

Molecular Flask for Solid State Electrochemistry and Photochemistry

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Summary: In a tight molecular solid made of polysaccharide and water, a very conventional electrochemical reactions took place for the first time the same as in a pure water. Photoinduced electron transfer from Ru(bpy)₃²⁺ to methylviologen (MV²⁺) took place also in this solid by a dynamic mechanism.

In chemical reactions taking place in a liquid, diffusion of reactants is of primary importance. Chemical reactions can also take place in a solid, but in such case the reactants do not diffuse at all or move only slightly, so that chemical reactions in a solid are usually entirely different from those in a pure liquid. If chemical reactions can occur in a stable and tight solid the same as in a pure liquid, it leads to new and wide applications. We have now found that electrochemical and photochemical reactions in tight and stable solids made of polysaccharide and water can take place the same as in water. As for the polysaccharide, κ -Carrageenan¹ and agarose² were used.

Electrochemical behavior of redox molecules in thin polymer films and gels coated on an electrode has been investigated^{1,3-12}, but they have been studied in the presence of outer electrolyte solution. The diffusion coefficient (D) of the redox substrate in these films or solids coated on an electrode has usually been very small³⁻¹². Entirely solid state voltammogram by using a conventional three electrode system has not been achieved yet. We have succeeded in achieving electrochemical reactions in a tight molecular solid made of polysaccharide and water. In this solid very conventional electrochemical reaction and measurement could be performed using a normal three electrodes system the same as in pure water without any outer water phase and vessel, and the electrochemical reactivity and diffusion of the redox compound were the same as in pure water.

Four weight % κ -carrageenan powder was put in pure water, and heated to entirely solubilize the material. After cooling the clear solution to room temperature, a tight, elastic and clear solid was obtained. In preparing a 1 wt% agarose/water (4ml) solution, tris(2,2'-bipyridine) ruthenium(II) dichloride (Ru(bpy)₃²⁺) and KNO₃ were added so as to have their concentration 1 mmoldm⁻³ and 0.1 moldm⁻³, respectively. In a viscous state of the mixture before entire cooling, transparent indium tin oxide (ITO) working, platinum counter, and Ag-AgCl reference electrodes were soaked in the solution. The cyclic voltammogram in the solid shows almost the same feature as in a liquid water including redox potential, peak separation, and peak currents. The D value of the Ru complex in a 1 wt% agarose solid (5.88x10⁻⁶cm²s⁻¹) was the same order of magnitude as in a liquid water (4.28x10⁻⁶cm²s⁻¹). In a Nafion film containing adsorbed Ru(bpy)₃²⁺ in the water phase in the hydrophilic column coated on an ITO electrode and soaked in a 0.1 moldm⁻³ KNO₃ aqueous solution, D was 10⁻¹⁰ cm²s⁻¹, four orders magnitude lower than that in the above solids.

To investigate photochemical reaction in the solid, electron transfer from a photoexcited state Ru(bpy)₃²⁺ to methylviologen (MV²⁺) was studied in the polysaccharide solid containing a large excess water. Electron transfer from a photoexcited Ru(bpy)₃²⁺ to MV²⁺ in a dry solid

matrix was first reported by one of the present authors by adsorbing the compounds on a cellulose sheet¹³, and the mechanism of such electron transfer in a dry polymer solid phase has later been established to be a static one in which the reaction components do not move at all for the electron transfer to occur^{14,15}. Now in a 2 wt% carrageenan /water solid containing both Ru(bpy)₃²⁺ (50 μ moldm⁻³) and MV²⁺ (from 50 to 400 μ moldm⁻³), electron transfer from the photoexcited Ru(bpy)₃²⁺ to MV²⁺ was investigated under irradiation with the wavelength of 453 nm (λ_{max}) at 25°C. The Stern-Volmer plots^{14,15} of the relative emission intensity (Io/I, where Io is the emission intensity at 627 nm without MV²⁺ and I with MV²⁺) from the photoexcited Ru complex as well as relative emission lifetime (τ_o / τ) (τ_o being the lifetime without MV²⁺) in the carrageenan solid are obtained, and both the plots of Io/I and τ_o / τ fell on almost the same line showing that the electron transfer takes place by a dynamic mechanism^{14,15} in which the molecules at first diffuse and react after collision. The second order rate constant of the electron transfer obtained by dividing the slope of the plots by τ_o (447 ns), 4.54x10⁹ dm³mol⁻¹s⁻¹, is almost a diffusion-controlled value, and even one order of magnitude larger than that in a pure water (3.1x10⁸ dm³mol⁻¹s⁻¹). On the contrary, a static mechanism took place in both dry and wet Nafion films containing adsorbed Ru(bpy)₃²⁺ and MV²⁺ for which the Stern-Volmer plots based on τ_o / τ gave no slope.

The polysaccharide is supposed to form a molecular network that contains a large amount of water. Applications of these solid state electrochemistry and photochemistry to photoelectrochemical devices are now under way.

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