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Amirhossein Droudian, Mahesh Lokesh, Seul Ki Youn, Hyung Gyu Park



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### ACCEPTED MANUSCRIPT

## Gas concentration polarization and transport mechanism transition near thin polymeric membranes

Amirhossein Droudian, Mahesh Lokesh, Seul Ki Youn, Hyung Gyu Park\*

Eidgenössische Technische Hochschule (ETH) Zürich, Zürich CH-8092, Switzerland

\* E-mail: parkh@ethz.ch

### Abstract

Advanced material engineering gave rise to cutting-edge characteristics of sustainable separation by fabrication of high permeable and gas selective membranes. A developed fabrication process of ultrathin polymers with controlled microporosity helps understanding pore size dependent transport and performance of thin membranes with constant pore number from continuum to free-molecular to solution-diffusion regimes. Fabrication of polymer layers with controlled pore size was realized by stage-wise physical vapor deposition of dimethylsiloxane oligomers onto porous alumina support. Single process step forms high permeable porous films of 13 nm in thickness. Further deposition allows fabrication of up to 120 nm nanopore-free uniform layers with defined gas selectivity. Permeances as high as 1300 GPU through gas-selective, uniform dense films results in gas concentration polarization and apparent selectivity loss, so far only observed for porous materials. Our fabrication process enabled observation of two unseen separation regimes in the transport physics transition from (nano) channel flow to solution diffusion supported by mathematical model derived for transport through ultra-thin membranes.

**Keywords**: Transition flow, Concentration polarization, Vapor deposition, Porous polymer, Ultra-thin membrane

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