

Spectrum of anode galvanoluminescence of aluminum

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It is shown that the anode galvanoluminescence spectrum of aluminum in a nonaqueous electrolyte does not depend on the impurities in the metal. It is indicated that the hypotheses advanced so far concerning the nature of this phenomenon are not consistent.

The anode galvanoluminescence (AG) spectrum of aluminum has been investigated so far by many workers^[1-9] only in aqueous solutions. We therefore deemed it of interest to plot the AG spectrum in a non-aqueous electrolyte. Our investigations, however, have led to unexpected results, which cast doubts on the existing concepts concerning the physical nature of this phenomenon.

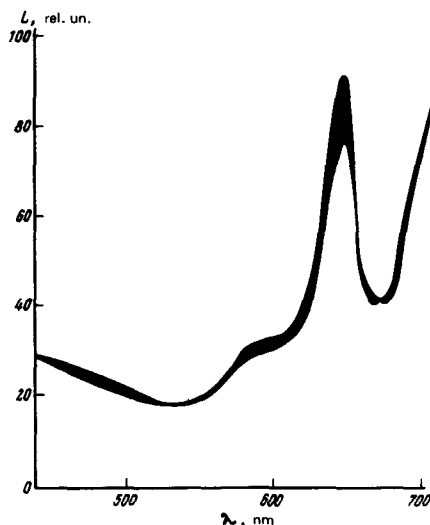
We used aluminum of different purity: ultrapure (99.999% Al) and technical (99.62% Al, 0.20% Fe, 0.15% Si, 0.02% Cu, 0.04% Mn + Mg).

To select a suitable electrolyte, the measurements were performed in different non-aqueous solutions used as non-dissolving electrolytes in capacitor manufacture. We selected a 0.5 N solution of adipinate in ethylene-glycol, in which the luminescence was of relatively high intensity. The AG was investigated with the electrolyte thermostatically controlled (10 °C) and stirred, and a constant current density (10 mA/cm²), was maintained with an electronic galvanostat. The anodizing process was stopped at voltages 10–20 V lower than the sparking voltage. The spectra of the emitted light were recorded by the well known method of cumulative quantitative spectrography. We used a spectrograph with glass optics and an effective dispersion (mm/nm) of 1.8 (at 450 nm), 0.8 (550 nm), and 0.35 (650 nm), respectively. The AG spectra together with the reference lines from a mercury or a sodium lamp were photographed on ultrasensitive panchromatic film (Kodak 2475) and interpreted with an automatic plotting microdensitometer (Joyce-Loebl MK-111-C). The customary corrections were introduced for the spectral sensitivity of the employed photographic film and for the nonlinear distribution of the exposure. The intrinsic absorption of the light-filtering electrolyte, determined with an automatic recording spectrophotometer (Perkin-Elmer 137-UV) turned out to be quite negligible in the visible region. The AG was taken from many electrodes in order to accumulate a sufficient exposure.

As seen from the figure, there is no difference in the spectral distributions of the emission energies of the AG for both types of aluminum. In other words, the AG spectrum is not peculiar to the impurities contained in the main metal, in contrast to statements made by a number of authors.^[1-4] In addition, the spectral distribution of the AG intensity, plotted with the same exposure (12 hours) and represented in identical relative units, indicates that the intensities are commensurate, in spite of the fact that in technical aluminum the content of impurities is larger by hundreds of times than in the "pure" aluminum. All this contradicts the experi-

mental results that illustrate the connection between the spectrum and the impurities of the metal.^[1-4] Nor does it agree with the electroluminescence model of AG, which for a long time has been regarded as firmly established.^[5] According to this model, the AG occurs in the anode oxide film that coats the metal, and the radiative recombination is generated by the impurities that penetrate into the oxide (a review is given in^[4,5]).

In fact, our results agree with the recently published papers in which independence of the spectrum of the impurities was first noted, as well as the fact that the spectrum is identical for different metals (Al, Ta, Zr, Sr).^[6-9] Nor is there a difference in the spectral distribution of the light emission when different non-dissolving electrolytes are used,^[7] including electrolytes that introduce anions into the formed anode film.^[9] On this basis, a hypothesis has been advanced that the AG is a certain form of electrically-generated chemiluminescence connected with a process that is independent of the chemical nature of the electrolyte.^[6-9] It should be noted, however, that the AG spectrum observed by us differs to a considerable degree from the spectrum proposed as "universal" for "non-dissolving" aqueous electrolytes. Since the non-aqueous electrolyte used by us was non-dissolving, we must reject the statement that the AG spectrum is independent of the type of electrolyte. On the other hand, it is also necessary to forgo the possibility of regarding AG as electrically-generated chemiluminescence, since this contradicts the dependence of the AG brightness on the thickness of the oxide



Spectral distribution of the galvanoluminescence for ultrapure and technical aluminum.

film of the metal, which was confirmed many times^[5] and has so far given no cause for doubt.

In conclusion it can be stated that the results cannot be explained within the framework of the existing hypotheses concerning the origin and mechanism of the AG, and that a serious reversion of these hypotheses is necessary.

¹M. Zentnerszwer and K. Guminski, *Fund. Radiol.* **4**, 18 (1939).

²Z. Ruziewicz, *Bull. Acad. Polon. Sci. C1* **3**, 8, 661 (1960).

³W. P. Ganley, P. M. Mooney, and D. Huminik, *Thin Solid Films* **3**, 337 (1969).

⁴W. P. Ganley, *Thin Solid Films* **11**, 91 (1972).

⁵H. F. Ivey, *Electroluminescence and Related Effects*, Academic Press, New York (1963).

⁶L. L. Odynets and Yu. E. Gardin, *Izv. Vyssh. Uchenb. Zaved. Ser. Fiz.* **13**, 151 (1970).

⁷Yu. E. Gardin and L. L. Odynets, in: *Elektrolyuminestsentsiya tverdykh tel* (Electroluminescence of Solids), Nauka, Kiev (1971), p. 215.

⁸Yu. E. Gardin, V. M. Kulabykhov, L. L. Odynets, and G. A. Pershina, *Élektrokhimiya* **7**, 1184 (1971).

⁹Yu. E. Gardin, V. M. Kulabykhov, and V. A. Legostaev, *Élektronnaya tekhnika Ser. 5*, **27**, 83 (1972).