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Characteristic luminescence of mercury and mercury-like ions at electrodes covered with insulating films

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Intense electrogenerated luminescence of tin, indium and mercury at Al/Al$_2$O$_3$, Be/BeO, Mg/MgO and Mg/MgF$_2$ electrodes was observed, and a mechanism of direct excitation of mercury-like centres by reduction with hot electrons was proposed.

Cathodic polarisation of insulating film-coated electrodes proceeds with the participation of hot electrons, and these processes can result in light emission.[1] Because of the barrier properties of Al$_2$O$_3$, ac electrolysis with an aluminium electrode is a versatile technique for generating electroluminescence (EL).[2–7] Various heavy metals can exhibit EL at Al/Al$_2$O$_3$. Indium,[7] tin[8] and mercury[3,5,9] show the most intense emission. An attempt to induce EL of these activators at different insulator-covered electrodes is undertaken here. The dependence of EL on the electrode material has two basic aspects. First, the energetic structure of a barrier layer determines the type of the energy distribution function of cathodic electrons. In some sense the alternation of electrode materials in the case of EL is similar to a shift of the wavelength of excitation light in the case of photoluminescence (PL). Second for, In, Sn and Hg, the barrier layer probably plays a role of the base of a surface phosphor.[7] It is known that hydrated In, Sn and Hg ions do not exhibit PL at room temperature. Therefore, it seems reasonable that the EL of these metals is a solid-state electroluminescence and strongly depends on the nature of an insulating film.

Preliminary experiments with Al/Al$_2$O$_3$, Mg/MgO, Mg/MgF$_2$, Be/BeO, Ca/CaF$_2$, Y/Y$_2$O$_3$ and Zr/ZrO$_2$ revealed that only aluminium, magnesium and beryllium electrodes are suitable for inducing the characteristic EL of tin, indium and mercury. Thus, only the results concerning Al/Al$_2$O$_3$, Mg/MgO, Mg/MgF$_2$ and Be/BeO will be discussed below. Note that Mg/MgF$_2$ and Be/BeO electrodes were not used for EL generation before. A Mg/MgO electrode was utilised to induce electrochemiluminescence.[10]

The three-electrode electrochemical cell (Figure 1) in a quartz cuvette *1* was positioned in front of a MDR-3 monochromator. Working electrode *2* (99.99% Al, 99.985% Mg or 99.98% Be) was fixed against a 8 mm diameter window in the wall of Teflon sample holder *3* by Teflon screw *4*. Graphite rod *5* was used as an auxiliary electrode. Working and auxiliary electrode compartments were separated by sample holder *3*. All potentials were measured against a saturated Ag/AgCl reference electrode. Rectangular potential pulses were applied to the EL cell using a PI-50-1.1 potentiostat. In some cases continuous ac electrolysis was used, or 0.5 s periods of electrolysis were alternated with 5 s pauses. The response of a PM tube was recorded with an L154 PC data acquisition board. The integrated signal from a fixed number (several hundreds) of cathodic pulses was used as the EL intensity in spectra. The spectra were measured in a range from 300 to 700 nm and corrected for the spectral sensitivity of the recording system.

A preliminary deposition procedure[9] was used to study the EL of mercury at Mg/MgO and Al/Al$_2$O$_3$ electrodes. After cementation of mercury from a 0.001 M Hg(NO$_3$)$_2$ solution in 0.5 M NaCl, the electrode was washed with distilled water and transferred to a cell filled with 0.02 M NaBrO$_3$ for EL generation. In all other cases an activator was added directly to the solution in which the EL generation was carried out.

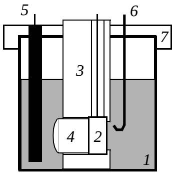

Figure 1 Schematic diagram of the EL cell: (*1*) quartz cuvette, (2) working electrode, (*3*) sample holder, (*4*) screw, (*5*) auxiliary electrode, (*6*) Luggin capillary, (*7*) cover.

The conditions of EL generation (Table 1) were optimised to provide the most intense and stable luminescence. The most intense emission (systems 1, 2 and 4) was visible in daylight. The cathodic current densities varied from less than 0.03 A cm^{-2} for bromate solutions (systems 7 and 9) or 0.2 A cm^{-2} for ammonium fluoride solutions (systems 3, 5 and 8) to 1 A cm^{-2} for H$_3$PO$_4$ solutions (systems 1, 2 and 4).

It is impossible to induce the EL of Sn and In at Mg/MgO because, on the one hand, the hydrolysis of Sn^{II}, Sn^{IV} and In^{III} inhibits the generation, and, on the other hand, MgO is readily soluble in acids. Thus, only a Mg/MgF$_2$ electrode can be used for the generation of Sn and In electroluminescence.

As can be seen in Figure 2 and Table 1, the spectra and intensities of the EL of Al$_2$O$_3$–Sn (curve *1*) and BeO–Sn (curve *2*) practically coincide. Note that the EL spectra are very similar to the PL spectra[12] of solid phosphates doped with Sn^{2+}. It seems reasonable that Sn^{2+}, which is extensively used as an activator in phosphors, also acts as an emitter in the case of EL. The maximum of the MgF$_2$–Sn spectrum (curve *3*) is shifted by about 30 nm towards the short-wave region. This fact is probably associated with a fluoride environment of Sn^{2+} in this system.

The EL spectrum of indium is complex and can vary depending on experimental conditions.[7] As Figure 2 indicates, the spectra of Al$_2$O$_3$–In (curve *4*) and MgF$_2$–In (curve *5*) contain strong blue components and weak yellow components that manifest themselves as shoulders. The EL spectrum of BeO–In (curve *6*) has a maximum at 580 nm, which corresponds to the shoulders in curves *4* and *5*, whereas there are no peaks in the blue–green region in curve *6*. As follows from a comparison with the PL data,[13,14] the blue component is associated with the 5*sp* → 5*s*^{2} transition in In$^+$. The yellow component appears to be associated with the luminescence of In^{2+}. This assumption is in agreement with the results of PL measurements carried out in glasses doped with In$^+$ under conditions of powerful laser irradiation.[14] It was found that an increase of the yellow component in PL spectra corresponds to the production of In^{2+}, which results from the photoionization of In$^+$ centres.[14]

The EL of mercury can be observed at Al/Al$_2$O$_3$, Mg/MgF$_2$ and Mg/MgO electrodes rather than at a Be/BeO electrode. As Table 1 indicates the intensity of EL is maximum for Mg/MgF$_2$ and minimum for Mg/MgO. The spectra of Al$_2$O$_3$–Hg (Figure 2, curve *7*) and MgF$_2$–Hg (Figure 2, curve *8*) are rather similar, whereas in the spectrum of Mg/MgO–Hg (Figure 2, curve *9*) the peak is strongly broadened and shifted to the long-wave region. The similarity of curves *7* and *8* and the dissimilarity of curves *7* and *9* are surprising when it is considered that the initial forms in which mercury was introduced are different for the first couple of curves and coincide for the second one (Table 1).

Meulenkamp *et al.* suggested[5] that the Hg^{2+} cation is responsible for the EL at an Al/Al$_2$O$_3$ electrode. However, as distinct from other *d*^{10} ions, there is no information on the PL of Hg^{2+}. In our opinion,[9] the mercury atom with the *d*^{10}*s*^{2} structure produces EL. The fact that the EL intensity of mercury is at least

Table 1 Conditions of EL generation.

no.	Barrier film–activator	Cathodic pulse		Anodic pulse		Solution	Intensity (arbitrary units)
		Length/ms	Potential/V	Length/ms	Potential/V		
1	Al_2O_3–Sn	5	–6	5	3	0.01 M Sn^{IV} in 1 M H_3PO_4	12
2	BeO–Sn	1	–7	0.5	4.5	0.005 M Sn^{IV} in 0.2 M H_3PO_4	12
3	MgF_2–Sn	1	–8	1	1	0.002 M In^{III} in 0.35 M $NH_4F\cdot HF$	3
4	Al_2O_3–In	5	–6	5	3	0.02 M In^{III} in 1 M H_3PO_4	15
5	MgF_2–In	1	–8	0.5	2.5	0.002 M In^{III} in 0.35 M $NH_4F\cdot HF$	2
6	BeO–In	2	–8	1	5	0.02 M In^{III} in 1 M H_3PO_4	3
7	Al_2O_3–Hg	5	–8	5	4	Hg film at Al in 0.02 M $NaBrO_3$	4
8	MgF_2–Hg	1	–8	0.5	0.5	0.001 M $Hg(NO_3)_2$ in 0.35 M $NH_4F\cdot HF$	5
9	MgO–Hg	5	–8	1	8	Hg film at Mg in 0.02 M $NaBrO_3$	1

by two orders of magnitude higher than that for other d^{10} emitters[5] and is close to that of $d^{10}s^2$ ions is evidence in favour of this assumption. The production of excited mercury atoms and excited mercury-like ions (Sn^{2+} and In^+), apparently, proceeds as the reduction of oxidised species with the d^{10} structure (Hg^{II}, Sn^{IV} and In^{III}) by hot electrons according to the scheme:

$$\begin{tikzcd}
 & d^{10}p \arrow[rr, "e"] \arrow[dr, "I"] & & d^{10}sp \arrow[dr, "II"] & \\
d^{10} \arrow[ur, "e^*"] \arrow[rr, "e"'] & & d^{10}s \arrow[ur, "e^*"] \arrow[rr, "e"'] & & d^{10}s^2
\end{tikzcd}$$

When mercury is introduced as Hg^0, an oxidant is required for EL generation. The active intermediate products of bromate reduction convert Hg^0 into Hg^{2+}; next, the above scheme is valid.

Thus, two ways can lead to light emission. Way I appears to be of secondary importance with respect to way II, because of very short lifetimes of intermediate species (Sn^{3+}, In^{2+} or Hg^+). Nevertheless, the contribution of In^{2+} to the EL spectrum is significant. As there is no information on the Sn^{3+} or Hg^+ luminescence, we assume that Sn^{2+} or Hg^0 are the main EL emitters. Because luminescence centres are localised in a solid insulating film, it is reasonable to expect that EL is sensitive to its properties. This sensitivity is evident in comparison of the EL at a Be/BeO electrode with other cases. Mercury does not exhibit EL at a Be/BeO electrode, and the spectrum of BeO–In (Figure 2, curve *6*) dramatically differs from the spectra of Al_2O_3–In (curve *4*) and MgF_2–In (curve *5*). This is likely due to great differences in size between a very small Be^{2+} cation (0.034 nm) and rather large Hg^{2+} (0.11 nm) and In^{3+} (0.092 nm) cations, which makes their incorporation into a BeO lattice difficult. The Sn^{4+} cation appears to exhibit a rather small size (0.067 nm) to enter into a BeO film. The surprising thing is that the structural selectivity is observed only in the case of a drastic difference in size between host and guest cations. Probably, an easy incorporation of guest cations into a barrier layer is facilitated by defects produced by impacts of hot electrons. Moreover, during a cathodic pulse, the entry of guest cations into the film is promoted by a high electric field. Note that a high electric field strength (several V nm^{-1}) can result in a significant Stark effect on EL spectra.

Thus, not only an Al/Al_2O_3 electrode is appropriate to induce the EL of mercury-like species. In our opinion, the EL of mercury-like species at insulating film-coated electrodes is a special type of recombination luminescence that occurred in thin solid layers when electrons injected from a metal directly interact with d^{10} cations sorbed from the solution. By now, the elements exhibiting EL upon electrochemical reduction from d^{10} to $d^{10}s^2$ species are Hg, Sn, Pb, Ga, In and Tl,[3,5,6] and it is likely that this range will be extended.

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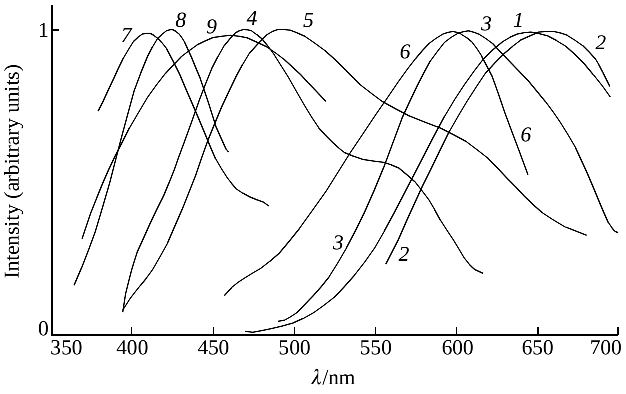

Figure 2 EL spectra (curve numbers correspond to those in Table 1).

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