Nanotube Membrane Sensors A New Paradigm in Electrochemical Sensing

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We have been exploring the transport and electrochemical properties of nanotube membranes (1-7) prepared by the template method (6,7), a general approach for preparing nanomaterials. One possible application for these nanotube membranes is in electroanalytical chemistry where the membrane is used to sense analyte species (3). In our prior work, membranes containing gold nanotubes with inside diameters that approached molecular dimensions (1 nm to 4 nm) were used (3). The Au nanotube membrane was placed between two salt solutions and a constant transmembrane potential was applied. The resulting transmembrane current, associated with migration of ions through the nanotubes, was measured. When an analyte molecule whose diameter was comparable to the inside diameter of the nanotubes was added to one salt solution, this molecule partitioned into the nanotubes and partially occluded the pathway for ion transport. This resulted in a decrease in the transmembrane current, and the magnitude of the drop in current was found to be proportional to the concentration of the analyte (3). In this experiment, a baseline transmembrane current was established, and the analyte molecule, in essence, turned off this current. It occurred to us that there might be an advantage in doing the opposite; i.e., starting with an ideally zero current situation and having the analyte molecule switch on the ion current. That is, we would like to make a synthetic membrane that mimics the function of a ligand-gated ion channel. An example is the acetylcholine-gated ion channel (8), which is closed (off state) in the absence of acetylcholine but opens (and supports an ion current, on state) when acetylcholine binds to the channel. This concept of ion-channel mimetic sensing, as originally proposed by Umezawas group (9), has been of considerable interest in analytical chemistry (10-12). There is also considerable interest in using naturally-occurring and genetically-engineered protein channels as sensors (see (13) and references therein). We describe here results of experiments that provide proof of the basic concept that an analyte molecule can switch on an ion current in a synthetic membrane-based ion-channel mimic. The membrane used for most experiments was a commercially available microporous alumina filter. The pores in this membrane were made hydrophobic by reaction with an 18-carbon (C18) alkyl silane. When placed between two salt solutions, the pores in this C18derivatized membrane are not wetted by water, yielding the off state for the membrane. When exposed to a solution containing a sufficiently high concentration of a long chain ionic surfactant (the analyte), the surfactant molecules partition into the hydrophobic membrane, and ultimately cause the pores to flood with water and electrolyte. As a result, the membrane will now support an ion current, and the channel-mimetic membrane is switched to its on state. Cationic drug molecules can also switch this membrane from the off to the on state. Furthermore, when a hydrophobic COOH-containing silane is used, the off/on transition can be induced by controlling the pH of the contacting solution phases. This analyte-induced switching of the membrane between the off and on states was investigated using an AC impedance method, transport methods and by direct measurements of the transmembrane ion current.

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