

Electrochemical Proton Time-of-Flight, a Dual Microelectrode Generator-Sensor Method with Potentiometric Detection

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Electrochemical time-of-flight (ETOF) is a family of techniques involving measurements of the signal vs time transients due to diffusion of electrochemically generated species between two narrowly spaced micro-electrodes of a lithographically fabricated device. In most ETOF experiments, electro-active species are generated at a constant potential and their arrival at the sensor is monitored amperometrically.^{1,2} We have recently described a modification to this scheme: generation of the diffusing species is done under controlled rate conditions (galvanostatically), and a potentiometric sensor (operating at open circuit) is used to record the E-t transients.³ One application of this methodology that we are interested in developing is a novel signal transduction mode in biological sensors. A general scheme is illustrated in Figure 1. The ETOF experiment is carried out in a narrow channel lined, for example, with a lipid bilayer carrying receptor sites selected to bind a targeted pathogen. Specific binding of the pathogen can then be detected by the change in the E-t transient that stem from a faster ions diffusion in the channel of partially restricted volume.

To fully understand ion diffusion in such channels and the related sensor response we have examined generation, diffusion and sensor response of silver ions and protons. In the later case, electro-oxidation of water served as the mechanism of proton generation and electrochemically formed IrO₂ films on gold as micro-electrode pH sensors. In Figure 2, we show direct comparison between the experimental and the digitally simulated E-t transients for two proton ETOF experiments carried out in an open face configuration where radial rather than linear diffusion governs transport between generator and sensor. The delay in the sensor response observed at pH 6.9 is related to the double-layer charging of the potentiometric sensor of a finite surface area and interfacial capacitance.³ Such delays are most vivid when a relatively high base pH results in a large change of the sensor potential in response to an initially small flux of protons arriving at the sensor. The subsequent, rapid increase of the sensor potential, of ca. 30 V/s, appears to be kinetically rather than mass transport controlled. Analysis of the maximum, intrinsic rates of IrO₂ sensor potential rise may allow us to elucidate the mechanism underlying the pH sensitivity of this class of sensors.

Reference:

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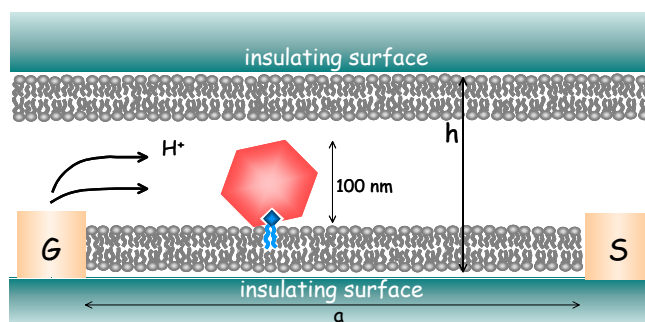


Figure 1. A schematic diagram of a biological sensor relying on the rate of proton transport as a signal transduction mode. It features two micro-electrodes, the generator (G) operated at constant current, and a potentiometric sensor (S). Selective binding of a pathogen species results in changes in the rate of proton diffusion through the channel of partially restricted void volume.

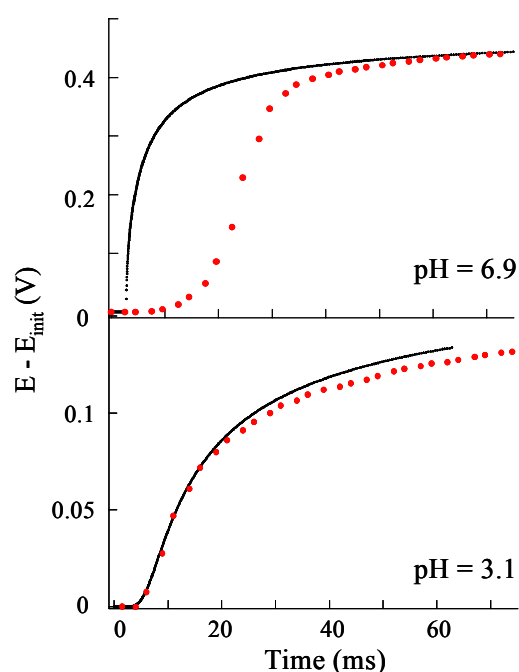


Figure 2. Comparison of the experimental (dots) and digitally simulated (continuous line) E-t transients in the proton ETOF experiments carried out at two different base pH values. An open face ETOF device was used with a 20 μm inter-electrode gap. The gold generator ($A=5\times 10^{-5}\text{ cm}^2$) and IrO₂ coated gold micro-sensor (with a Nernstian slope of $76 \pm 2\text{ mV/pH}$) electrodes were used; generator current was 0.5 mA. An experimentally determined proton diffusion coefficient of $6.9\times 10^{-5}\text{ cm}^2/\text{s}$ was used in the digital simulations described in ref. 3.