

Microscopic Measurement of Diffusion

The phenomenon of diffusion has been known for centuries. For example, the ancients who dyed fabrics certainly noticed the leading edge of their turquoise dye propagating through their cotton cloth, and biologists have long been aware of osmosis through various membranes. With our century's advances in engineered materials, scientists and engineers are now able to design diffusive layers to provide controlled rates and selectivity of diffusion. There are a number of applications of engineered diffusion in current technology. Some are medical: drug patches allowing sustained slow release of a pharmaceutical, and membranes are used in dialysis and various laboratory separation procedures. Similar to the use of drug patches is the agricultural use of slow release nodules to provide sustained fertilisation of soil. Industrial production of chemicals and foodstuffs often depend on separations with various membranes. Other applications are of a less organic nature, as in the separation of gases by selective diffusion through membranes, and of ions through a solid, which might be part of a battery or other electronic device. Sometimes, diffusion is an undesirable phenomenon, as when we wish to store gases dissolved in a solid, and they can diffuse out over time, or when diffusion of oxygen into a semiconductor crystal can depreciate the performance of an electronic device.

In order to engineer materials with controlled diffusive properties, we need to be able to measure the diffusive process *in situ*. If we want to measure diffusion on a microscopic scale, there are not many analytical tools available. Ideally, we would like a technique that provides molecular information with resolution on a microscopic scale, that is non destructive of the samples, and can be set up and used on a laboratory bench top with a minimum of time and effort involved in sample preparation.

Raman microprobe spectroscopy is an ideal candidate for this type of studies. Use of visible light combined with a confocal microscope provides a probe with spatial resolution of a micron or better, and coupling of such a microscope to a modern Raman spectrometer equipped with holographic notch filters and CCD multi channel detectors allows rapid acquisition of Raman spectra which can be correlated with the chemical state of the species and its physical environment.

Confocal microscopy is an invention of the 1950's that has now become popular in a variety of scientific applications, as documented in various published articles, e.g. Scientific American of August 1994, and Photonics Spectra of February 1995. The Raman microprobe, which involves the injection of a laser beam into a confocal microscope, and the coupling of the spatially resolved output of this microscope to a Raman spectrometer, was developed in the early 1980's, and by now has been shown to provide otherwise unobtainable information on various types of samples with in-homogeneities on a scale of micrometers. In comparison, infrared microscopes, because of the longer wavelength of the probing radiation, have resolution of, at best, 5 to 10 micrometers.

Here, we would like to demonstrate the utility of the Raman microprobe by discussion of a single set of measurements, conducted on a model for a microbattery diffusion layer.

Example: Diffusion in Microbatteries

Microbatteries are an integral part of miniaturisation of all types of electronic devices. Batteries used in portable electronic devices must themselves be compact and light enough to be portable. Microbatteries currently used in popular laptop computers use ionic conductivity instead of electrons to conduct charge, and lithium, in the upper left corner of the periodic table, is often the ion of choice. The components of the battery must, of course, allow movement of the lithium ions.

In the battery model probed in our demonstration, a layer of poly(ethylene oxide) was cast on a vanadium oxide ceramic substrate, which served as the model electrode. The lithium ions conduct charge by diffusing from the electrode through the polymer layer. The lithium ions, being positively charged, need a static counterion in the diffusion layer to provide electrical neutrality, and in this system the trifluoromethanesulfonate («triflate») anion is used. The Raman spectrum of trifluoromethanesulfonic acid dissolved in water, seen in Figure 1, shows several sharp bands. In particular, note the sharp single bands at 766 and 1034 cm^{-1} .

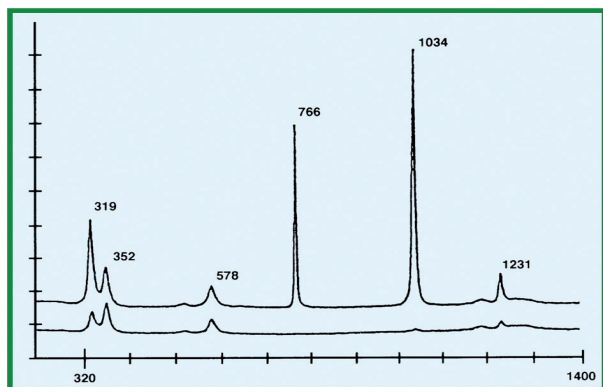


Figure 1: Spectrum of Triflate in Water

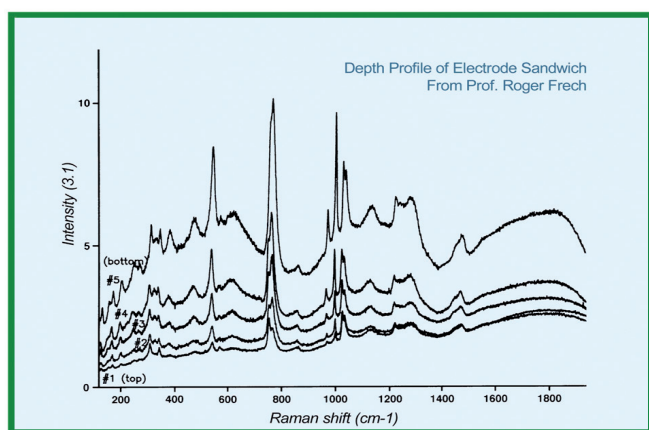


Figure 2: Spectra taken at different depths within the polymer layer

The poly(ethyleneoxide) layer, here about 20 micrometers thick, is transparent to visible light. Therefore, the excitation laser beam could be focussed at different depths in the sample simply by changing the height of the microscope stage. Figure 2 shows spectra collected from five different focal positions within the layer, ranging through the depth of the film.

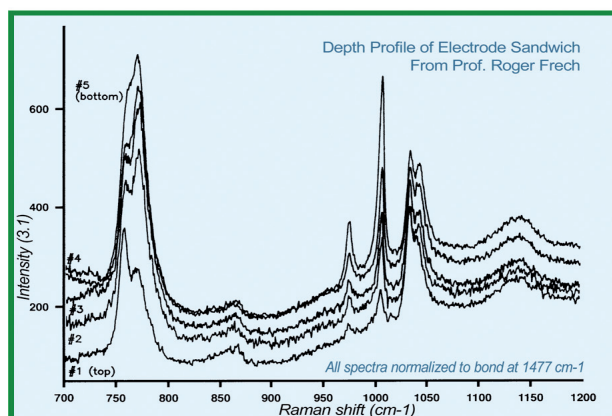


Figure 3: Spectra taken at different depths within the polymer layer with normalized spectra

A separate measurement of the index of refraction of the poly(ethyleneoxide) medium would have allowed us to correct the calibrated stage displacement to determine the exact depths of focus. Nevertheless, one can clearly see a progression of spectra in this Figure. The data become more interesting when we correct the raw spectra for the decrease in absolute intensity due to varied path length of both the laser and scattered radiation through the medium that is either absorbing or scattering; we do this by normalising all spectra to one of the bands of the polymer matrix, specifically the one at 1477 cm^{-1} . The results are plotted in Figure 3. Now we see that two triflate bands which appeared as singlets in the aqueous spectra, at 766 and 1034 cm^{-1} , are each split into two overlapped bands. Moreover, the relative proportions of the two components of the doublet at 766 cm^{-1} changes with depth in the sample, with the higher frequency component of the doublet increasing in relative intensity as the bottom of the polymer layer, and the interface with the ceramic electrode, is approached.

A crystal structure of this particular polymer electrolyte system was published by P. Lightfoot and co workers (Science 262, 883 (1993)). They found that the lithium ions are coordinated to five oxygen atoms, from either triflate ions or the host polymer, and that the oxygen atoms of the triflate could be either coordinated to lithium or uncoordinated. We could thus interpret the splitting of the triflate bands as arising from separate populations of coordinated and uncoordinated oxygen atoms, with the coordination shifting the Raman frequency. The more lithium ions that are present, the greater would be the population of triflate oxygen atoms with charged neighbors. A separate study of homogeneous samples of triflate ion in the presence of various concentrations of lithium, combined with analysis of the doublet progression with either curve-fitting or chemometrics software, would provide specific information concerning the chemical environment of the triflate ion, and, presumably the lithium concentration, as a function of the depth. These measurements were performed with a sample with zero applied voltage; more interesting successive studies would study the spectra at fixed depth as a function of applied voltage and/or time of the applied voltage.

Similarly, the spatial and temporal dependencies of various other diffusion processes through transparent media can be quantified. In cases in which the sample can be sliced or microtomed, the automated mapping stage driven by SpectraMax software can allow automatic collection of spectra as a function of depth, providing a «Raman map» of spectra as a function of depth. This provides one example of the use of Raman microscopy to obtain useful, and otherwise unobtainable, information about a sample with a concentration gradient which results from a diffusion process



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