Spatially resolved electrochemiluminescence on an array of electrodes for the investigation of the development of diffusion layers with time

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For arrays where the electrodes are operated at an identical potential, the total response of the array depends not only on the size of the electrodes in the array, but also on the interelectrode distance d.[1] If the time of the experiment is sufficiently short for the individual diffusion length δ to be extremely small with respect to the radius r of the electrode and if the interelectrode spacing d is large compared to δ developed at the electrodes of the array ($d > \delta << r$) the response of the array is the sum of the individual Cottrell responses of the electrodes in the array. At longer times, the diffusion length δ gets larger with respect to r.

We were interested in using an array of electrodes in the amplification steady state regime, viz., when $d > \delta >> r$, as the array current is, under these circumstances, the sum of the steady state currents of its individual electrodes. In some cases can the interelectrode distance d be artificially varied by connecting only a fraction of the individual electrodes. Thus, it was shown that by statistically connecting only 20-30% of the electrodes of such arrays, the entire array functioned in the steady state amplified mode.[2-4] Similarly, the use of an insulating paint[5] to decrease the dimension of each individual electrode of such arrays produced the same result by increasing the d/r ratio, with the advantage that the hexagonal symmetry arrangement of optical fibers in the array was retained.[6] The disadvantage is that the relatively low stability of the paint insulation requires that the potential window be rather limited (e.g., E > -0.2V vs. Ag for reductions) to avoid irreversible dissolution of the paint with resulting exposure of the full electrode surface.

We wish to demonstrate that for a given array, diffusional de-coupling between individual electrodes may be achieved by adjusting δ through control of the time scale of the experiment. This concept will be illustrated by using an electrochemical array formed through chemical etching of optical fiber bundles. The chemical etching of a fiber bundle's distal end results in arrays of either tips or wells, depending on the composition of the core relative to the cladding and have been used to develop optical nanoarrays.[7,8] Through pulsing experiments, the size of the diffusion layer can be varied from the situation where diffusion layers interpenetrate and the array behaves like a continuous planar macroelectrode, to the situation where the response of the array is the sum of the individual Cottrell responses of the electrodes. The overlap of diffusion layers with time was investigated using ruthenium complexes as they produce electrochemiluminescence (ECL) with a good quantum yield even in the presence of oxygen and water.

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