Preparation and electrochemical performance of chemical-activated carbon foam

1 | INTRODUCTION

In the area of electrochemical energy storage, various carbon materials have been used as high stable electrode materials of electrical double-layer capacitor, presenting high power density and long durability [1–3]. The functional carbon materials have been well designed and prepared for the purposes of applications [4]. Various transition metal oxides and conductive polymers are developed as high active electrode materials of Faradaic supercapacitor, presenting high capacitance performance [5-10]. Porous carbon has been widely investigated as active electrode materials for supercapacitor electrodes, keeping excellent chemical stability which has excellent acid and alkali resistance and oxidation resistance for electrochemical applications [19]. Porous carbon materials are applied for supercapacitor electrodes, keeping excellent cyclic stability and good resistance to electrochemical corrosion [20–22]. These porous carbon materials mainly reveal the electrical double-layer capacitance behaviour with the limited areal specific capacitance which is restricted by the active electrode surface area and the pore size distribution [23]. Both the areal specific capacitance and rate capability of porous carbon electrode materials is still needed to be improved. High graphitization degree of carbon materials is beneficial to enhance the electrical conductivity [24, 25]. The capacitance performance can be further improved by catalytic thermal activation of porous carbon.

Carbon foam is typical porous carbon material, showing a three-dimensional porous network structure, large specific surface area, and low preparation cost [26, 27]. Carbon foam is usually used as catalyst carriers, battery electrode materials, microwave absorbing materials, and so on. Carbon foam preparation methods include organic polymer pyrolysis, foaming, sol-gel, Pocofoam, and template methods. The thermal carbonization method is similar to the pyrolysis of organic matters [28, 29]. It is feasible to increase the degree of graphitization by thermal activation in an inert gas atmosphere [30]. Normal carbon foam has moderate electrical conductivity and low capacitance performance, due to the low electrochemical active site [31, 32]. The catalytic activation treatment can be utilized to improve the graphitization of porous carbon foam materials. Generally, the activation methods include physical activation, chemical activation, and physio-chemical activation. The KOH activation is used to improve the surface area and tailor the pore texture of mesoporous carbon by adjusting KOH/carbon mass ratio as well as activation time [33]. The CO2 activation treatment could cause the increase of specific surface area and micropore volume of carbon foam [34]. However, a large number of disorderly accumulation voids replace the previously clear and ordered pore structure along with the extended activation time, leading to the decrease of electrochemical activity of porous carbon materials. The Ni(NO3)2 activation treatment could catalyze the thermal pyrolysis of melamine glucose to prepare nitrogen-doped porous graphitic carbon [35]. So, these activation methods have the guiding significance. The chemical activation treatment leads to the increase of specific surface area and enhanced the reaction activity of carbon foam.

In this study, porous carbon foam materials are fabricated by thermal pyrolysis of melamine foam polymer [28]. The KOH or Ni(NO3)2 catalyzed thermal pyrolysis of melamine foam is also carried out to further improve the graphitization degree and electrical conductivity of carbon foam. It is expected that the chemical-activated carbon foam has the higher electrochemical performance for potential energy storage application.

2 | EXPERIMENTAL

2.1 | Fabrication of carbon foam

Porous carbon foam is fabricated by thermal pyrolysis of melamine foam. Melamine foam with a cubic shape of 10 × 3 × 0.5 cm was fully washed with acetone, alcohol, and deionized water. The dried melamine foam was placed into a corundum boat. Thermal carbonization treatment was carried out in tubular furnace which was supplied with pure argon gas at a flow rate of 60 ml min⁻¹. The temperature increased up to 700, 800, and 900°C at a heating rate was 5°C min⁻¹. The carbonization process is kept for 2 h at above constant temperature. Bare
carbon foam was obtained. The chemical-activated carbon foam was fabricated through KOH-catalyzed or Ni(NO$_3$)$_2$-catalyzed graphitization process. The cleaned melamine foam with a cubic shape of 10 x 3 x 0.5 cm was immersed in 0.1 mM Ni(NO$_3$)$_2$ or 0.1 mM KOH aqueous solution for 6 h. The pretreated melamine foam conducted thermal carbonization treatment at 900°C for 2 h in pure argon atmosphere. Ni(NO$_3$)$_2$-activated carbon foam and KOH-activated carbon foam were obtained.

2.2 Characterization and measurement

The morphological microstructure and energy-dispersive X-ray (EDX) spectrum were characterized by a scanning electron microscopy (SEM; Zeiss Ultra Plus). The crystal phase structure was conducted by X-ray diffractometer (XRD; D8 ADVANCE, Cu Kα radiation, 40 kV, 200 mA). Raman spectroscopy (Raman, Oceanoptics Benchtop Raman System) of the electrode materials was conducted using He-Ne laser emitting at 532 nm excitation in the wave number range of 0–2000 cm$^{-1}$. The cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) performances were tested using an electrochemical workstation (CHI 760C, CH Instruments), which was conducted in 1.0 M H$_2$SO$_4$ aqueous solution under a controlled scan rate, current density, and potential window. All electrochemical measurements were carried out 25°C in a three-electrode system where different carbon foam electrodes were used as the working electrode, Pt sheet as a counter electrode, and the saturated calomel electrode. The mechanical stability and flexibility of carbon foam are assessed through 180° completely folding test for 1000 cycles.

3 RESULTS AND DISCUSSION: MORPHOLOGY AND MICROSTRUCTURE

Figure 1A shows photograph and SEM image of carbon foam prepared by carbonization treatment of melamine foam at 900°C. Obviously, carbon foam has much smaller shape size than melamine foam, which is due to the volumetric shrinkage during carbonization process. Comparatively, the higher temperature causes more shrinkage of carbon foam, which is due to higher carbonization degree. Thermal carbonization causes the partial breakdown of some carbon framework. Furthermore, carbon foam could be fully bended and almost keep physical intact, revealing its good mechanical stability. The SEM images show carbon foam is composited of the cross-linked fibres. These carbon fibres are overlapped layer-by-layer, presenting a three-dimensional porous structure. The melamine polymer could conduct the volume shrinkage in the carbonization process, which causes some broken frameworks of carbon fibres. The carbon foam prepared at 900°C is used as the optimal electrode material for further study due to higher graphitization degree. Such an activated carbon foam also keeps good mechanical stability and flexibility in the continuous folding process.

Figure 1B,C shows photograph and SEM images of KOH-activated carbon foam and Ni(NO$_3$)$_2$-activated carbon foam. Both carbon foams still keep the interconnected fibres with 3D porous structure. Comparatively, the activated carbon foam shows much more breakdown of carbon framework than bare carbon foam. Ni(NO$_3$)$_2$-activated carbon foam demonstrates more shrinkage volume and more fractured fibres than KOH-activated carbon foam. On the surface of carbon fibres appears many tiny micropores. It implies that the graphitization degree of Ni(NO$_3$)$_2$-activated carbonization is more complete than that of KOH-activated carbon foam. The higher graphitization degree contributes to improving the electrical conductivity. However, the more breakdown of carbon framework leads to lowering mechanical strength and stability.

The increase of carbonization temperature is beneficial to improving graphitization degree and meanwhile lowering mechanical stability of carbon foam. Ni(NO$_3$)$_2$-activation is more effective to enhance graphitization degree and meanwhile lowering mechanical stability of KOH-activation carbon foam.

3.1 EDX spectrum analysis

Figure 2 shows EDX spectra of bare, KOH-activated and Ni(NO$_3$)$_2$-activated carbon foams. The inset shows the atomic
and mass ratio of elements in both chemical-activated carbon foams. The characteristic energy dispersive peaks at 0.346 and 0.258 KeV are ascribed to N and C elements, respectively. The C and N atomic content are 67.2% and 32.8% with C/N ratio of 2.07 for bare carbon foam. They become 63.5% and 29.3% with C/N ratio of 2.17 for KOH-activated carbon foam. They become 69.6% and 21.5% with high C/N ratio of 3.23 for Ni(NO₃)₂-activated carbon foam. So, the activated carbon foam has higher carbonization degree than bare one. Furthermore, Ni(NO₃)₂-activated carbon foam exhibits higher carbon ratio than KOH-activated one. Additionally, the characteristic energy-dispersive peak at 0.512 KeV is observed which is ascribed to O element of residual oxides products adsorbed on the activated carbon foams during the activated graphitization process. Comparatively, bare carbon foam almost does exhibit the energy-dispersive peak of O element. On the other hand, very high N contents in all carbon foams are associated with the incomplete graphitization. So, all carbon foams present relatively low conductivity in comparation with pure graphite carbon.

3.2 | X-ray diffraction analysis

Figure 3 shows XRD patterns of bare, KOH-activated and Ni(NO₃)₂-activated carbon foams. All samples show the similar board diffraction peak at 23.5–26.5°, which is ascribed to the graphite carbon. The wide and coarse shape of diffraction peak indicates its uncompleted graphitization with the scattering characteristic. Other characteristic peaks are not observed. So, bare, KOH-activated and Ni(NO₃)₂-activated carbon foams still have the low graphitization level. Comparatively, the peak half-width of bare carbon foam is somewhat larger than that of two activated ones, presenting higher crystallized graphitization. This result agrees with that of EDX spectra analysis result.

3.3 | Raman spectrum analysis

Figure 4 shows Raman spectra of bare, KOH-activated and Ni(NO₃)₂-activated carbon foams at Raman shift of 1000–2000 cm⁻¹. The characteristic Raman peaks at 1360 and 1580 cm⁻¹ are ascribed to the D (disorder) peak and G (graphite) peak. D peak correlates with the defects in the carbon lattice and the extent of sp³ hybridization, referring to the disordered carbon structure. The G peak correlates with the graphitic network and the extent of sp² hybridization, referring to the ordered graphitic structure. The corresponding peak intensity ratio (I_D/I_G) is 0.987, 0.959, and 0.947, respectively. Bare carbon foam involves higher defect ratio than the two activated carbon foams. So, KOH and Ni(NO₃)₂-activation carbon foams show the improved graphitization degree. Furthermore, Ni(NO₃)₂-activated carbon foam reveals higher graphitization degree than KOH-activated carbon foam, presenting higher conductivity. So, the XRD analysis result is similar to the Raman analysis result.

3.4 | Electrical resistance

Table 1 lists electrical resistance of bare carbon foam prepared at different carbonization temperature. Obviously, the electrical resistance of bare carbon foam declines along with increasing carbonization temperature, which is due to the improved graphitization degree. Meanwhile, the mechanical stability of carbon foam was descended and even directly crushed at higher temperature above 900°C. So, the following activation carbonization temperature is controlled at 900°C. Table 2 lists electrical resistance of bare, KOH-activated and Ni(NO₃)₂-activated carbon foams formed at the carbonization
temperature of 900°C. Obviously, both activated carbon foams show much lower electrical resistance than bare carbon foam. The activated carbonization contributes to improving the graphitization degree and accordingly electrical conductivity. Furthermore, Ni(NO₃)ₓ-activated carbon foam reveals even lower electrical resistance than KOH-activated carbon foam. So, Ni(NO₃)ₓ-activation is more effective than KOH-activation for carbon foam electrode material.

3.5 Cyclic voltammetry properties

Figure 5 shows CV curves of bare, KOH-activated, Ni(NO₃)ₓ-activated carbon foams at different scan rates. The CV-based average current density (i(CV)) and specific capacitance (Cₛ(CV)) of electrode materials can be calculated using the following equations.

\[
i(CV) = \left[ \int_{V_a}^{V_c} i(v) \right] / (V_c - V_a), \tag{1}\n\]

\[
C_s(CV) = i(CV)/\upsilon = \left[ \int_{V_a}^{V_c} i(v) \right] / (V_c - V_a) / \upsilon, \tag{2}\n\]

where \(i(\upsilon)\) is instantaneous current density of CV (mA cm⁻²), \(\upsilon\) is potential sweep rate (mV s⁻¹), \(i(CV)\) is average current density obtained through integrating the area of the CV curves (mA)

| Carbon foam | Bare | KOH activated | Ni(NO₃)ₓ activated |
|-------------|------|---------------|--------------------|
| Resistance (Ω cm⁻¹) | 305 | 198 | 58 |
Herein, \( i(CV) \) is defined as \( \left( \int_{V_a}^{V_c} i(V) \, dV \right) / (V_c - V_a) \), where \( V_a \) and \( V_c \) represent the lowest and highest voltage (mV), respectively [12]. \( C_s(CV) \) is CV-based specific capacitance (mF cm\(^{-2}\)). Table 3 lists the response current density of three kinds of carbon foam electrodes at different scan rates. Figure 5A–C show CV curves of three kinds of carbon foam electrodes. They are very close to an ideal rectangular shape without an obvious distortion at a potential window of 0–0.6 in 1.0 M H\(_2\)SO\(_4\) electrolyte. It indicates that electrochemical polarization of carbon foam electrodes is not significant at a potential window of 0–0.6 V. Considering the electrochemical stable properties, carbon foam electrode usually presents electrical double-layer capacitance behaviour through reversible electrolyte ion adsorption-desorption in a charge–discharge process. At the same scan rate, the average current density increases at the order of bare carbon foam < KOH-activated one < Ni(NO\(_3\))\(_2\)-activated one. So, both activated carbon foam electrodes have higher electrical conductivity than bare carbon foam electrode. Ni(NO\(_3\))\(_2\)-activated carbon foam electrode is more electroactive than KOH-activated one. Figure 5D shows the CV-based capacitance of three kinds of carbon foam electrodes. The capacitance of bare, KOH-activated, Ni(NO\(_3\))\(_2\)-activated carbon foam electrode declines from 1.4 to 0.34 mF cm\(^{-2}\) with the capacity retention of 24.3\%, from 1.8 to 0.76 mF cm\(^{-2}\) with the capacity retention of 42.2\%, from 2.8 to 1.45 mF cm\(^{-2}\) with the capacity retention of 51.8\%. So, KOH-activated and Ni(NO\(_3\))\(_2\)-activated carbon foams show higher rate capability than bare carbon foam.

### Table 3  Response current density of three kinds of carbon foams at different scan rates

| Scan rate (mV s\(^{-1}\)) | Bare     | KOH activated | Ni(NO\(_3\))\(_2\) activated |
|--------------------------|----------|---------------|-----------------------------|
| 5                        | 0.007    | 0.009         | 0.014                       |
| 10                       | 0.009    | 0.014         | 0.023                       |
| 20                       | 0.011    | 0.023         | 0.039                       |
| 40                       | 0.016    | 0.039         | 0.067                       |
| 60                       | 0.019    | 0.054         | 0.094                       |
| 80                       | 0.028    | 0.067         | 0.121                       |
| 100                      | 0.034    | 0.076         | 0.145                       |

**3.6 Galvanostatic charge–discharge properties**

The GCD-based specific capacitance \( C_s(GCD) \) can be calculated using the following equation.

\[
C_s(GCD) = \frac{I \times \Delta V}{\Delta t},
\]

where \( I \) is constant current density of GCD (mA cm\(^{-2}\)), \( \Delta V \) is potential window (V), \( \Delta t \) is the discharge time (s). Figure 6A–C shows GCD curves of bare, KOH-activated, and Ni(NO\(_3\))\(_2\)-activated carbon foam electrodes at different current densities. They illustrate a good symmetric characteristic between the charge section and the discharge section without the potential plateau. The carbon foam electrodes mostly present electrical double-layer capacitance performance. Figure 6D shows corresponding capacitance curves in terms of current density.
The bare, KOH-activated and Ni(NO$_3$)$_2$-activated carbon foam electrodes reveal the specific capacitance of 0.371, 0.905, and 1.267 mF/cm$^2$ at the low current density of 0.1 mA/cm$^2$. Such capacitance quickly declines along with the increase of GCD current density and then approaches the stable low level of 0.005, 0.027, and 0.033 mF/cm$^2$ at the current density of 2.0 mA/cm$^2$, presenting the quite low capacitance retention. So, low electrical conductivity of bare carbon foam causes rate capability. Comparatively, the activated carbon foams exhibit the higher capacitance than bare one. Furthermore, Ni(NO$_3$)$_2$-activated carbon foam keeps higher capacitance than KOH-activated carbon foam. It implies that the activation thermal treatment is still regarded as an effective way to improve the electroactivity of carbon foam.

4 | CONCLUSIONS

3D porous carbon foam is well fabricated by thermal carbonization of melamine foam in argon atmosphere at 900°C, which is composed of the interconnected fibres. It keeps high electrical resistance of 305 Ω cm$^{-1}$, high mechanical stability, and flexibility. KOH-activated and Ni(NO$_3$)$_2$-activated carbon foams keep the lowered electrical resistance of 198 and 58 Ω cm$^{-1}$. The fibres also show partially fractured framework. EDS and Raman spectrum measurement results prove that Ni(NO$_3$)$_2$-activated carbon foam shows the higher graphitization degree, which contributes to its higher CV response current than KOH-activated carbon foam. GCD measurement results prove that the specific capacitance can increase from 0.371 mF cm$^{-2}$ for bare carbon foam to 0.905 mF cm$^{-2}$ for KOH-activated one and 1.267 mF cm$^{-2}$ for Ni(NO$_3$)$_2$-activated one at the current density of 0.1 mA cm$^{-2}$. The KOH and Ni(NO$_3$)$_2$-catalyzed thermal pyrolysis can enhance carbonization degree of melamine foam and accordingly improve the electroactivity of carbon foam. Furthermore, Ni(NO$_3$)$_2$-activated carbon foam has higher capacitance than KOH-activated carbon foam. All carbon foams still keep a low capacitance and low rate capability level due to the overall low conductivity. Comparatively, Ni(NO$_3$)$_2$-activation is more effective approach to improve the graphitization degree and electrochemical capacitance performance of carbon foam as well. Ni(NO$_3$)$_2$-activation carbon foam becomes potential electrochemical energy storage electrode material.

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