

## RESEARCH NEWS

# Evidence of electrochemiluminescence as a pumping mechanism for a dye laser

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An important advancement in the technology of continuous wave dye lasers was reported by a group of scientists at NTT Basic Research Laboratories, Japan<sup>1</sup>. They claim to have realised an idea, proposed about twenty five years ago, of improvising the process of pumping a dye laser, thereby making the family of dye lasers easier to maintain, cost effective, and user-friendly.

For any medium to act as a laser, it is essential that the number of molecules

in the excited state exceeds the number of molecules in the lower state. This condition is called 'Population Inversion'. In ordinary circumstances, the energy levels are populated according to the Maxwell Boltzmann distribution. This distribution rules that the population of any energy level is inversely proportional to the exponential of its energy. Furthermore, the excited states have a very short lifetime, and the molecules in the excited state decay

rapidly to the lower state, destroying the population inversion. So, to hold a large number of molecules in the excited state, one is required to supply a lot of energy. The minimum energy required to invert the population is called the threshold energy. The obvious sources of such large energies are flashlamps. However, flashlamps can deliver energies only in short pulses, and cannot perform continuously. They are used, therefore, in pulsed dye lasers. And this

is where continuous wave dye lasers run into problems.

The active medium in dye lasers is a fluorescent dye, the molecules of which absorb energy in the blue part of the spectrum, and emit in the red part. Every electronic energy level of the dye consists of a stack of vibrational levels which are closely spaced and almost form a continuum of states. Hence both the absorption and emission spectra are continuous. That makes the dye lasers tunable, i.e. one can obtain a laser emission at any wavelength within the fluorescence spectrum. This is a powerful advantage over other lasers.

Dye lasers, being the tunable type, are vastly used in areas such as spectroscopy, light scattering and find applications in medicine, communications etc. However, these dye lasers can prove to be a liability than an asset, because of the pumping requirements.

The source which can deliver high energies continuously is a laser itself. So, to build a continuous wave dye laser, other lasers are used as pumping sources. Effectively, the maintenance of such a dye laser involves the maintenance of two lasers, and this also renders it unreasonable pricewise.

One of the solutions to this disadvantage was conceived and proposed about twenty five years ago<sup>2-4</sup>. It was suggested that energy obtained by the process of electrochemiluminescence (ECL) can be used as a pump for such dye lasers. Efforts were made to realise this idea, but the maximum energy generated was two orders of magnitude lower than the threshold. Recently, Hirouchi *et al.*<sup>1</sup> succeeded in building a device which enhances the efficiency of ECL leading to observation of laser action.

When the anion and cation radicals of a species react with each other, the electron transfer between them excites the atom that absorbs the electron. The energy carried off by the electron is equal to the energy that is expended in creating the two radicals. The excited atom then decays by radiating this energy as light. This is called chemiluminescence. If the radicals are electrochemically generated, that is, under the influence of an electric field, the process is called electrochemiluminescence. Clearly, it is the energy of the electric field that is converted into light energy.

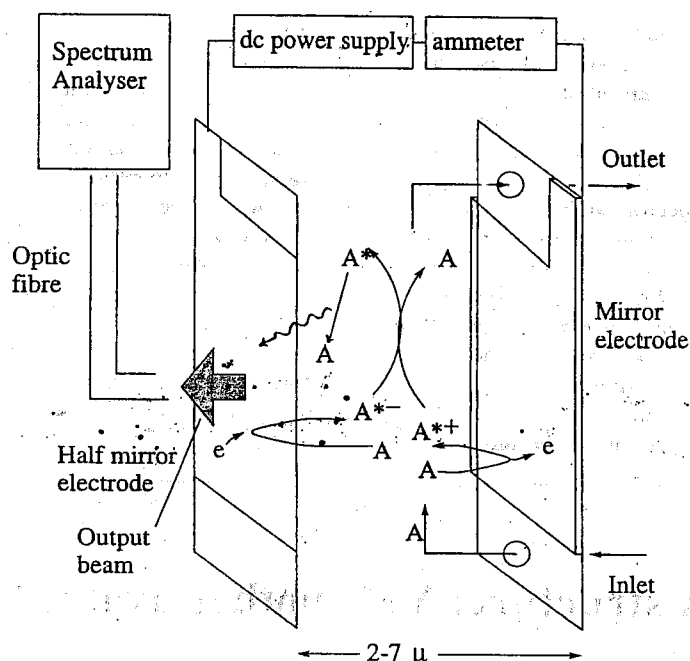


Figure 1. The dye is allowed to flow between the electrodes. The schematic of the chemical reaction is shown in the figure. A, A\*, A\*<sup>-</sup> and A\*<sup>+</sup> stand for the ground state, excited state, anion radical and cation radical states of the dye molecule respectively.

The dye used in the experiment of Hirouchi *et al.*<sup>1</sup> was Diphenylanthracene (DPA) dissolved in Dimethylformamide (DMF). This dye, when used as a lasing medium, is pumped by a nitrogen laser<sup>5</sup>. The oxidation potential of the molecule of this dye is 1.3 V and the reduction potential is -1.7 V. Both these numbers are with reference to Ag/AgCl. The energy given out when the two radicals combine is equal to the potential difference, which is 3 V. The wavelength corresponding to this energy is ~400 nm, that lies in the blue region of the spectrum. The dye molecules can absorb this energy and fluoresce.

A special cell was engineered to drive the chemiluminescent reaction (Figure 1). A thin layer of platinum was deposited on two quartz substrates (each of area 2 mm × 2 mm). The thickness of the deposition was such that one of them was totally reflecting, and the other had 99.2% reflectance. These two substrates formed the opposite faces of a rectangular cell. The separation between the two faces was about 2-7 microns. The platinum layers also acted as electrodes. The dye was allowed to flow through this cell, and an optical fibre was placed outside the semireflecting mirror to collect the light generated.

The electric field electrolysed the ground state molecules into anion and

cation radicals. These radicals released energy in the form of fluorescent radiation on recombination according to the fluorescence spectrum of the dye. The spectrum peaked at 445 nm. Moreover, the fluorescence showed some special features.

The fluorescence spectrum of the dye was seen to be modulated by thin sharp equidistant peaks, which were detected to be the Fabry Perot resonances of the cavity formed by the two mirrors. These resonances occur when light is repeatedly reflected between two parallel mirrors, and the separation between the two mirrors enables certain wavelengths to interfere constructively, resulting in intense lines at corresponding wavelengths.

The dependence of ECL on the current was examined. The intensity of the peaks in the fluorescence spectrum, was measured at different current values in a steady state. Theoretically, the ECL intensity should be proportional to the square of the current. However, the observed intensity could not be represented as a quadratic function of the current. Initially, the intensity showed a very gradual increase with current, up to about 0.45 mA. After that, it grew rapidly with current, showing a clear threshold at 0.45 mA. This dependence of intensity on current is similar to the

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one observed in semiconductor lasers. An empirical relation was used to estimate the threshold current to be 0.41 mA for the cell, which fairly matched with the experimental value of 0.45 mA.

Two spectra were obtained at two different current values, one above the threshold and the other below the threshold. The peak positions were almost the same for the two spectra, however, the peak heights of the spectrum above threshold were much greater than those below threshold, and the envelope of the spectrum above threshold nar-

rowed. This envelope narrowing effect is similar to that observed in ordinary lasers. This happens because the peaked wavelength starts growing in intensity at the cost of other wavelengths, which are consequently suppressed. This narrowing, called 'line narrowing' is a clear indicator of laser action.

These observations confirm that the emission from the cell was indeed a 'laser', driven by an electrochemical reaction. Thus, ECL can prove to be an easier alternative to pump continuous wave dye lasers in the near future.

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