

Controlling Diffusion in Sol-Gel Derived Solids
Maryanne M. Collinson and Mandakini Kanungo
Department of Chemistry
Kansas State University
Manhattan, KS 66506-3701

3. Diffusion of Redox Probes in Hydrated Sol-Gel Derived Glasses. Effect of Gel Structure. Kanungo, Mandakini; Collinson, Maryanne M. *Analytical Chemistry*, **2003**, 75(23); 6555-6559.

The sol-gel process has been routinely used to prepare silicate materials for a variety of applications including chemical sensors, photonic materials, and solid state electrochemical devices [1]. In a typical procedure, tetramethoxysilane (TMOS) is mixed with water in a mutual solvent such as methanol followed by addition of a catalyst such as hydrochloric acid. During sol-gel formation, the viscosity of the solution gradually increases as the sol becomes interconnected to form a rigid, porous structure - the gel [1-2]. Specific reagents can be readily entrapped within the inorganic framework via the addition of the dopant to the sol prior to its gelation [2]. The molecular diffusion of these entrapped species within the gels becomes very important in solid-state, catalysis, and chemical sensor applications.

In this work, ultramicroelectrodes have been embedded into the silicate matrix and used to evaluate the diffusional mobility of gel-entrapped redox probes during the sol-gel-xerogel transformation [3]. Examples of redox probes employed include potassium ferricyanide, cobalt (II) tris(bipyridine), and ferrocene derivatives. Potential step chronoamperometry coupled with slow scan cyclic voltammetry was used to measure the diffusion coefficient of entrapped probe during gel drying.

In the first part of this work, redox probes have been trapped in gels prepared either from (1) tetramethoxysilane (TMOS) catalyzed with either HCl, NaF, or NH₃, (2) TMOS cohydrolyzed and condensed with an organoalkoxysilane precursor (R-Si(OCH₃)₃, R = CH₃ or -NR₃⁺), (3) Ludox colloidal silica, and (4) titanium isobutoxide. The magnitude of the diffusion coefficient (D_{app}) and the rate at which it changes with drying time was a strong function of the extent of intermolecular interactions between the guest and the host. The diffusion rate of the encapsulated guest can be controlled by judiciously choosing the type of functional group immobilized in the porous framework. At one extreme the encapsulated probes diffused at rates similar to solution where at the other extreme, an order of magnitude drop in D_{app} was observed.

In this presentation, these results as well as other approaches to controlling diffusion in hydrated sol-gel glasses will be presented and discussed.

References

1. "Structure, Chemistry, and Applications of Sol-Gel Derived Materials". Collinson, M.M. "Handbook of Advanced Electronic and Photonic Materials", Ed., H.S. Nalwa. Vol. 5: Chalcogenides Glasses and Sol-gel Materials, Academic Press, 2001.
2. Organic Chemistry within Ceramic Matrices: Doped Sol-Gel Materials. Avnir, D. *Acc. Chem. Res.* **1995**, 28, 328-334.