Abstract:

Solar fuels generators operate under non-steady state conditions, however the permeability of the membranes used in them is represented using solubility and diffusivities obtained as fitting parameters from steady state measurements. Our work examines fundamental material properties and processes in order to build a model of membrane permeation from physical chemistry that is realistic, valid at all times, and predictive for both steady state and non-steady state conditions. The multiscale reaction – diffusion scheme is described, and we summarize recent results from 3 recent studies that investigate fundamental aspects of time-dependent permeation. The studies are of CO₂ and N₂ permeation through rubbery and glassy polymers, which illustrates the influence of the rigidity of the matrix when the solutes only interact weakly, and of methanol through Nafion, which examines a system that characterized by strong interactions. Permeation in all 3 systems is characterized by real-time membrane polymetric responses as the permeants are absorbed. This indicates that simple descriptions of membranes used in solar fuels generator models may not be sufficiently detailed to predict performance during the diurnal cycle, and that new studies of time-dependent polymer-solute interactions would be valuable.

Introduction

Permeability theory

for dense polymers is given by the solution-diffusion model.

Permeability = Diffusivity \times Solubility

To be able to optimize a solar fuels conversion system, it is crucial to understand the details of counter-propagating ionic and molecular fluxes through a selectively permeable membrane under fluctuating solar illumination. Membrane permeation theory describes transport of single solutes through membranes and is not extendable to this level of complexity. Using 3 prototypical cases, we have established stochastic multiscale reaction-diffusion simulations as an alternative method to characterize membrane properties under realistic conditions. The models are fully validated, physically based and predictive, and extendable to the more complex, real systems.

Results, Highlights, and Accomplishments

Integrated simulation-experimental studies

Gas permeation

Liquid sorption

General multiscale reaction-diffusion scheme

Gas-polymer Interface

Collision frequency from kinetic gas theory.

Sticking coefficient from molecular dynamics.

Liquid-polymer Interface

Sorption frequency from solution phase diffusion and Smoluchowski equation

Gas-polymer sticking

Interfaceal processes are assumed to be non-rate-limiting in permeability theory, however they cannot be neglected in the multiscale model. Measurements of gas-polymer sticking probabilities are not available so are calculated. Typical values are in the range of 0.5 – gas uptake by rubbers and glasses is facile.

Polymer-solute interactions influence solubility and diffusivity in real time

General finding: The maximum solute concentration in a polymer membrane is proportional to its upstream concentration (Henry’s Law), however the time required to reach this maximum depends on the polymer’s structure and how strongly the solute interacts with the polymer. Therefore, if an upstream solute concentration varies with time, its permeability also varies on a timescale that depends on the specific polymer-solute chemical interactions. Even N₂ is not inert enough in the polymer environment.

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