**Cellulose-developed Carbon Molecular Sieving Hollow Fiber Membranes for Gas Separation**

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**Highlights**

* Carbon hollow fiber membranes were developed from sustainable cellulose.
* 239 Barrer CO2 permeability and 186 CO2/CH4 selectivity were obtained.
* The membrane exhibited attractive performances in 10% CO2 -90% CH4 mixed gas.

**1. Introduction**

Membrane systems are expected to apply in different gas separations such as oxygen recovery from air, natural gas sweetening and CO2 capture from flue gas, thanks to the small footprint, low energy consumption, low capital and operating cost and process flexibility. Among different membrane materials, carbon molecular sieving (CMS) membrane is one of the most promising materials due to its high separation performance and good compatibility in some harsh operating situations (such as high pressures, high temperatures). Different polymers, like polyimide[1], cellulose acetate[2] and cellulose[3], have been employed as precursors for CMS membranes. Cellulose, as an inexhaustible and biorenewable material, could be a suitable precursor for large-scale producing CMS membranes. In this work, cellulose-based carbon hollow fiber membranes (CHFMs) were developed from cellulose/ionic liquid system.

**2. Methods**

Microcrystalline cellulose (MCC) was dissolved in 1-Ethyl-3-methylimidazolium acetate (EmimAc) and dimethyl sulfoxide (DMSO) solution at 50 °C with mechanical stirring in a glove box as a dope solution for spinning. Then, the defect-free cellulose hollow fiber precursors were fabricated by a dry-wet spinning, as shown in Figure 1a. The dried cellulose hollow fibers were carbonized in a tubular furnace by applying a specific carbonization protocol for preparing the CHFMs. Single gas permeation data were determined at room temperature with a feeding pressure of 2 bar. CO2/CH4 separation performance was evaluated by mixed gas tests (10% CO2/90% CH4) at different temperature and pressures.

**3. Results and discussion**

XRD and FTIR characterization confirmed that a crystalline structure transition from cellulose I (MCC) to cellulose II (cellulose hollow fibers) occurred during the cellulose dissolution and spinning process. Additionally, due to the transition of crystalline structure, the cellulose hollow fibers retained a higher carbon yield of 22.9% than the MCC after carbonization[3]. Single gas (e.g., CO2, O2, N2, and CH4) permeation testing indicated that the molecular sieving mechanism is dominating the gas transport through the CHFMs. In addition, the CO2 permeability and CO2/CH4 selectivity of 239 Barrer and 186 were obtained in the single gas permeation, which presents a high separation performance cross the 2008 Robeson Upper Bound as shown in the Figure 1b. Moreover, it maintains attractive CO2/CH4 separation performances in 10% CO2 -90% CH4 mixed gas permeation testing at increasing temperatures and raising pressures.



**Figure 1.** Schematic diagram of the spinning process, b) Gas permeation results for CO2/CH4 in prepared CHFM and comparison with the 2008 upper bound plot, c) Cross-sectional SEM images of a fabricated CHFM.

**4. Conclusions**

This study provides a suitable way to directly fabricate CHFMs using cellulose hollow fiber precursors spun from cellulose/(EmimAc + DMSO)/H2O ternary system. The developed novel CHFMs shows attractive separation performance especially CO2 removal from high pressure natural gas, as well as provides a new way for fabricating CMS membranes from sustainable and green materials.

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