

Supporting Information

Ion-transfer electrochemistry at arrays of nanoscale interfaces between two immiscible electrolyte solutions arranged in hexagonal format

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Experimental voltammograms were recorded as cyclic voltammograms (CVs), with a typical example shown in Figure S1. The results show that well-behaved cyclic voltammograms were obtained. The background CV (Figure S1, 0 μM of tetrapropylammonium, TPrA⁺) shows a response consistent with capacitive behaviour, which can be attributed to capacitance of the array of nano-ITIES and of the solid state membrane itself, as discussed previously.¹ This capacitive effect was removed by background subtraction. The role of background subtraction was to simplify the voltammograms so that only the ion-transfer current associated with TPrA⁺ is present, as this is the parameter of interest in this report. The CVs in Figure S1 for different concentrations of TPrA⁺ show that ion transfer occurs on the forward scan but no apparent peak or process attributable to a reverse ion scan is seen.

This is consistent with ion transfer voltammetry in which thin membranes are used to support the interface and radial diffusion occurs on both sides of the membrane. As we are interested in the impact of mass transport on the TPrA⁺ ion transfer current, we therefore choose to study only the forward scans of the CVs. As a result, voltammetric data are displayed in the main paper as forward scans only, as these displayed the ion transfer current of interest.

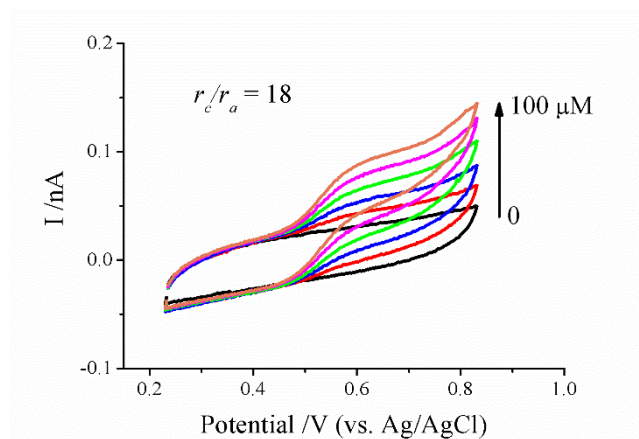


Figure S1. Exemplar cyclic voltammograms of tetrapropylammonium ion (concentrations in aqueous phase = 0, 20, 40, 60, 80 and 100 μM) transfer at an array of nanoITIES formed at a SiN membrane with $r_c/r_a = 18$ (corresponding to Figures 2A & 3A of the main paper). Scan rate: 5 mV s^{-1} .

¹ M. Sairi, J. Strutwolf, R.A. Mitchell, D.S. Silvester, D.W.M. Arrigan, Chronoamperometric response at nanoscale liquid-liquid interface arrays, *Electrochimica Acta*, **101** (2013) 177-185.