308a Non-Destructive, Quantitative Characterization of Microporous Thin Film Polycrystallinity for Elucidating Structure-Properties Relations

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Rational design of new microporous films and fine tailoring of current materials demands understanding of the structure-properties relations governing molecular transport through realistic membranes. The crystallinity of microporous materials at short length scales (i.e., single crystal level) that deems zeolite membranes attractive for high-resolution gas separations, ultimately gives rise to a complex permeation landscape (i.e., grains separated by grain boundaries) at the device level. While the current modeling paradigm focuses almost exclusively at the single crystal level, a persistent challenge has been the prediction of permeation performance for real membranes that exhibit diffusion anomalies (e.g., unexpectedly low selectivities and deviations from single-crystal theory). Such anomalies in membrane permeation are often tacitly attributed to membrane polycrystallinity. Fluorescence confocal optical microscopy (FCOM) studies [1, 2] have revealed the substantial extent of this polycrystallinity in zeolite membranes, but quantitative interpretation of FCOM images has remained relatively elusive. Recent gradient kinetic Monte Carlo simulations [3] of diffusion through model polycrystalline membranes (e.g., NaX) have revealed how even moderate polycrystallinity can reduce the flux by nearly an order of a magnitude. This underscores the need for more quantitative characterization of microporous membrane polycrystallinity.

In this talk, we develop new protocols for pushing the limits of FCOM as a quantitative, non-destructive characterization technique. Molecular mechanics calculations are first carried out to rationally screen preferential dye adsorption based upon steric compatibility and energetic interactions with zeolitic (e.g., silicalite-1 and NaX) pores and dominant crystal surfaces [4]. FCOM imaging of novel standards with nanometer scale features are employed for calibrating feature size and density with fluorescence intensity and its spatial decay. Such protocols, in conjunction with correlative FCOM and SEM studies [2] using separate and sequential adsorption of dyes, quantify the size and distribution of polycrystalline features, and link them directly to the crystal morphology.

Here, we apply the new FCOM protocols to study both purely siliceous silicalite-1 and, for the first time, NaX zeolite membranes. In particular, we explain variations in separation performance associated with membrane orientation (in the case of silicalite-1) and growth conditions based upon membrane polycrystallinity. Ultimately, we illustrate the capabilities of more quantitative, non-destructive FCOM imaging for elucidating structure-properties relations for polycrystalline zeolite membranes.

References:

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3. Snyder, M.A. and D.G. Vlachos, in preparation, (2005).

4. Diaz, I., et al., Chemistry of Materials, 16(2004), 5226-5232.