurs at 230 °C [Fig. 3(c)]. The degree of cyclization can be described by the cyclization index  $\eta$ , calculated as [21].

 $\eta = I_{1600} / (I_{1600} + I_{2242}), (1)$ 

where  $I_{1600}$  and  $I_{2242}$  represent the peak intensities at 1600 cm<sup>-1</sup> and 2242 cm<sup>-1</sup>, respectively. From Fig. 3(a), the  $\eta$  value for P 230 is 0.975, close to 1, suggesting a great degree of cyclization. Fig. 3(b) depicts the FT-IR spectra of F-P 25 and F-P 230. The peaks in the FT-IR spectrum of F-P 25 are typical for both PAN and Fe(acac)<sub>3</sub>. Peaks at 2242 cm<sup>-1</sup> and 1450 cm<sup>-1</sup> originate from PAN; other peaks result from the vibration of functional groups in Fe(acac)<sub>3</sub>. [Fig. 3(d)]. Among the characteristic absorption peaks of Fe(acac)<sub>3</sub>, the peaks at 1571 and 1522 cm<sup>-1</sup> originate from the coupling vibration of C=O and C=C (labeled as functional groups 1 and 2). The peak at 1441 cm<sup>-1</sup> is the stretching vibration



Fig. 4. STEM images of F-P 25 (a) and F-P 230 (c) with corresponding EDS maps of C, N, O and Fe (b, d).

peak of C-O (labeled as functional group 3) [22]. The peaks at 1363 and 1273 cm<sup>-1</sup> result from bending vibrations of C-H in CH<sub>3</sub> as well as the coupling vibration of C-CH<sub>3</sub> (labeled as functional group 4) and C=C. The peak corresponding to 774 cm<sup>-1</sup> is caused by C=C-H<sub>2</sub> stretching vibrations. The peak at ~ 543 cm<sup>-1</sup> is assigned to the Fe-O stretching

vibration (labeled as functional group 5). As for the spectrum of F-P 230, the peak at 1600 cm<sup>-1</sup> derives from the stretching vibration peak of C—N in the cyclized PAN. The peak at 1365 cm<sup>-1</sup> is caused by overlapping of the bending vibration of C—C in cyclized PAN and C-H in Fe (acac)<sub>3</sub>. The peak at 543 cm<sup>-1</sup> is the stretching vibration peak of Fe-O in



Fig. 5. Typical BF TEM image (a) and HRTEM image (b) of F-P 230. The inset in (a) shows the SAED pattern obtained from F-P 230.



Fig. 6. High-resolution XPS spectra of the Fe 2p for F-P 25 (a) and F-P 230 (b).



Fig. 7. EELS spectra of Fe L<sub>2,3</sub> edges acquired from F-P 25 (a) and F-P 230 (b). Normalized and fitted EELS spectra of Fe L<sub>2,3</sub> edges acquired from F-P 25 (c) and F-P 230 (d).

Fe(acac)<sub>3</sub>. Comparing the FT-IR spectra of F-P 25 and F-P 230, the C-O stretching vibration peak at 1441 cm<sup>-1</sup> in Fe(acac)<sub>3</sub> almost disappears at 230 °C, indicating that most C-O bonds are broken. The stretching vibration peak of Fe-O (543 cm<sup>-1</sup>) in F-P 230 implies that bonding between iron and oxygen takes place during the pre-oxidation process. Therefore, the decomposition product of Fe(acac)<sub>3</sub> in PAN fibers after pre-oxidation mainly consists of iron oxides.

Fig. 4 shows EDS elemental maps of F-P 25 and F-P 230. Fig. 4(a) displays a typical STEM image of F-P 25, and the corresponding EDS mapping images for elements C, N, O, and Fe are presented in Fig. 4(b). It can be seen that C, N, O and Fe are evenly distributed across the fibers in F-P 25. Fig. 4(c) and (d) show STEM images of F-P 230 and corresponding EDS maps of C, N, O and Fe. It should be noted that C and N are evenly distributed across the whole fiber, whereas O and Fe are mostly

distributed in the middle of the fiber, which differs from the elemental distribution in F-P 25.

TEM was used to further study the microstructure of F-P 230. Fig. 5 (a) shows a BF TEM image of F-P 230. The contrast on both sides of the fiber is lighter, whereas it is darker in the middle of the fiber. This indicates that heavier Fe atoms are distributed in the middle of the fiber, in good agreement with EDS mapping [Fig. 4(d)]. The selected-area electron diffraction (SAED) pattern of F-P 230 [inset in Fig. 5(a)] shows diffuse diffraction rings, indicating that F-P 230 is mainly amorphous. HRTEM was used to further characterize the microstructure of F-P 230. From the HRTEM image of F-P 230 [Fig. 5(b)], aggregations are observed in the area with darker contrast (labeled by white dashed lines), and no nanocrystallites are observed, further confirming that F-P 230 is completely amorphous. Additionally, no aggregations appear

within 20 nm of the outer surface of the fiber. Combining our HRTEM images with the elemental mapping of F-P 230 [Fig. 4(d)], we suspect that the aggregations are composed of Fe and O.

XPS was conducted to investigate the valence states of Fe in F-P 25 and F-P 230. Fig. 6(a) and (b) display the XPS spectra of Fe 2*p* for F-P 25 and F-P 230, respectively. In Fig. 6(a), the Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  peaks at 721.1  $\pm$  0.1 eV and 708.7  $\pm$  0.1 eV fit well with those of Fe<sup>3+</sup>. The two satellite peaks at 728.1  $\pm$  0.1 eV and 713.4  $\pm$  0.1 eV originate from Fe<sup>3+</sup>. [23] Therefore, F-P 25 contains trivalent Fe. In Fig. 6(b), Fe  $2p_{1/2}$ and Fe  $2p_{3/2}$  peaks are located at 721.1  $\pm$  0.1 eV and 708.7  $\pm$  0.1 eV, which match those of Fe<sup>3+</sup> and Fe<sup>2+</sup> [23]. The peaks at 723.2  $\pm$  0.1 eV and 709.6  $\pm$  0.1 eV correspond to characteristic peaks of Fe<sup>3+</sup>, while the peaks at 721.6  $\pm$  0.1 eV and 708.1  $\pm$  0.1 eV are characteristic peaks of Fe<sup>2+</sup>. [24] This indicates that Fe<sup>2+</sup> and Fe<sup>3+</sup> co-exist in F-P 230. Therefore, the valence state of Fe in the PAN fiber converts from trivalent (Fe<sup>3+</sup>) to mixed valence (Fe<sup>3+</sup> and Fe<sup>2+</sup>) after the pre-oxidation process.

To verify the valence state of Fe in F-P 25 and F-P 230, extensive EELS examinations were also carried out. The Fe  $L_{2r,3}$  edges of F-P 25 and F-P 230 are shown in Fig. 7(a) and (b), exhibiting a rather similar profile. To compare the valence state of Fe in F-P 25 and F-P 230, the peak intensity ratio  $(L_3/L_2)$  and peak spacing between  $L_3$  and  $L_2$  are calculated. The peak intensity ratio  $(L_3/L_2)$  is calculated to be 3.2:1 and 2.9:1 for F-P 25 and F-P 230, respectively, and the peak spacing between  $L_3$  and  $L_2$  is measured to be 13.2 eV and 13.1 eV. The higher the peak intensity ratio  $L_3/L_2$ , and the wider the peak spacing, the higher the Fe valence state. [25] Thus, it can be inferred that the Fe valence state of F-P 25 is higher than that of F-P 230. In addition, a slight difference in the shoulder peak at ~716 eV (labeled by black arrows) can be observed. To clearly compare the difference in the shoulder peak between the F-P 25 and F-P 230, their Fe  $L_{2,3}$  edges are normalized and fitted, as shown in Fig. 7(c) and (d). Compared with F-P 25, the intensity of the shoulder peak for F-P 230 is reduced by 28 %. In previous research [26], it was found that intensity of shoulder peak for pure  ${\rm Fe}^{3+}$  is stronger than that of mixed  $Fe^{3+}$  and  $Fe^{2+}$ , because  $Fe^{2+}$  has no shoulder peak. Thus, the intensity decrease in shoulder peak for F-P 230 indicates that Fe<sup>3+</sup> has partially converted into Fe<sup>2+</sup> after pre-oxidation. Moreover, Colliex et al. [27] reported that the shoulder peak of Fe<sub>3</sub>O<sub>4</sub> is barely visible, which greatly differs from our observations of F-P 230. Hence, Fe<sub>3</sub>O<sub>4</sub> is not present in F-P 230. We conclude that only amorphous FeO and Fe<sub>2</sub>O<sub>3</sub> exist in F-P 230. The co-existence of FeO and Fe<sub>2</sub>O<sub>3</sub> can be explained by the fact that an individual fiber is divided into two different parts after stabilization, *i.e.*, outer and inner parts along the radial direction. The outer part of the fiber is exposed to oxygen, where Fe(acac)<sub>3</sub> decomposes and transforms into amorphous Fe<sub>2</sub>O<sub>3</sub>. The inner part has limited access to oxygen, so Fe(acac)<sub>3</sub> is decomposed and reduced to amorphous FeO by surrounding carbon in the fiber.

#### 4. Conclusions

In summary, Fe(acac)<sub>3</sub>-PAN fibers have been fabricated using electrospinning. The morphologies and microstructure evolutions of Fe (acac)<sub>3</sub>-PAN fibers were studied before and after stabilization. The average fiber diameter shrank from 712 nm to 546 nm after stabilization, and numerous amorphous aggregations were produced in the middle parts of fibers which were ascribed to the formation of iron oxides. Through XPS, FT-IR and EELS characterizations, we observed an amorphous microstructure composed of both FeO and Fe<sub>2</sub>O<sub>3</sub>. This study provides novel insight into the morphology and microstructure of Fe (acac)<sub>3</sub> in PAN fibers subjected to the pre-oxidation process, thereby contributing significantly to our understanding of chemical reactions and phase transitions during pre-oxidation. These electrospun fiber membranes have many potential applications in catalysis, energy storage, and magnetic devices.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### References

- [1] L. Sabantina, M.A. Rodríguez-Cano, M. Klöcker, F.J. García-Mateos, J.J. Ternero-Hidalgo, A. Mamun, F. Beermann, M. Schwakenberg, A.L. Voigt, J. Rodríguez-Mirasol, T. Cordero, A. Ehrmann, Fixing PAN nanofiber mats during stabilization for carbonization and creating novel metal/carbon composites, Polymers 10 (2018) 735.
- [2] P. Carol, P. Ramakrishnan, B. John, G. Cheruvally, Preparation and characterization of electrospun poly(acrylonitrile) fibrous membrane based gel polymer electrolytes for lithium-ion batteries, J. Power Sources 196 (2011) 10156–10162.
- [3] K. Gupta, T.Y. Liu, R. Kavian, H.G. Chae, G.H. Ryu, Z. Lee, S.W. Lee, S. Kumar, High surface area carbon from polyacrylonitrile for high-performance electrochemical capacitive energy storage, J. Mater. Chem. A 4 (2016) 18294–18299.
- [4] R. Zhao, X. Li, Y.M. Li, Y.Z. Li, B.L. Sun, N. Zhang, S. Chao, C. Wang, Functionalized magnetic iron oxide/polyacrylonitrile composite electrospun fibers as effective chromium (VI) adsorbents for water purification, J. Colloid Interf. Sci. 505 (2017) 1018–1030.
- [5] L.G. Guo, H. Sun, C.Q. Qin, W. Li, F. Wang, W.L. Song, J. Du, F. Zhong, Y. Ding, Flexible Fe<sub>3</sub>O<sub>4</sub> nanoparticles/N-doped carbon nanofibers hybrid film as binder-free anode materials for lithium-ion batteries, Appl. Surf. Sci. 459 (2018) 263–270.
- [6] H. Wang, W.Y. Wang, H.J. Wang, X. Jin, H.T. Niu, H.X. Wang, H. Zhou, T. Lin, High performance supercapacitor electrode materials from electrospun carbon nanofibers in situ activated by high decomposition temperature polymer, ACS Appl. Energ. Mater. 1 (2018) 431–439.
- [7] X.L. Sheng, T. Li, M. Sun, G.J. Liu, Q.Y. Zhang, Z.B. Ling, S.W. Gao, F.Y. Diao, J. Z. Zhang, F. Rosei, Y.Q. Wang, Flexible electrospun iron compounds/carbon fibers: Phase transformation and electrochemical properties, Electrochim. Acta 407 (2022), 139892.
- [8] B. Barua, M.C. Saha, Investigation on jet stability, fiber diameter, and tensile properties of electrospun polyacrylonitrile nanofibrous yarns, J. Appl. Polym. Sci. 132 (2015) 41918.
- [9] J.C. Chen, I.R. Harrison, Modification of polyacrylonitrile (PAN) carbon fiber precursor via post-spinning plasticization and stretching in dimethylformamide (DMF), Carbon 40 (2002) 25–45.
- [10] H. Khayyam, R.N. Jazar, S. Nunna, G. Golkarnarenji, K. Badii, S.M. Fakhrhoseini, S. Kumar, M. Naebe, PAN precursor fabrication, applications and thermal stabilization process in carbon fiber production: Experimental and mathematical modelling, Prog. Mater Sci. 107 (2020), 100575.
- [11] D.X. Ji, S.J. Peng, J. Lu, L.L. Li, S.Y. Yang, G.R. Yang, X.H. Qin, M. Srinivasan, S. Ramakrishna, Design and synthesis of porous channel-rich carbon nanofibers for self-standing oxygen reduction reaction and hydrogen evolution reaction bifunctional catalysts in alkaline medium, J. Mater. Chem. A 5 (2017) 7507–7515.
- [12] Y. Yang, Z. Guo, H. Zhang, D. Huang, J. Gu, Z. Huang, F. Kang, T. Alan Hatton, G. C. Rutledge, Electrospun magnetic carbon composite fibers: Synthesis and electromagnetic wave absorption characteristics, J. Appl. Polym. Sci. 127 (2013) 4288–4295.
- [13] Y. Yang, Z. Guo, H. Zhang, D.Q. Huang, J.L. Gu, Z.H. Huang, F.Y. Kang, T. A. Hatton, G.C. Rutledge, Electrospun magnetic carbon composite fibers: Synthesis and electromagnetic wave absorption characteristics, J. Appl. Polym. Sci. 127 (2013) 4288–4295.
- [14] M. Akia, N. Salinas, S. Luna, E. Medina, A. Valdez, J. Lopez, J. Ayala, M. Alcoutlabi, K. Lozano, In situ synthesis of Fe<sub>3</sub>O<sub>4</sub>-reinforced carbon fiber composites as anodes in lithium-ion batteries, J. Mater. Sci. 54 (2019) 13479–13490.

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- [15] T. Zhang, D.Q. Huang, Y. Yang, F.Y. Kang, J.L. Gu, Influence of iron (III) acetylacetonate on structure and electrical conductivity of Fe3O4/carbon composite nanofibers, Polymer 53 (2012) 6000–6007.
- [17] M. Yurdakoç, M. Akçay, Y. Tonbul, F. Ok, K. Yurdakoç, Preparation and characterization of Cr- and Fe-pillared bentonites by using CrCl3, FeCl3, Cr(acac)3 and Fe(acac)3 as precursors, Micropor. Mesopor. Mater. 111 (2008) 211–218.
- [18] A. Lennartson, Optical resolution and racemisation of Fe(acac)3, Inorg. Chim. Acta 365 (2011) 451–453.
- [19] S. Patel, G. Hota, Iron oxide nanoparticle-immobilized PAN nanofibers: Synthesis and adsorption studies, RSC Adv. 6 (2016) 15402–15414.
- [20] M. Zhou, H.M. Luo, Effects of Y-doping on the formation, structure and properties of iron oxide, J. Alloy. Compd. 255 (1997) 239–242.
- [21] Y. Zhu, M.A. Wilding, S.K. Mukhopadhyay, Estimation, using infrared spectroscopy, of the cyclization of poly(acrylonitrile) during the stabilization stage of carbon fibre production, J. Mater. Sci. 31 (1996) 3831–3837.

- [22] M. Devi, S. Ganguly, B. Bhuyan, S.S. Dhar, S. Vadivel, A novel Fe(acac)3 interspersed g-C3N4 heterostructure for environmentally benign visible-lightdriven oxidation of alcohols, Eur. J. Inorg. Chem. 44 (2018) 4819–4825.
- [23] J.J. Wang, X.Y. Xue, Y.Q. Wang, Tuning the structural and magnetic properties of electrospun strontium-iron-oxide nanofibers with different stoichiometry, Mater Charact 200 (2023), 112884.
- [24] T. Yamashita, P. Hayes, Analysis of XPS spectra of Fe2+ and Fe3+ ions in oxide materials, Appl. Surf. Sci. 254 (2008) 2441–2449.
- [25] H.K. Schmid, W. Mader, Oxidation states of Mn and Fe in various compound oxide systems, Micron 37 (2006) 426–432.
- [26] C. Wang, Y.Q. Wang, X.H. Liu, H.W. Yang, J.R. Sun, L. Yuan, G.W. Zhou, F. Rosei, Structure versus properties in α-Fe<sub>2</sub>O<sub>3</sub> nanowires and nanoblades, Nanotechnology 27 (2016), 035702.
- [27] C. Colliex, T. Manoubi, C. Ortiz, Electron-energy-loss-spectroscopy near-edge fine structures in the iron-oxygen system, Phys. Rev. B 44 (1991) 11402–11411.