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Electrochemiluminescence Interferometry at Microelectrodes

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Electrochemiluminescence (ECL) is the production of light from electrochemically generated reagents.[1-3] This technique has been extensively studied for several reasons including the possibility of obtaining fundamental information about highly energetic electron-transfer reactions.[1-3] Recently we have investigated ECL on the microsecond time scale by applying a rapidly alternating square wave to a microelectrode.[4] This method of reactant generation allows the measurement time scale to approach that of the kinetics of the light-producing reaction. With the exception of Van Duyne and co-workers in the 1970s,[5,6] very little attention has been applied to the investigation of ECL at high frequencies. A number of distinct advantages are obtained by reducing the time scale of the experiment, including greater light production and improved reactant stability.[4] In addition, the rapid time scale maintains the ECL reaction layer close to the electrode surface. In this work we report on the presence of distinct interference patterns in the ECL curves obtained at high frequencies due to the reflection of light from the electrode surface. The presence of these patterns provides unique experimental evidence of the position, shape, and movement of the ECL reaction layer through the course of reactant generation.

In these experiments, a microelectrode is sequentially pulsed between the oxidation and reduction potentials of the precursor compound in deoxygenated solution, *i.e.*, 9,10-diphenylanthracene (DPA) or ruthenium(II) tris(bipyridine) ($Ru(bpy)_3^{2+}$), to alternatively generate the radical-ion reagents.[2,3,7] The experimental[8] and simulated[9] ECL curves for 5.6 mM DPA at an r = 5 μm Au electrode are shown in Figure 1 (upper) for a step time of 200 μs. The emission displays a maximum at early times in the step which decays as predicted by classical, diffusion-based theory.[10-12] However, a damped oscillation is superimposed on the decaying experimental emission. Similar results are obtained using 4.3 mM $Ru(bpy)_3^{2+}$, Figure 1, with the exception that the oscillations are of lower frequency.[13]

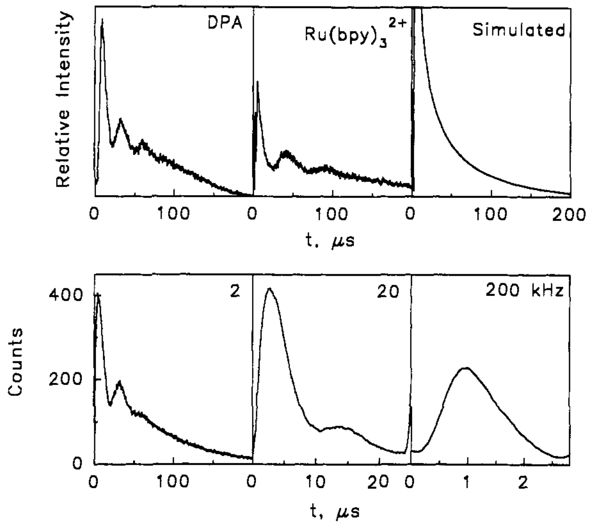

Figure 1. Upper: ECL curves from 5.6 mM DPA in 50:50 acetonitrile–toluene and 4.3 mM $Ru(bpy)_3^{2+}$ in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) at a gold disk (r = 5 μm) at 2.5 kHz (t_f = 200 μs); the simulated curve for the DPA data with an experimentally determined RC_{dl} time constant of 1.1 μs. Lower: ECL curves from 5.9 mM DPA in 50:50 acetonitrile–toluene containing 0.1 M TBAH as a function of applied frequency at a Pt disk (r = 1 μm). The simulation (not shown) predicts the delay caused by the time constant (0.1 μs) but does not predict the slow rise in emission especially apparent at 200 kHz.

The oscillations of the ECL intensity have the appearance of an optical interference pattern resulting from the reflection of light off the metal electrode surface.[14,15] At high concentrations, the electrochemically generated reagents react to produce an emitting species in a thin plane at the location where the inward and outward fluxes meet.[10-12] Digital simulations[9,12] show that the ECL reaction layer broadens and moves away from the electrode surface in a manner that is nearly linear with time, Figure 2 inset. Thus on these time scales, the emitting plane is located at a distance that is comparable to the wavelength of the emission, allowing strong interaction with the metal surface. An ECL interferogram (intensity vs distance) was obtained by dividing the experimental ECL curve with the simulated curve[9] and converting time into distance. The Fourier transform (FT) of the resultant interference pattern produces the frequency spectrum[16] of the emitting species in solution as shown in Figure 2 for DPA and $Ru(bpy)_3^{2+}$. The distance traveled by the emission limits the resolution to *ca.* 5000 cm^{-1}.[14] In addition, the FT spectra are broadened because of uncertainty in the position of the emitting species due to the finite width of the ECL reaction layer and the electrode surface roughness. Within these bounds, however, the spectra are in agreement with their corresponding ECL emission spectra measured conventionally.

Prior theoretical and experimental work supports the concept that the emission from a molecule near a reflecting surface (*i.e.*, within a wavelength of light) can directly interact with its reflected

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(8) The experimental arrangement was identical to that described previously.[4] *e.g*, flow-injection analysis based system with single-photon counting equipment. To prevent any possible artifacts caused by current measurement, the working microelectrode was connected to ground and the voltage pulses from a Wavetek function generator were applied to a silver counter electrode ($A \sim 0.3$ cm^2).

(9) The program was written in Pascal using a Hopscotch algorithm, and simulations were performed on a 80486 computer. The simulation contained a number of parameters which were determined experimentally (t_f, RC_{dl}, iR, D, C, $E°_{red}$, $E°_{ox}$). The reaction kinetics were assumed to be diffusion-controlled, and the results from the fifth cycle are shown. At this point, the ECL is pseudo-steady-state. Additional details regarding the simulation will be published elsewhere.

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(13) When the working electrode is connected to an ultrafast current amplifier rather than directly to ground, no oscillations can be observed in either the faradaic or charging current.

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(16) The experimental wavenumbers were calculated by converting the FT index to wavenumbers and then dividing the result by the factor 2η, where η corresponds to the refractive index of the medium, 1.34 for ACN or 1.42 for 50:50 toluene-ACN.

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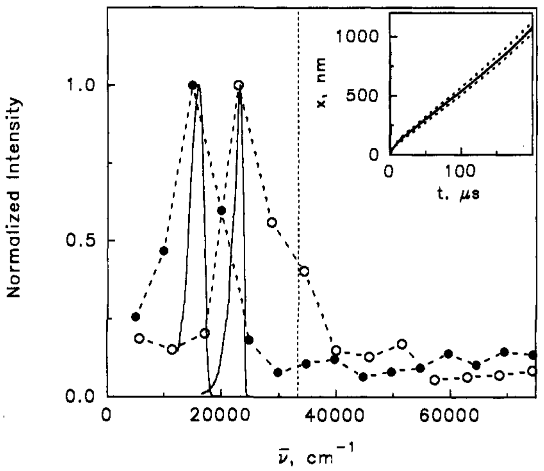

Figure 2. Fourier transforms of interference patterns obtained from 6.4 mM DPA at a platinum disk (r = 2.5 μm) (open circles) and 4.3 mM $Ru(bpy)_3^{2+}$ at a gold disk (r = 5.4 μm) (closed circles). The dashed line corresponds to the upper frequency limit imposed by the glass optical window in the ECL cell. Wavenumber maxima[16] are 15 000 cm^{-1} (670 nm) for $Ru(bpy)_3^{2+}$ and 23 000 cm^{-1} (440 nm) for DPA. For comparison, ECL spectra from $Ru(bpy)_3^{2+}$ and DPA acquired with a SPEX fluorimeter via double-band microelectrode geometry[23] are shown. Inset: Digital simulations of the position (solid line) and the width at half-height (dashed lines) of the ECL reaction layer during a 200-μs potential step; simulations for kt_fC = 22 000. RC_{dl} = 375 ns.

field.[17-20] Strong damping of the excited state by the metallic surface is predicted at small distances while distinct oscillations in the fluorescence lifetime of the emitting species are predicted at long distances. Previous experimental work, in which a fluorescent molecule was tethered at various distances from a reflecting metal surface, attributed these phenomena to nonradiative energy transfer and interference between the dipole emitter and its reflected field.[17-20] The exact positions of interference maxima and minima were found to depend on several variables including the reflection coefficients, the emission wavelength, and the refractive index of the intervening material.[18-20] The ECL experiments differ from those described above in that the emitting layer is moving during the experiment.

When the applied frequency is increased, the interference pattern disappears and significant quenching of the integrated light intensity relative to simulated curves is observed, Figure 1 (lower). At high frequencies, the ECL reaction layer is located within a quarter-wavelength from the electrode surface where only strong quenching of the ECL intensity occurs. When a carbon-fiber microelectrode is used, both the oscillatory behavior and intensity quenching are less pronounced, consistent with carbon's lower reflectivity and density of states.[21] Distinct interference patterns are also not observed in ECL curves obtained from dilute solutions because the ECL reaction layer is not a thin plane as a result of the finite, second-order kinetics.[4,10] However, significant quenching of the ECL intensity is still apparent in this case. Furthermore, the interference patterns are diminished when the electrode surface is roughened with 9-μm alumina or 6-μm diamond paste. Under these conditions, the surface roughness features are considerably larger than the wavelength of light. The effective broadening of the ECL reaction layer by these features and the additional reflectivity/scattering would cause the interference pattern to be less distinguishable. The most distinct patterns have been obtained using gold or platinum electrodes polished with 0.05-μm alumina on a napless cloth.

In conclusion, the use of high-frequency voltage waveforms for generation of ECL reagents results in a reaction layer which is very close to the electrode. As a result, large interactions between the emission and the surface occur. Careful consideration must be given to the interpretation of ECL data generated under such conditions. Specifically, the derivation of kinetic or mechanistic information from a pulse shape analysis of the high-frequency ECL decay curves requires that this can be accounted for. It is interesting that constructive interference can be used to partially offset the quenching of the excited states. This suggests that an electrode placed at a strategic point from a second electrode could produce an *ca.* 1.2–1.3 enhancement factor in the ECL intensity. In addition, since the emission intensity is high (calculated to be *ca.* 10^7 photons/s[22]), a miniature version of this probe would make a suitable source for near-field microscopy. Indeed, the ECL intensity pattern which would be a direct function of substrate–tip spacing could provide a measurement of distance from the surface.

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