ABSTRACT: A thin body of active material in the form of anthracene or naphthalene generates light when a current is passed through it by the injection of electrons from an electrode containing negative ions of a similar material e.g. anthracene, naphthalene or tetracene) to a base electrode to which an external positive potential relative to the electron-injecting electrode is applied. The base electrode may be solid and transparent for transmission of light generated in the active material or at its interface with the base electrode. This device also acts as a rectifier, since virtually no current will flow if the externally applied potential is reversed.
ELECTROLUMINESCENT DEVICE WITH LIGHT EMITTING AROMATIC, HYDROCARBON MATERIAL

This invention relates to electroluminescent devices. Electroluminescence over a considerable wavelength region is possible using inorganic semiconductor systems. However, at least as versatile in this respect are systems using organic materials as the active elements. Such organic materials are normally highly electrically nonconducting, however, so that before electroluminescence can be achieved it is necessary to find the correct conditions for injecting electric charges (electrons or holes) into the materials.

While, as indicated below, the present invention is not restricted in its broad scope to the injection of charges into any one or two particular materials, it will be convenient to take as typical materials anthracene and naphthalene, whether in the form of single crystals or as powder or in a matrix.

Injection of electric charge carriers into such materials has been achieved using liquid electrodes. See for example H. Kallman et al., J. Chem. Phys., 32, 300 (1960); M. Popel et al., J. Chem. Phys., Vol. 36, No. 9, May 1, 1962, pages 2486 et seq.; and W. Helfrich et al. U.S. Pat. No. 3,457,153 issued July 22, 1969. Only in the latter reference were sufficient currents reported to generate any observable luminescence. Emission from an anthracene crystal occurred primarily in the blue spectral region, and is believed to have been generated by the direct recombination in the body of the crystal of electrons and holes injected from the opposite faces of the crystal by the respective liquid electrodes.

These liquid electrodes are, however, opaque and it has been necessary to remove the light from the system through the edges of the active crystals. This is inconvenient and relatively inefficient, especially since for best performance the crystal will normally be made as a very thin wafer, the liquid electrodes obscuring most or all of the flat faces. Also only relatively short term stability was available due to dissolving the active material in the electrode solutions.

The principal objects of the present invention are to provide a method of injecting carriers into such materials by means of electrodes at least one of which is a transparent solid through which the light generated in the active material can readily emerge, and to give long-term stability to the system.

Another object is to obtain more light than has previously been possible with devices of this type of comparable size and operating conditions.

Yet another object is to produce a device that will act as a rectifier as well as to produce light.

The present invention consists of an electroluminescent device comprising:

a. a thin body of light-generating, aromatic, electrically nonconducting, hydrocarbon material;

b. a first electrode having an electrically conducting surface contacting a first surface of said light-generating material, and

c. a second electrode contacting a second surface of said light-generating material, said second electrode containing negative ions of an aromatic hydrocarbon material capable of injecting electrons into said second surface upon the application of a negative potential to said second electrode relative to a potential applied to said electrically conducting surface of the first electrode;

d. at least one of the said electrodes being in solid phase and transparent for the transmission therethrough of light generated in said light-generating material by recombination of said injected electrons with holes.

The single figure of the accompanying drawing shows diagrammatically and by way of example a cross section of one device constructed in accordance with the present invention.

This device comprises a base 10 of conducting glass; then a layer 11 of the active material; then a layer 12 of negative electrode material 12 held within a glass-retaining ring 13, if necessary; and finally a body of encapsulating wax 14. Leads 15 and 16 connect to external terminals to which either relative positive or negative direct voltage is applied as illustrated.

That is the glass 10 will always be positive relatively to the electrode 12, the potential of these parts relative to ground being unimportant.

The base 10 is of glass, at least the upper surface of which has been made conducting by one of the known surface treatment methods, to form a first electrode. Alternatively, this conducting glass surface electrode can be replaced by silver or gold paste. However, since these materials are opaque, they would have to be constructed with windows to permit the light emission.

The light-generating active material 11 should be kept as thin as possible, since the light generated is proportional to the current, and the current is proportional to the square of the voltage and inversely as the cube of the thickness of the material. A thickness of the order of 1 to 200 microns is preferred. This active material may take the form of a crystal or may be in powder or other form. For example, the following materials have been used satisfactorily as the active material:

a. Anthracene sublimation flakes.

b. Anthracene melt grown single crystals.

c. Anthracene powder.

d. Anthracene powder in a matrix of methyl methacrylate plastic.

e. Naphthalene sublimation flakes.

The chemical form should be of high purity for maximum emission intensity, and, although anthracene and naphthalene have been taken as the most convenient and readily available substances, the active material can theoretically be any aromatic hydrocarbon in a relatively pure chemical form. In practice, however, only those materials having a high quantum efficiency of fluorescence can be used with advantage.

The electrode material 12 will preferably consist of solid material made by evaporation from a solution containing negative ions of a hydrocarbon similar to that used as the active material. For example, if the active material 11 is anthracene, the electrode material 12 can be the evaporation product of anthracene dissolved in a solvent such as will produce stable negative anthracene ions, e.g. tetrahydrofuran, dimethoxyethane, dimethyl sulfoxide or dimethyl formamide.

The material can be prepared by interacting the solution with metallic sodium or other alkali metal, care being taken to keep the material under an inert atmosphere such as nitrogen during production. Direct production of this electrode material 12 by reduction of the active material 11 at its surface is also possible by sublimation of the reductant, e.g. sodium metal.

If the active material 11 is naphthalene, the electrode material 12 can likewise be a similar evaporated product of a negative ion producing solution of naphthalene. While it is convenient to use the same hydrocarbon for both materials this is not essential. For example, the electrode material 12 can be naphthalene or tetracen while the active material 11 is anthracene.

The retaining ring 13 is solely physical in function and will be unnecessary if the electrode material 12 is deposited upon the light-emitting material surface by other techniques, e.g. sublimation. The wax 14 can be replaced by any other inert substance or means for preventing access of air.

Upon application of the relative voltages shown, light is emitted downwardly either through the glass base 10 or upwardly through the electrode material 12 and wax 14, if these are sufficiently transparent, or in both directions. There will also be emission from the edges of the active material 11 unless this is deliberately discouraged by some opaque material.

The wavelength of the emitted light may be varied by the choice of hydrocarbon for the active material. Naphthalene will emit in the ultraviolet range mainly from approximately 3500 to 4000A., and anthracene in the blue range mainly from approximately 4000 down to 3000A. Wavelength changes can be achieved by doping. For example, anthracene doped with one part per million of tetracene gives a green-blue emission at approximately 4800-5000A. It has also been found that color...
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variations can be obtained by varying the voltage or the dopant concentration.

If the externally applied potential is reversed, virtually no current flows, so that the device acts as a rectifier. The forward and reverse current ratio is of the order of $10^9$.

Under the condition of flow of injected electrons from the second electrode 12 to the first electrode 10 the latter must be able to supply sufficient holes to recombine with a sufficient number of electrons to produce the required intensity of electroluminescence. Many electrode materials satisfy this criteria, for example conducting glass, silver paste and gold paste. If there is substituted a solid substance capable of injecting holes into the lower surface of the active material 11, for example anthracene positive ions or naphthalene positive ions, a current will flow, light will be generated, and also a rectifying action will be observed. The positive ion electrodes, however, are opaque and only permit light emitted from the sides of the device to be observed.

We claim:

1. An electroluminescent device comprising:
   a. a thin body of light-generating, aromatic, electrically non-conducting, hydrocarbon material,
   b. a first solid phase electrode having an electrically conducting surface contacting a first surface of said light-generating material,
   c. a second solid phase electrode contacting a second surface of said light-generating material, said second electrode containing negative ions of an aromatic hydrocarbon material capable of injecting electrons into said second surface when a potential is applied to said second electrode relative to a potential applied to said electrically conducting surface of the first electrode, and
   d. at least one of said electrodes being transparent for the transmission therethrough of light generated in said light-generating material by recombination of said injected electrons with holes.

2. A device according to claim 1, wherein said light-generating material is anthracene and said second electrode includes negative anthracene ions.

3. A device according to claim 1, wherein said light-generating material is anthracene and said second electrode includes negative naphthalene ions.

4. A device according to claim 1, wherein said light-generating material is anthracene and said second electrode includes negative tetracene ions.

5. A device according to claim 1, wherein said light-generating material is anthracene and said second electrode includes negative tetracene ions.

6. A device according to claim 1, wherein said first electrode is formed of electrically conducting glass.

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