Electrostatically Self-Assembled Polyelectrolyte Monolayer as a Novel pH-Permselective Ion Switch

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Development of stimuli-responsive porous membranes has been extensively pursued in the past few decades for potential applications, including controlled release, selective separation, chemical sensors, and biosensors. Recently, polyelectrolyte multilayer (PEM) films deposited onto a solid substrate by means of electrostatic self-assembly[1] combined with stimuli-responsive functions[2-4] were introduced, and their development is emerging as a promising field for sophisticated applications, such as filtration systems, membrane-based separation, bio-separation, and sensors.

In the present presentation, we introduce the development of a new pH-switchable membrane system comprising a copolymer of acrylic acid and [1,3]oxazine-bearing acrylate (POA). The pH-responsive membrane relies on the homogeneous dispersal of the oxazine groups (OX), which are known to open, yielding either a positively charged cation (IC) at low pH or a negatively charged anion (NA) at high pH[5]. Ionic permeability through a POA monolayer film deposited on an amino-functionalized ITO electrode (ITO/POA) by the electrostatic self-assembly method was electrochemically investigated under different pH conditions using redox probe molecules, anionic Fe(CN)$_6^{3-}$ or cationic Ru(NH$_3$)$_6^{3+}$, as shown in Figure 1. The POA film was permeable (“On”) to the negatively charged probe, Fe(CN)$_6^{3-}$, at pH 3.0, but impermeable (“Off”) to the probe at pH 10.0. In contrast, the POA film was closed to the positively charged probe, Ru(NH$_3$)$_6^{3+}$ at pH 3.0, but open to the probe at pH 10.0. The origin of the excellent ion-transport selectivity in the 1 nm-thick ultrathin POA membrane is discussed in terms of alternating charges of the aromatic zwitterionic group, oxazine, in the polyelectrolyte membrane.

Figure 1. Schematic illustration of the pH-switchable On/Off function of the POA monolayer film.