

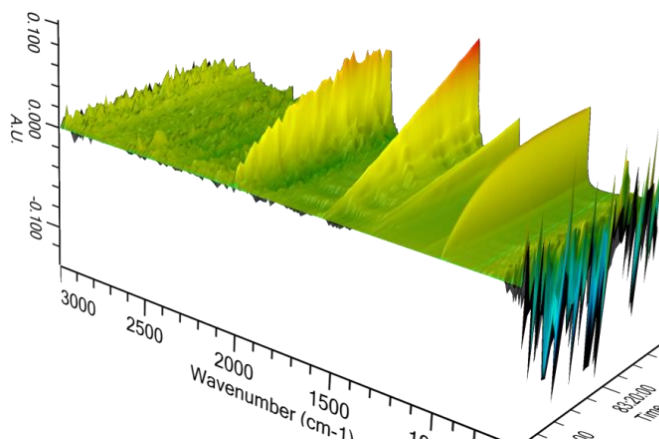
MONITORING MULTICOMPONENT TRANSPORT USING IN-SITU FTIR SPECTROSCOPY

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The permeation of aqueous solutes through membranes is of critical importance in many applications, including fuel cells and solar-driven electrochemical cells. In these devices, the undesirable crossover of small organics through a membrane separating halves of the electrochemical cell reduces device efficiency. The techniques traditionally used to measure organic permeation through a membrane, such as gas chromatography, typically require aliquot sampling and are limited by the chromatograph's capability to resolve analytes and water. In-situ FTIR spectroscopy, is capable of quantitative measurement of organic permeation through membranes in a simple diffusion cell without aliquot sampling. Furthermore, in-situ FTIR is capable of the simultaneous measurement of multicomponent permeation, provided that each analyte has a distinct IR signature.

Within the context of devices for solar fuel production, membranes are desired that facilitate the ion transport necessary to feed the electrochemical reactions while meeting various additional selectivity and permeability demands. For example, in an artificial photosynthesis device, water is oxidized to O_2 and CO_2 is reduced to a liquid transportation fuel, such as methanol or ethanol. However, the catalysts responsible for CO_2 reduction are non-specific, producing a library of small molecule products. Here, we demonstrate the use of in-situ FTIR spectroscopy to quantitatively determine the concentration of single and multicomponent mixtures of various CO_2 reduction products including methanol, formate and acetate. We then apply this methodology to the in-situ monitoring of the permeation of single and multicomponent mixtures across commercially available membranes, such as Nafion 117 and Selemion AMV, using a diffusion cell. Membrane permeabilities are extracted from time-resolved half-cell concentration data using free volume models. Membrane permeabilities and selectivities calculated from the single component permeation experiments are compared to those calculated for solutes in multicomponent permeation experiments. In some instances, the membrane permeability to an organic solute changes substantially, sometimes by orders of magnitude, when co-solutes are present. These results and their implications will be discussed in the context of next-generation energy devices.



Evolution of IR absorbance peaks corresponding to organic solute permeation through an ion exchange membrane.