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# Control on Pore Structure and Strength of Tubular Carbon Membrane by Introducing Additives

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**Abstract**

The pore structure and strength of carbon membrane are controlled by introducing different additives into raw materials. It is indicated that sesbania powder has an obvious effect on the pore structure of carbon membrane, and the obtained pores have the maximum diameter of 0.723 μm, average diameter of 0.319 μm and minimum diameter of 0.241 μm, respectively; whereas, medium temperature pitch has an obvious effect on the strength of carbon membrane, and increases the linear pressure and flexural strength to 13.68 N/mm and 19.80 MPa, respectively.

**Keywords:** Tabular carbon membrane, Petroleum coke, Additive, Pore size, Strength

## Preface

Carbon membrane, a new inorganic separation membrane that has developed since the mid-1980s, is composed of carbon materials. In recent years, with more and more research in this field, carbon membrane has been industrialized in France, and China has made a remarkable progress in its research and development (Ash R et al, 1967, p. 434-454; Ash R et al, 1968, p. 407-425; Wang, Tonghua et al, 2000, p. 6-11; Wang, Shuseng et al, 1995, p. 90-95; Wei, Wei et al, 2004, p. 5-8).

With petroleum coke as the main material, this paper has prepared a carbon membrane by altering the type and dose of the additives, and investigated the effects of additives on the performances of tabular carbon membrane.

## 1. Experiment

### *1.1 Raw materials*

Main raw material: petroleum coke, from Tianjin Tongxiang Carbon Factory. Its performance indexes are listed in table 1.

### *1.2 Preparation of carbon membrane*

Evenly blend petroleum coke of a given particle size with additive and binder at a certain ratio, knead in water until the mixture becomes a loose mud, and force it out at a certain pressure from an extruder to obtain a tabular original membrane of internal diameter 8.5 mm and wall thickness 1.45 mm. Dry the original membrane in air, and heat in nitrogen medium to obtain a tabular carbon membrane.

*1.3 Characterization of carbon membrane*

At room temperature, measure the diameter and diameter distribution of pore by the bubble method with isopropanol as wetting agent and nitrogen as permeation gas, then calculate the average diameter and diameter distribution of pore of carbon membrane according to the method reported by Wei et al (2004, p. 20-23).

The strength of tabular carbon membrane is characterized by the maximum linear pressure measured with KC-2A digital strength tester, and the maximum flexural strength measured with SK2 digital anti-rupture tester.

**2. Results and discussions**

*2.1 Particle size distribution and structure of petroleum coke*

The particle size distribution of petroleum coke after 2 hours of ball milling is shown in table 2. Figure 1 and figure 2 exhibit the SEM image and the particle size distribution of petroleum coke after 2 hours of ball milling, respectively. The average diameter of petroleum coke [D (v, 0.5)] is 46.49 μm. The SEM image indicates an obvious difference in the particle size; however, the large particles and small particles make up only a very small portion.

*2.2 Effect of additive on pore size of carbon membrane*

Figure 3 exhibits the SEM images of carbon membranes containing different additives.

From figure 3, we can see that the surface of additive-contained carbon membrane is smoother than that of additive-free carbon membrane; the carbon membranes containing phenolic resin or sesbania powder appear obvious pores on the surface; however, the carbon membranes containing iron powder or starch appear cracks, but no pores, on the surface; particularly, the pores on the medium temperature pitch-contained carbon membrane are smaller than those on the additive-free membrane, it's probably because the uncombined small particles inside the pore fall off and aggregate with the rise of pressure during measurement of pore size, in turn lead to the decrease of pore size.

Table 3 reveals the pore size of additive-contained carbon membrane. It indicates that except medium temperature pitch, the average and minimum pore sizes of the other four additive-contained membranes are larger than those of the additive-free membrane. For example, the average and minimum pore sizes of sesbania powder-contained membrane increase from 0.214 μm and 0.167 μm to 0.319 μm and 0.241 μm, respectively. However, those of medium temperature pitch-contained membrane decrease from 0.214 μm and 0.174 μm to 0.167 μm and 0.136 μm, respectively. As to the maximum pore size, the additive-contained membranes, except for iron powder (0.482 μm), are larger than the additive-free membrane. For example, the maximum pore sizes of carbon membranes containing phenolic resin or sesbania powder are up to 0.723 μm.

Figure 4 exhibits the pore size distribution of additive-contained carbon membranes. It demonstrates that the pore size of tabular carbon membrane is mainly in the range between the minimum and the average, which contributes about 70 percent of the total.

*2.3 Effect of additive on strength of carbon membrane*

2.3.1 Effect of additive on linear pressure of carbon membrane

Table 4 reveals the effect of additive on the linear pressure of carbon membrane. It demonstrates that the linear pressures of carbon membranes containing medium temperature pitch or starch are higher than that of original carbon membrane, and increase from previous 8.58 N to 13.68 N and 9.85 N, respectively. However, the linear pressures of carbon membranes containing iron powder, phenolic resin or sesbania powder decrease to 7.19 N, 7.66 N and 4.40 N, respectively. It is concluded that medium temperature pitch has the most positive effect on the increase of linear pressure of carbon membrane; the increase of linear pressure resulted from medium temperature pitch is almost two times of that from iron powder or phenolic resin, and three times of that from sesbania powder.

2.3.2 Effect of additive on flexural strength of carbon membrane

Table 5 reveals the effect of additive on the flexural strength of carbon membrane. It demonstrates that the flexural strength of carbon membranes containing iron powder or sesbania powder are lower than that of original carbon membrane, and decrease from previous 9.32 MPa to 7.87 MPa and 7.63 MPa, respectively. However, the flexural strength of carbon membranes containing medium temperature pitch, phenolic resin or starch increase from previous 9.32 MPa to 19.80 MPa, 10.19 MPa and 10.62 MPa, respectively. Therefore, it is still the medium temperature pitch that has the most positive effect on the increase of flexural strength of carbon membrane, which increases more than two times.

**3. Conclusion**

(1) Among the above-mentioned additives, sesbania powder has the most positive effect on the increase of pore size of the tabular carbon membrane, and causes the maximum, average and minimum pore sizes to increase from previous 0.482 μm, 0.214 μm and 0.167 μm to 0.723 μm, 0.319 μm and 0.241 μm, respectively. However, medium temperature

pitch causes the average and minimum pore sizes of carbon membrane to decrease to 0.174 μm and 0.136 μm, respectively.

(2) Among the above-mentioned additives, medium temperature pitch has the most positive effect on the increase of strength of the tabular carbon membrane, and causes the linear pressure and flexural strength to increase from previous 8.58 N and 9.32 MPa to 13.68 N and 19.80 MPa, respectively. However, the linear pressure and flexural strength of sesbania powder-contained carbon membrane decrease to 4.40 N and 7.63 MPa, respectively.

(3) Based on the above conclusions, we have tried to introduce the mixture of sesbania powder and medium temperature pitch into the tabular carbon membrane. As a result, both the pore size and the strength of the obtained carbon membrane increase.

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Table 1. The performance indexes of petroleum coke

| | |
|---|---|
| Total water content | 0.85% |
| Ash content | 0.44% |
| True density | 0.9399 g/cm$^3$ |
| Volatile content | 9.88% |
| Particle size | Adjustable according to the requirements of experiment |

Table 2. The particle size distribution of petroleum coke

| Ball-milling time | Average diameter (μm) | | |
|---|---|---|---|
| | D (v, 0.1) | D (v, 0.5) | D (v, 0.9) |
| 2 h | 35.70 | 46.69 | 61.55 |

Table 3. The pore size of additive-contained carbon membrane

| Additives | $r_{max}$ (μm) | $r_{ave}$ (μm) | $r_{min}$ (μm) |
|---|---|---|---|
| No additive | 0.482 | 0.214 | 0.167 |
| Iron powder | 0.482 | 0.299 | 0.207 |
| Medium temperature pitch | 0.543 | 0.174 | 0.136 |
| Phenolic resin | 0.723 | 0.282 | 0.241 |
| Sesbania powder | 0.723 | 0.319 | 0.241 |
| Starch | 0.543 | 0.299 | 0.197 |

Table 4. The effect of additive on the linear pressure of carbon membrane

| Additives | Strength (N) | | | Average strength (N) | Diameter (mm) | Average linear pressure (N) |
|---|---|---|---|---|---|---|
| No additive | 62.8 | 69.1 | 64.3 | 65.40 | 7.62 | 8.58 |
| Iron powder | 58.4 | 58.5 | 53.1 | 56.67 | 7.88 | 7.19 |
| Medium temperature pitch | 104.2 | 104.6 | 105.5 | 104.77 | 7.66 | 13.68 |
| Phenolic resin | 61.9 | 58.6 | 57.0 | 59.17 | 7.72 | 7.66 |
| Sesbania powder | 35.5 | 31.8 | 30.7 | 32.67 | 7.42 | 4.40 |
| Starch | 74.9 | 72.8 | 73.9 | 73.87 | 7.50 | 9.85 |

Table 5. The effect of additive on the flexural strength of carbon membrane

| Additives | Strength (N) | | | Average strength (N) | Diameter (mm) | Average flexural strength (MPa) |
|---|---|---|---|---|---|---|
| No additive | 67 | 74 | 72 | 71.00 | 7.62 | 9.32 |
| Iron powder | 62 | 54 | 70 | 62.00 | 7.88 | 7.87 |
| Medium temperature pitch | 125 | 152 | 178 | 151.67 | 7.66 | 19.80 |
| Phenolic resin | 70 | 72 | 94 | 78.67 | 7.72 | 10.19 |
| Sesbania powder | 54 | 62 | 54 | 32.67 | 7.42 | 7.63 |
| Starch | 82 | 82 | 75 | 79.67 | 7.50 | 10.62 |

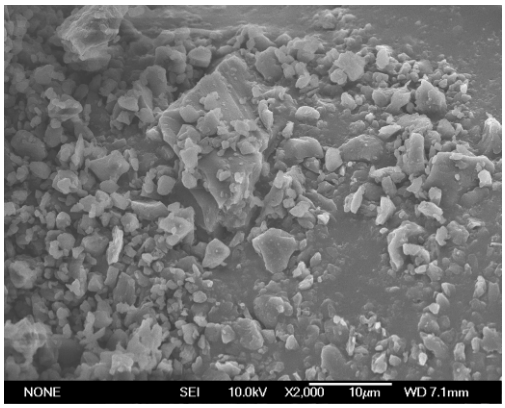



Figure 1. The SEM image of petroleum coke

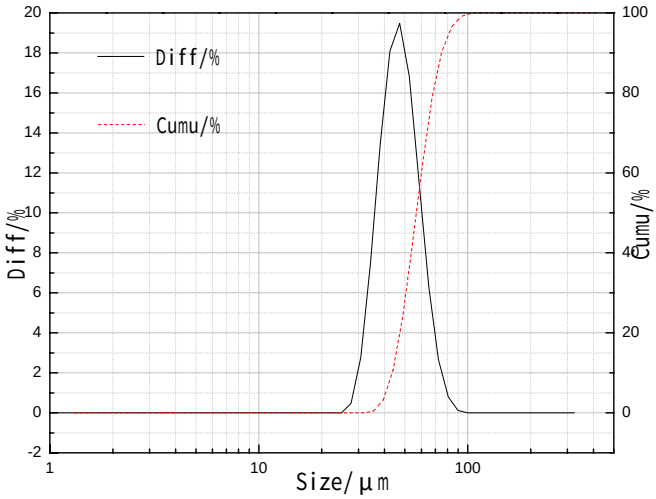
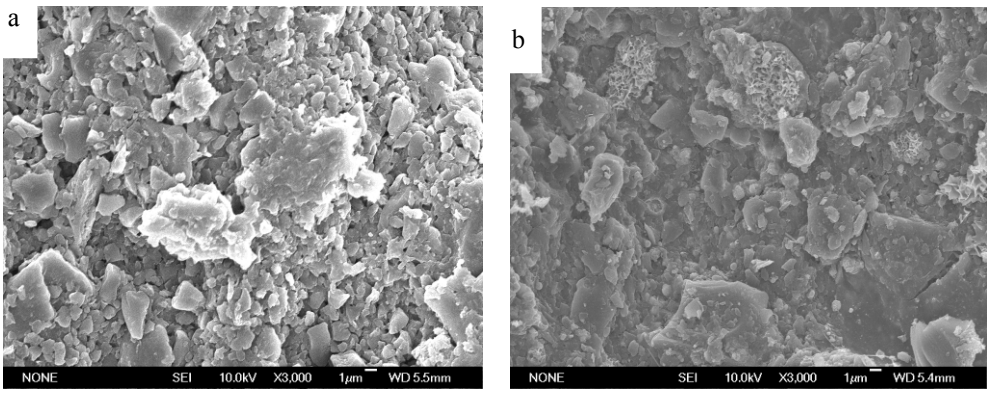
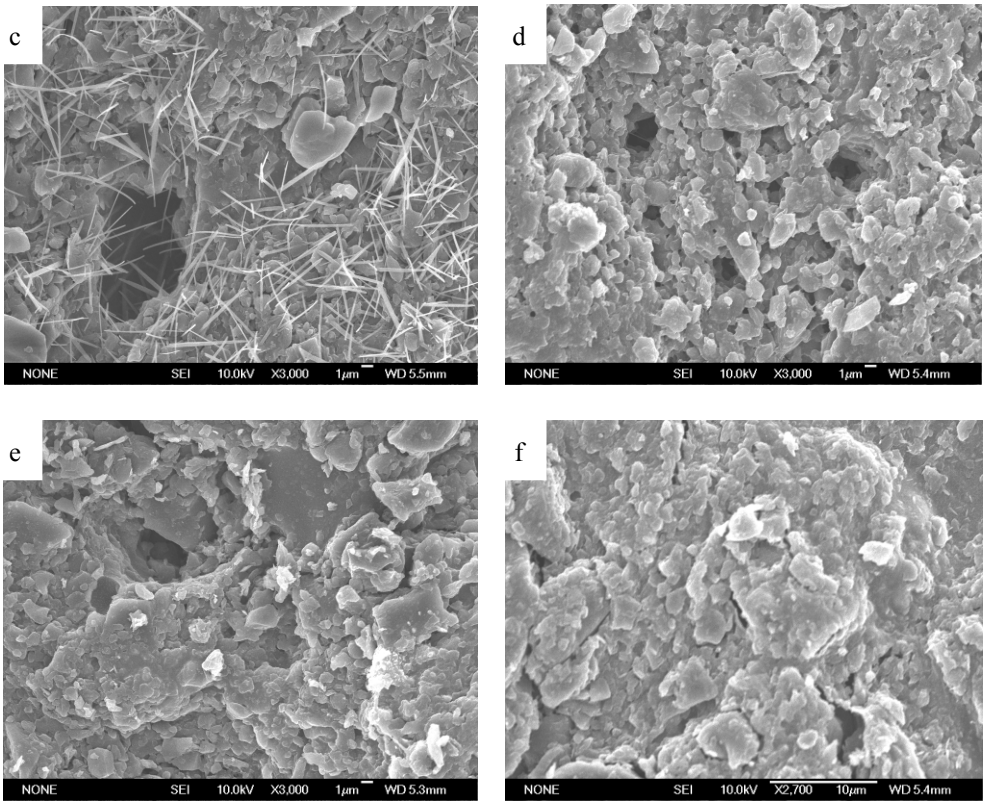



Figure 2. The particle size distribution of petroleum coke






a–no additive; b–iron powder; c–medium temperature pitch;
d–phenolic resin; e–sesbania powder; f–starch

Figure 3. The SEM images of carbon membranes containing different additives

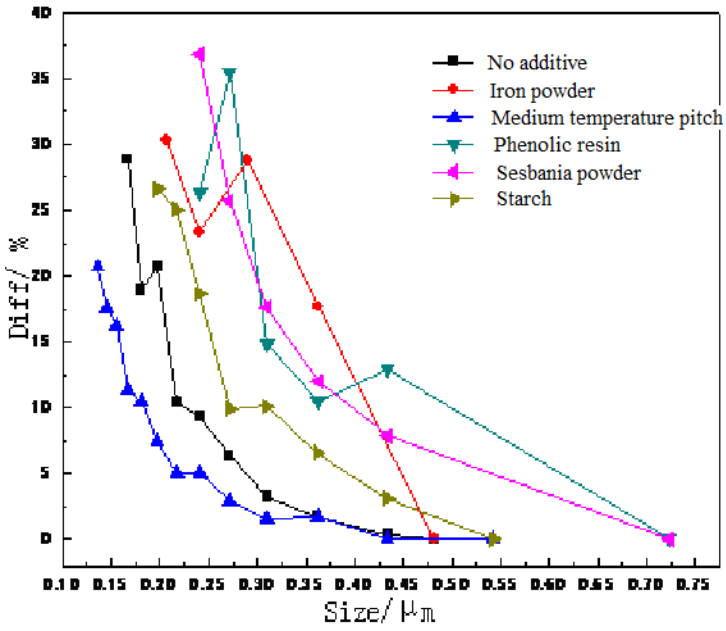



Figure 4. The pore size distribution of additive-contained carbon membranes