



# Fabrication of Silicon Carbide Ultrafiltration Membranes via Low-Pressure Chemical Vapor Deposition for Oil-in-Water Emulsion Separation

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## Introduction

SiC UF membranes are well-known for their hydrophilic properties, allowing them to achieve notable permeate flux rates and find wide applications. Their ability to consistently produce high-quality permeate, regardless of fluctuations in feed water composition, highlights their reliability under dynamic operational conditions. Additionally, these membranes exhibit exceptional stability against varying pressure differentials and pH gradients, ensuring their effectiveness over prolonged operational periods [1,2].

Traditional fabrication methods, such as the sol-gel technique, require numerous coating procedures and energy-intensive sintering steps, which contribute to manufacturing complexities [3]. In contrast, Low-Pressure Chemical Vapor Deposition (LPCVD) offers a more streamlined production pathway by eliminating the need for sintering. We aimed to potentially reduce the fabrication cost of commercial SiC membranes by preparing them at lower temperatures and using lower-cost supports like Al<sub>2</sub>O<sub>3</sub>. Specifically, the SiC-deposited Al<sub>2</sub>O<sub>3</sub> membranes were fabricated through LPCVD for oil-water separation.

Fouling stands as the primary obstacle in membrane-based separation applications. Although commercial SiC membranes are known for their low fouling characteristic, the fouling properties of these newly developed SiC-deposited ceramic membranes could be affected by factors such as the surface properties of the membranes and support, as well as characteristics of the feed and operational conditions. Our research efforts are specifically aimed at delving deeper into the performance of the newly developed SiC-deposited membranes by considering the deposition parameters of LPCVD and the properties of the ceramic membranes, such as surface charge, hydrophilicity, and pore size of SiC-coated UF membranes on the phenomenon of membrane fouling. Moreover, filtration mode and operational parameters and the long-term impact of the chemical cleaning applications are investigated.

## Methodology

The experiments employed commercial single-channel tubular Al<sub>2</sub>O<sub>3</sub> ceramic UF membranes as substrates for LPCVD of SiC. The membranes consisted of a 600 nm macroporous Al<sub>2</sub>O<sub>3</sub> support layer and a 100 nm Al<sub>2</sub>O<sub>3</sub> selective layer, specified by the manufacturer (CoorsTek, the Netherlands). The Al<sub>2</sub>O<sub>3</sub> membranes chosen for LPCVD exhibited similar permeabilities, ranging from 360 to 380 Lm<sup>-2</sup>h<sup>-1</sup>bar<sup>-1</sup>. Dichlorosilane (SiH<sub>2</sub>Cl<sub>2</sub>) and acetylene (C<sub>2</sub>H<sub>2</sub>) served as precursors for depositing SiC layers on Al<sub>2</sub>O<sub>3</sub> membranes. The deposition took place at temperatures of 750°C and 860°C, yielding polycrystalline SiC. Deposition times varied, i.e., 10, 15, 20, and 25 minutes were labeled H10, H15, H20, and H25, respectively.

Soybean oil, surfactants (sodium dodecyl sulfate, Span 80, Tween 80, hexadecyltrimethylammonium bromide), calcium chloride, and sodium chloride (Sigma-Aldrich, the Netherlands) were used to prepare oil-in-water microemulsions. Hydrochloric acid and sodium hydroxide were utilized for pH adjustment, while citric acid was employed for membrane cleaning. For the long-term chemical cleaning experiments, 12.5% sodium hypochlorite (NaClO) was obtained commercially (Sigma-Aldrich, the Netherlands). A 5% NaClO solution was then prepared by diluting the 12.5% stock solution while maintaining a pH of 12. All solutions were prepared using deionized water.



## Results and Discussion

Fig. 1 illustrates the TEM observation of the uniform SiC layer thickness on the Al<sub>2</sub>O<sub>3</sub> particle surface for the H20 membrane, measuring 18 ± 1 nm. The interface between the Al<sub>2</sub>O<sub>3</sub> particles and the SiC coating layer is prominently visible. The contrast in fouling tendencies between the Al<sub>2</sub>O<sub>3</sub> membrane (H0) and the four SiC-Al<sub>2</sub>O<sub>3</sub> membranes (H10, H15, H20, H25) during microemulsion filtration, all under a steady flux of 80 Lm<sup>-2</sup>h<sup>-1</sup> is displayed in (c). The H0 membrane exhibited the highest propensity for fouling. Nonetheless, it's noteworthy that the normalized TMP curves displayed resemblances among all membranes during the initial cycles. Subsequent to the initial cycle, the backwash proved effective, suggesting minimal irreversible fouling. However, as the number of filtration cycles increased, irreversible fouling gradually built up, leading to a quicker rise in TMP [4].

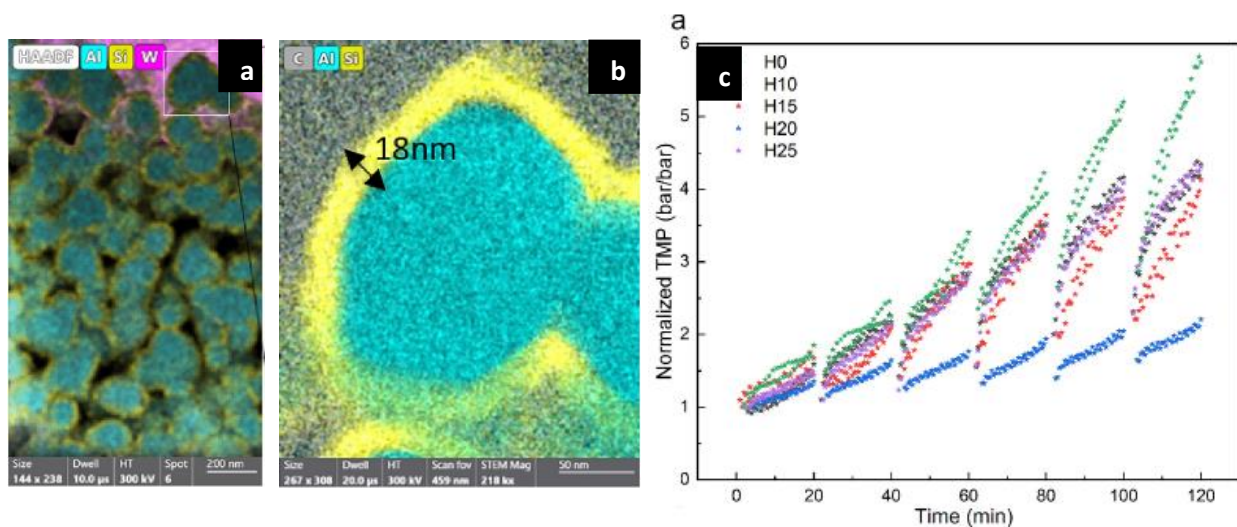


Fig. 1. (a) Net intensity maps of the cross-section of the H20 membrane obtained through STEM-EDX, (b) corresponding net intensity maps acquired via EDX depicting a SiC-coated alumina particle near the top, (c) the normalized TMP of the H0, the H10, the H15, the H20, and the H25 membrane for the filtration of microemulsion (500 mg/ L soybean oil with 50 mg/ L Span 80 and 50 mg/L Tween 80).

Our investigation revealed that the SiC-coated membranes, with varying deposition times, showed lower reversible fouling compared to pristine Al<sub>2</sub>O<sub>3</sub> membranes due to their more hydrophilic and negatively charged surface. The 20-minute SiC-coated membranes (H20) had the least reversible fouling, especially at higher pH levels, thanks to increased electrostatic repulsion. When filtering microemulsions stabilized with Span 80 and Tween 80/SDS, the SiC-coated Al<sub>2</sub>O<sub>3</sub> membranes outperformed the Al<sub>2</sub>O<sub>3</sub> membranes due to stronger electrostatic repulsion. However, for positively charged (CTAB-stabilized) microemulsions, the SiC-coated Al<sub>2</sub>O<sub>3</sub> membranes exhibited higher fouling, attributed to electrostatic interactions favoring attraction to the SiC-coated surface over the Al<sub>2</sub>O<sub>3</sub> membrane.

## References

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