

# Permeation through polymeric membranes far from steady state

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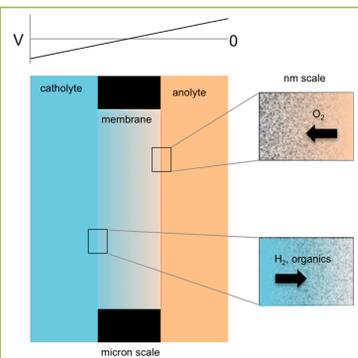
Technology, Pasadena, CA, 91125



## 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 selected results from 3 recent studies that investigate fundamental aspects of time-dependent permeation. The studies are of CO<sub>2</sub> and N<sub>2</sub> permeation through rubbery and glassy polymers, which examines 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 polymeric matrix 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



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.

## Papers

(1) Predictive simulation of non-steady-state transport of gases through rubbery polymer membranes, *Polymer* (2018) DOI: 10.1016/j.polymer.2017.11.055

(2) Swelling and diffusion during methanol sorption into hydrated Nafion, *J. Phys. Chem. B* (2018), DOI: 10.1021/acs.jpcc.8b03169

(3) Permeation of CO<sub>2</sub> and N<sub>2</sub> Through Glassy Poly(Dimethyl Phenylene Oxide) (PPO) under Steady and Pre-Steady State Conditions, *J. Polym. Sci.*, (2020) DOI: 10.1002/pol.20200053 (cover article)

## Acknowledgments

We are grateful to Dan Miller (LBNL) and Bill Hinsberg (Columbia Hill Technical Consulting) for their advice and assistance throughout this work. This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993. Funding from Bosch Energy Research Network, Grant Number: 07.23.CS.15; National Science Foundation Award Number: DGE 1106400.

## Results, Highlights, and Accomplishments

### Permeability theory

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

$$\text{Permeability} = \text{Diffusivity} \times \text{Solubility}$$

Diffusivity,  $D$ , and solubility,  $S$ , are obtained at steady state. Processes at the interface are assumed to be non-rate-limiting.

Permeability  $P$  is calculated from a fit to time-dependent data for a selected system,  $S$  is measured separately using a fully equilibrated membrane, and  $D$  is obtained from  $P/S$ .

### General multiscale reaction-diffusion scheme

Liquid-polymer Interface

Sorption frequency from solution phase diffusion and Smoluchowski equation

Gas-polymer Interface

Collision frequency from kinetic gas theory.

Sticking coefficient from molecular dynamics.

Diffusion and solubility from experimental data.

Gas/liquid-polymer Interface

Desorption rate constant from Arrhenius equation.

area of flux =  $\sim 1 \text{ cm}^2$

thickness  $\sim 100 \mu\text{m}$

gas collector volume  $\sim 100 \text{ cm}^3$

interface thickness = 1 nm

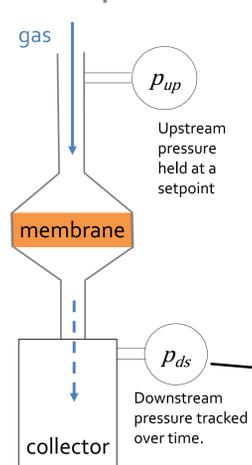
The system is a linear array of coupled compartments. Permeant concentration, polymer properties, diffusion, solubility and thickness can all vary with time.

Bunker et al. *Combust. Flame.* 23 (1974) 373. Gillespie. *J. Comput. Phys.* 22(1976) 403.

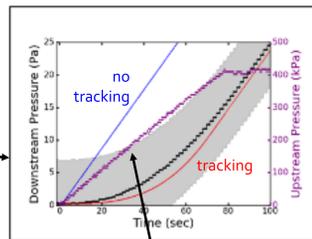
Kineticscope W. D. Hinsberg and F. A. Houle, <http://hinsberg.net/kineticscope/>

### Integrated simulation-experimental studies

Gas permeation

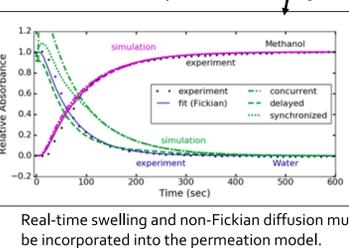
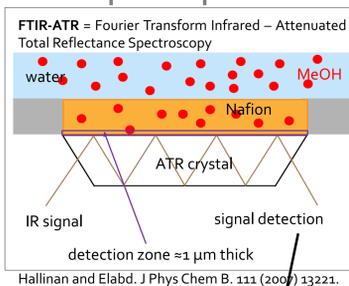


Time-dependent permeation data are calculated from the simulations, and directly compared to experimental measurements to validate the reaction-diffusion model.

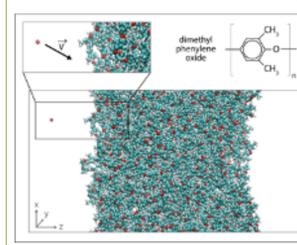


The concentration of CO<sub>2</sub> and N<sub>2</sub> in rubbery and glassy polymers during permeation tracks time-dependent  $p_{up}$ .

Liquid sorption

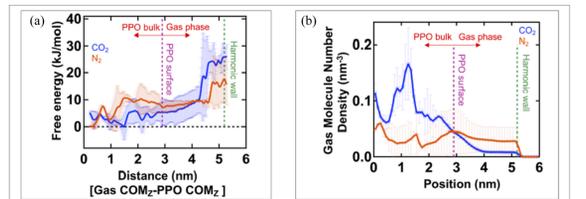


### Gas-polymer sticking



Sticking is determined from MD simulations, free energies are determined using molecular metadynamics.

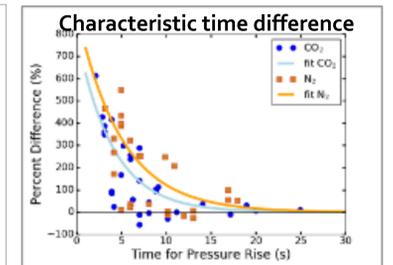
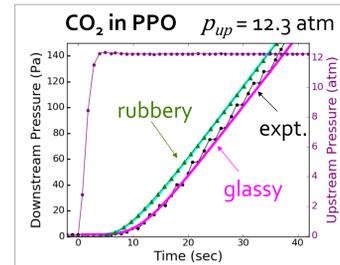
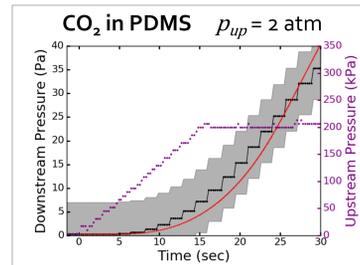
Interfacial processes are assumed to be non-rate-limiting in permeability theory, however they cannot be neglected in the multiscale model. Measurements of gas-polymer sticking probabilities are not available so are calculated. Typical values are in the range of 0.5 – gas uptake by rubbers and glasses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



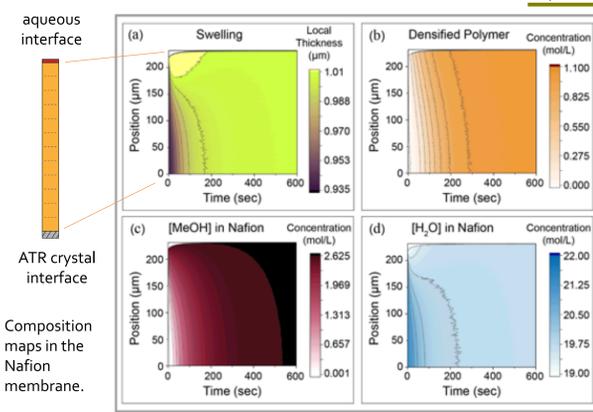
CO<sub>2</sub> and N<sub>2</sub> differ in their free energy in PPO relative to the gas phase. CO<sub>2</sub> has a higher affinity for the polymer bulk, consistent with higher diffusivity despite its larger size.

### Polymer-solute interactions influence solubility and diffusivity in real time

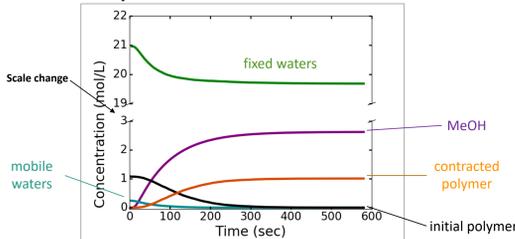
**General finding:** The maximum solute concentration in a polymer membrane is proportional to its upstream concentration (Henry's Law), however the time required to reach this maximum depends on the polymer's structure and how strongly the solute interacts with the polymer. Therefore, if an upstream solute concentration varies with time, its permeability also varies on a timescale that depends on the specific polymer-solute chemical interactions. Even N<sub>2</sub> is not inert enough in the polymer environment.



The detailed upstream pressure rise must be included in the model to correctly reproduce the downstream pressure for both rubbery and glassy polymers. In rubbery polymers the polymer response (sorbed gas concentration) is instantaneous on the timescale of the measurement, however in glasses there is a delay that is pressure rise time dependent. The delay is minimal when the pressure rise time is less than 15s, providing a characteristic PPO response time to the permeant.



Composition at the ATR interface



The simulations can only reproduce experiment if the model includes a continually increasing Nafion membrane thickness and a concurrent densification of the polymer matrix. Thickness vs time maps show that there is an initial high degree of swelling with little overall thickness change at the membrane surface, followed by uniform swelling as the methanol permeates. This may result in compressive strain that relaxes as the polymer densifies. Local solute concentrations vary dynamically.

The simulations capture the full evolution of the membrane in time. When can the simple assumption that Fickian diffusion controls local solute concentration  $C$  be made, and permeability is accurately predicted by solution-diffusion?

$$\frac{dC}{dt} = AD_m \nabla C$$

when the membrane's surface area does not change

when solubility is constant

when the diffusion coefficient is completely independent of changes in polymer structure and the presence of other solutes

when the membrane does not swell or shrink