

A New Technique for the Measurement of CO₂ Diffusion in Thin Polymer Films

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The adsorption and diffusion properties of CO₂ in solid sorbents are of great interest for gas separation and carbon capture. Much work has focused on the development of new physical sorbents (zeolites, carbons, metal organic frameworks) and chemical sorbents (amine-functionalized solids) for these applications. In most cases, these materials are rigid inorganic frameworks or substrates that retain their structure upon gas adsorption. Polymeric sorbents are also of interest for applications in gas separation as both bulk solids and thin film adsorbents or membranes. Polymers, however, offer some unique characterization challenges, due to their well-known tendency to undergo rheological changes resulting from cumulative sorbent-sorbate interactions. Polymeric sorbents can also behave quite differently in bulk and thin films due to heat effects and R_g (radius of gyration) compared to effective film thickness. Parameters of interest for gas adsorption may include sorption capacity, swelling, and diffusivity. Whereas conventional volumetric and gravimetric techniques can measure equilibrium uptake capacities with high accuracy, the measurement of rapid diffusion rates is difficult. Quartz Crystal Microbalance with Dissipation (QCM-D, Biolin Scientific) has proven to be a very useful method for *simultaneously* measuring capacity, and diffusivity in thin polymer films.

In this poster, we describe a QCM-D/gas manifold system that can be used to measure adsorption isotherms of CO₂ in several polymer thin films exhibiting variable degrees of rigidity. In addition we also present the results of CO₂ diffusion constant measurements in polydimethylsiloxane, polystyrene, polyallyl amine and PIM-1 (polymer of intrinsic microporosity) thin films. By comparing these gravimetric based diffusion constants with literature values and in-house measurements, we have determined that the adsorption isotherms obtained by QCM-D match very well with volumetric measurements for rapidly equilibrating systems. We have also found that upper limits exist in the ability of QCM-D to measure rapid diffusion rates. These limits are imposed by the polymer film thickness and floppiness resulting in long resonance decay times, and the minimum time interval that can be measured by the QCM-D system.