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Hollow-fiber membrane trapper for sulfur-free hydrogen source

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A polyimide hollow-fiber membrane trapper with adsorption channels that enables sulfur to be removed from hydrocarbon fuels could provide a sulfur-free hydrogen source for fuel-cell applications.

Currently, hydrogen is the cleanest source of sustainable energy. The question of how hydrogen can be used safely and efficiently, however, persists. Among the currently available options, fuel cells represent a promising way for the efficient and reliable use of hydrogen energy.[1,2] Hydrocarbon fuel, which can be converted to hydrogen for fuel-cell applications by a steam reforming process,[3] is an ideal hydrogen source for automotive fuel cells. However, to prevent the catalysts in fuel-cell systems from becoming poisoned by sulfur-containing substances and to reduce sulfur-dioxide emissions, it is highly desirable that the hydrocarbon fuel be sulfur-free.

Removing sulfur from liquid hydrocarbon fuels is, however, a challenging problem that conventional processes struggle with.[4] Sulfur-removal methods that have emerged in recent years include hydrodesulfurization, oxidation, extraction, biodesulfurization, and adsorption.[5] However, the sulfur-removal efficiency and cost of these processes are unsatisfactory.

In our work,[6] we thus seek to develop a method for the generation of sulfur-free fuel (i.e., that can be used as a hydrogen source without the creation of poisonous byproducts). To this end, we have proposed a hollow-fiber membrane trapper for the removal of sulfur from fuel. In our device, when the fuel feed—consisting of hydrocarbons and sulfur compounds—passes through the membrane (in which zeolites are enabling materials), the sulfur compounds are trapped. Thus, our hollow-fiber membrane trapper outputs a sulfur-free hydrogen source for fuel-cell applications (see Figure 1). Our device has a number of advantages, including its large surface area per unit volume, low separation module volume (due to compact fiber assembly), low cost of operation, and ease of on-board implementation.

To develop our sulfur-trapping device, we proposed a new strategy for the preparation of high-performance polyimide (PI) hollow-fiber membranes. In our approach, we tuned the imidization behavior of the PI. We used pyromellitic dianhydride and 4, 4′-diaminodiphenyl ether

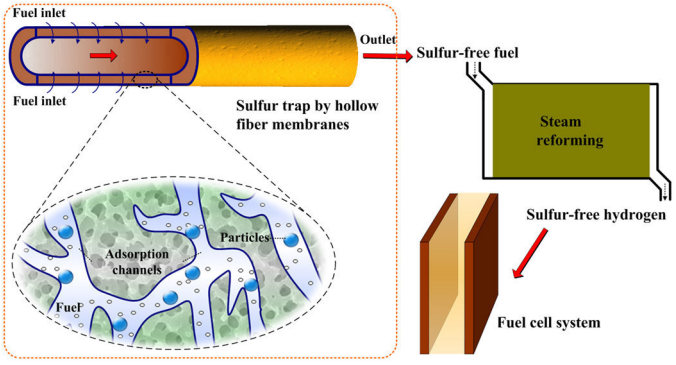

Figure 1. *Schematic diagram of our hollow-fiber membrane trapper for the creation of a sulfur-free hydrogen source. The hydrocarbon fuel, containing sulfur compounds, flows through the microporous adsorption channels within a membrane of the device. Here, silver-doped Y-type zeolite particles—embedded into the membranes as functional fillers—adsorb the sulfur, thus trapping it within the membrane. The outlet sulfur-free hydrocarbon fuel can then be subjected to a steam-reforming process, enabling the creation of sulfur-free hydrogen for use in a fuel-cell stack.*

as monomers to prepare the nascent polyamide acid (PAA) solution. Then, during the imidization process, we treated the nascent PAA membrane by heating stepwise at 100°C (1h), 150°C (1h), 200°C (1h), 250°C (1h), and 300°C (1h), successively. By thus controlling the imidization behavior, we were able to fabricate PI membranes with good heat resistance, solvent resistance, and mechanical strength. To introduce the sulfur-trapping functionality, we embedded silver-doped Y-type zeolite (AgY) particles into the membranes as functional fillers. Silver ions on the surface of the AgY zeolites combine with thiophenic sulfur via π-bonds. When the hydrocarbon fuel passes through the membranes within the device, sulfur adsorption occurs (as a result of the strong π-complexation binding force) and the outlet fuel is sulfur-free.

Figure 2 shows the excellent hollow structure and self-supported feed passageway that we obtained in the membranes using our fabrication approach. The outer diameter of the hollow-fiber membranes is

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about 1150μm, and each membrane is separated by a wall of $\sim$250μm (the polyimide matrix). The magnified images show that the membrane matrix has abundant pores (i.e., 3D working channels and microenvironments). The large number of channels provide paths for the feed flow, thus enabling a larger volume of fuel to be processed, which is key for high working efficiency.

The practical sulfur removal performance of our device is presented in Figure 3, as compared with a hollow-fiber device without zeolites. During treatment, the fuel permeates through the membrane in a continuous manner. The breakthrough point of the raw PI membranes appears first—see Figure 3(a)—which shows that the sulfur compounds are not bound, since there are no zeolite particles in the membrane matrix. In contrast, Figure 3(b–d) shows the breakthrough curves of our AgY-functionalized polyimide hollow-fiber membrane trappers (with two, four, and eight fibers). In all cases, the inlet feed can be desulfurized to below 0.1mg L^{-1}, which indicates that sulfur is binding effectively to the fibers.

In summary, we have designed and manufactured a hollow-fiber membrane trapper with multiple architectures (i.e., a self-supported passageway, adsorption channels, and binding sites) that enable organic molecules to be bound to AgY zeolites within the device. Our trapper thus allows the efficient removal of sulfur compounds from hydrocarbon fuels, presenting a potential alternative for the production of a sulfur-free hydrogen source for fuel-cell applications. We are now working on developing a membrane trapper with more hollow-fiber membranes to accelerate the scaled-up application of our device.

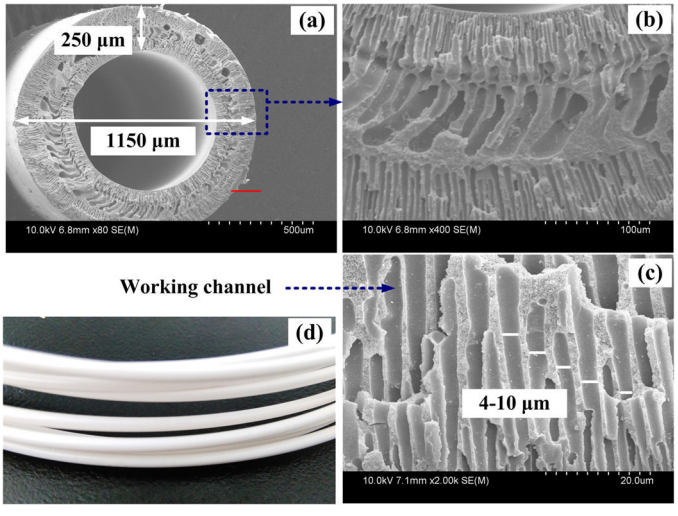

Figure 2. *Scanning electron microscope images showing the cross-section morphology of the polyimide hollow-fiber membranes at magnifications of (a) 80, (b) 400, and (c) 2000×. (d) A photograph showing prepared hollow-fiber membranes.*

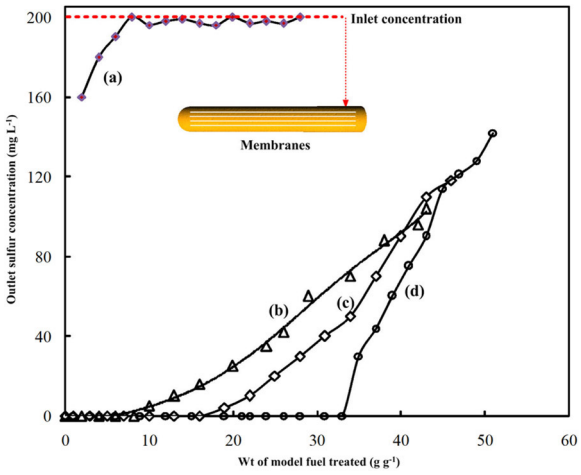

Figure 3. *Typical breakthrough curves of the hollow-fiber membrane trapper, with and without zeolites. (a) Two fibers with raw polyimide architecture (i.e., without zeolites). (b–d) Two, four, and eight fibers (with a zeolitic polyimide architecture), respectively.*

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