

Oxygen Reduction at Planar Solid Polymer Amperometric Sensors

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The electrochemistry of oxygen at solid polymer electrolyte (SPE)-based amperometric sensors, fabricated according to a recently introduced planar design concept, has been investigated as a function of both gas relative humidity (RH) and oxygen levels. The solid protonic conductors used were Nafion[®]-117 membranes and Polybenzimidazole (PBI) films, while the working and counter electrodes were non-porous Au and/or Pt layers sputtered on the same face of the solid electrolyte and in contact with the gas sample (see Figure 1). Such planar solid-state devices could offer potential advantages over sandwich-type gas sensors namely, reduction in precious metal electrode area (the detection takes place at the edge of the deposit) and simplified fabrication (avoiding labor-intensive component stacking steps).

Sensors based on both materials exhibited near-linear response to oxygen concentration changes and response times comparable to those of commercially available sensors, irrespective to sample relative humidity (Figure 2), but the magnitude of the signal did depend on the latter even after ohmic correction or at low currents.

The shape of the oxygen reduction current-potential curves observed (lack of mass transfer-limited current even after ohmic corrections and for oxygen levels down to 1000 ppm, Figure 3), as well as the dependence of the signal only on the electrode layer length parallel to the electrolyte path (and not on the total layer area) all point to high mass transport rates and the absence of a significant mass transport barrier and imply that the electroactive gas reacts at the line formed by the gas/solid electrolyte/metal layer interface.

A systematic study of the effect of humidity on oxygen reduction and Au surface electrochemistry at the Au/Nafion[®] and Au/PBI interfaces reveals, that the fall in the oxygen signal with decreasing humidity and the parallel decrease in surface oxide formation/stripping (Figure 4.) cannot be explained simply in terms of ohmic losses, but are related to the effect of water on the number of electroactive sites and their catalytic activity. Furthermore, the Tafel plots for oxygen reduction (Figure 4, inset) show a changing slope with changing humidity (from 524 mV per decade for 23% RH to 334 mV for 83.5% RH) which is higher in the case of humidified samples than the value of 152 mV obtained when Nafion was in direct contact with water.

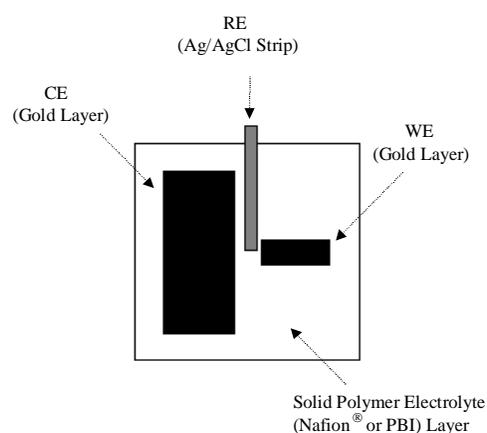


Figure 1 : Top-view drawing of the planar amperometric sensors used.

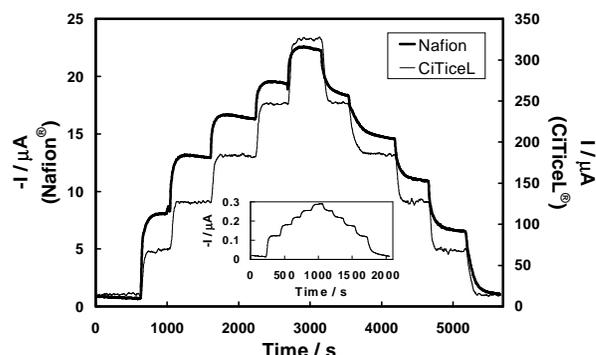


Figure 2 : Current-time response of the Au (vs. Ag/AgCl)/Nafion[®]/Au and CiTiceL (City Technology Ltd) sensors to oxygen concentration steps in water-saturated gas samples. The working electrode of our device was held at -0.10 V vs. Ag/AgCl.

Inset: Experiment was repeated at 40% RH. Working electrode was held at -0.5 V vs. Ag/AgCl

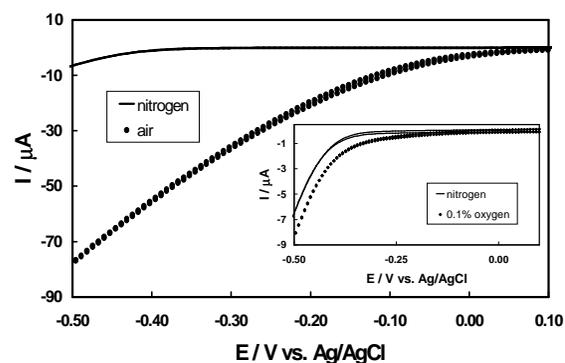


Figure 3 : Oxygen reduction curves at water saturated samples.

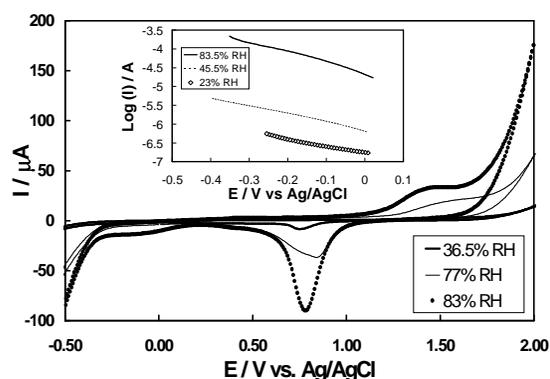


Figure 4 : Voltammogram recorded at 50 mV/s potential sweep rate in humidified nitrogen streams of 36.5%, 77% and 83% RH, at a three-electrode Au (vs. Ag/AgCl)/Nafion[®]/Au planar device

Inset : Tafel plot for oxygen reduction in streams of varied humidity.