

Sensing at the nanoscale: properties of nanoscale interfaces between immiscible liquids formed at the mouths of nanopore arrays

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Ion transfer electrochemistry at liquid-liquid interfaces can be employed for the successful detection and sensing of chemical and biochemical species that do not exhibit useful redox electrochemistry. By miniaturisation of these interfaces to the nanoscale, enhanced mass transport fluxes can be achieved to bring about better analytical sensitivity. However, the enhancement in diffusional flux may be off-set by other factors which impact on the performance.

In this report, the results of investigations into the properties and behavior of nanoscale liquid-liquid interface arrays formed by use of nanoporous silicon nitride membranes are presented. Potential step chronoamperometry (PSCA) of ion transfer across arrays of nanoscale interfaces between two immiscible electrolyte solutions was implemented at silicon nitride membranes containing 400 nanopores in a hexagonal close-packed arrangement and with pore radii of 75, 50 and 17 nm. The transfer of tetrapropylammonium cation across the nanopore array-supported water /1,6-dichlorohexane interface served as the model reaction. The cell time constants and charging time were determined prior to experimental PSCA. Charging times in the range of 0.08 s to 0.46 s were determined, with the membrane with smallest pores exhibiting the largest charging time. Steady-state current due to ion transfer were achieved at long times, but these were 30-50 % lower than current expected for inlaid disc nano-interfaces. This is attributed to diffusion zone overlap at adjacent interfaces. The response times of the three nano-interface arrays to a potential step were all in the region of 6 (+/- 1) s, (response time here defined as the time required to reach 95 % of the steady-state current). Subsequent studies by electrochemical impedance spectroscopy (EIS) confirmed that capacitance due to the presence of the silicon nitride membrane and large resistance due to the presence of organic phase-filled nanopores, impacted on the electrochemical performance.

As a result, careful selection of material and membrane design is required in order to achieve optimal sensor and biosensor performance of nanoscale interface arrays between immiscible liquids.