SPECTROSCOPIC STUDIES OF LUMINESCENCE AT THE CATHODE DURING ELECTROLYSIS.

By Iturô UHARA.

Received August 9th, 1935. Published December 28th, 1935.

Luminescence has been observed during electrolysis in many cases, mostly at the anode, and it is attributed to the formation of a thin film of insoluble matters, for examples, oxide, hydroxide, oxygen on aluminium electrode, mercurous chloride on the surface of mercury; and the spectra are continuous. There are a few examples of luminescence at the cathode. M. Fraymann[1] observed that, when a sulphuric acid solution was electrolysed in high current density with various metals as the cathode, arc lines of the metals and H_α- and often H_β-lines were emitted by sparking through the film of hydrogen on the cathode. A. W. Dumanski and his co-workers[2]

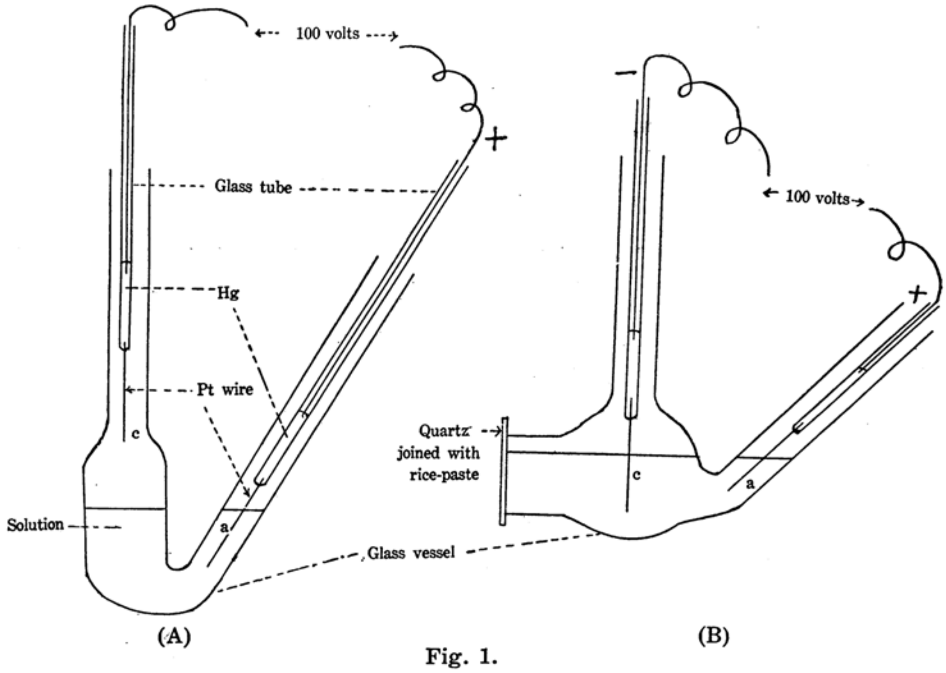

Fig. 1.

(1) M. Fraymann, *Recherches et Inventions*, **11**, 36–41; *Chem. Zentr.*, **101** (1930), I 1902.

(2) A. W. Dumanski, A. W. Banow, M. W. Lichoscherstow, *Chem. J. Ser. W. J. physik. Chem.*, **2** (1931), 806–813; *Chem. Zentr.*, **104** (1933), II, 1307.

observed very weak luminescence when the current was reversed during electrolysis of the solutions of zinc chloride, etc., with mercury electrodes, and calcium salts and magnesium nitrate with platinum electrodes; and he remarked that this was not explicable as an oxidation reaction as in the cases of luminescence at the anode.

The writer observed luminescence at the cathode during electrolysis of the solutions of many electrolytes with electrodes of platinum wire, and studied the spectra. The apparatus for electrolysis is shown in Fig. 1(A).

The solutions of Merck's and Kahlbaum's products in the concentration of 1–3 N, or 1.5–1 N for acid solutions, were electrolysed. When the platinum electrode (c) was immersed quietly in the solution, scintillation took place over the surface of the electrode with hydrogen evolution and noise. When the voltage was too low, or when the solution was too dilute, or when the circuit was closed after the cathode (c) was immersed in the solution, only violent electrolysis was observed. This suggests that the formation of a thin film of hydrogen over the cathode under high current density is necessary. The spectra of luminescence were studied under the following conditions with Hilger's glass spectrograph of constant deviation type: current 0.2–0.5 amperes or more; current density 0.6–1.5 amperes per sq. cm. or more; slit about 0.2 mm.; photographic plates Wratten hypersensitive panchromatic plates; exposure one hour (for intense lines like D-line from sodium salt solutions a few minutes is sufficient). The temperature of the solution rose to about 80°.

The spectra obtained consist of sharp lines and are independent of the anions (NaCl, $NaNO_3$, NaOH, and Na_2CO_3 gave the same spectra). Sometimes Na^+ and Ca^{++} go into the solution from the glass vessel during electrolysis and give their lines. The spectra are shown in Fig. 2, and the wave

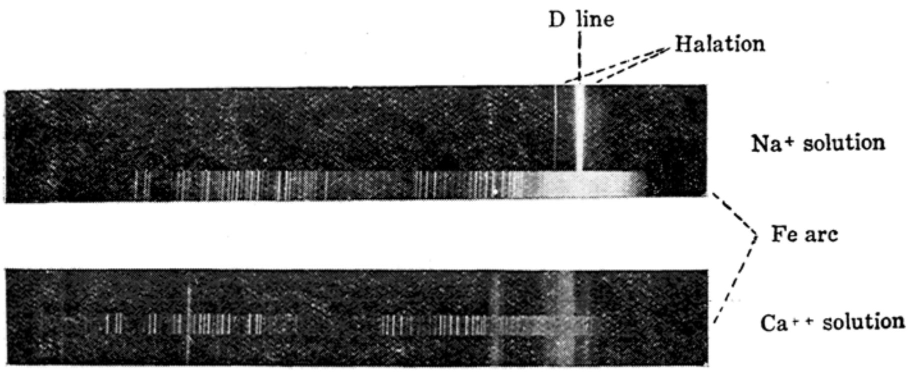

Fig. 2.

lengths (Å) of the observed lines are given in Table 1 (intensity is shown by asterisks).

Table 1.

Na^+ Solution.

Lines	Remarks
5890***, 4985, 4670, 5690**, 6164*	Due to Na I
6563* (H_α), 4860(H_β)	Due to H I
4227, 5140	Due to Ca I
3830	Due to Mg I

K^+ Solution.

4608, 4388, 4309, 4263, 4226, 4135, 4115	Spark lines of K
6563** (H_α), 4861* (H_β)	Due to H I
4849, 4654*	Due to H_2
5890**	Due to Na I
4418	Due to O(?); Kayser's table: O 4416.97; H_2 4412.25
4353	Kayser's table: Mg I 4352.1; O II 4351.38
4370	Kayser's table: O II 4369.28; O I 4368.30; Cs 4373.0
4593	Kayser's table: O II 4596.19, 4590.98; Cs 4593.2
4647	Kayser's table: O II 4649.15; Rb 4648.56
4829	Kayser's table: Cs 4830.2
4838	?

HCl Solution.

6563** (H_α), 4860 (H_β), 4340 (H_γ)	Due to H I
6032, 6327, 4491*, 4205*	Due to H_2
4520, 4548, 4165, 4120	Due to Pt; sometimes black powder of platinum is precipitated.
5896, 5688	Due to Na I
5855, 5270**, 5041, 4435	Due to Ca I
4150	Kayser's table: O II 4153.31; Al III 4150.1
6318	Due to Mg I

Table 1 (*Concluded*).

NH_4^+ Solution.

Lines	Remarks
6530* (H_α), 4860 (H_β), 4340 (H_γ)	Due to H I
5435, 4490, 5055, 4205	Due to H_2
4548	Due to Pt
6550	Due to O(?)
5270, 5350, 5140, 4455	Due to Ca

Ca^{++} Solution.

6494*, 6472**, 6470**, 6439**, 6162*, 6122*, 5858*, 5595**, 5589**, 5350, 5270**, 5189, 5042, 4878, 4586, 4455**, 4435**, 4426**, 4308*, 4303**, 4290*, 4227*	Due to Ca I
3969*, 3934*	Due to Ca II
6563(H_α)	Due to H I
5537**, 5505*, 6135*	Due to H_2
5890, 5688	Due to Na I
4390	Due to Mg II (?)
5455	Kayser's table : Sr I 5450.83 ; Hg I 5460.724

$Hg(NO_3)_2+HNO_3$ Solution.

5791, 5770, 5461**, 4358*	Due to Hg I
5890**	Due to Na I

To study the ultraviolet region an apparatus as shown in Fig. 1 (B) and Hilger's quartz spectrograph were used. Lines of metals and hydrogen were observed, but OH-band was not (this band was not observed when carbon arc was lit in hydrogen which had been passed through boiling water under one atmospheric pressure).

In electrolysis with the alternating current (100 volts) luminescence takes place sometimes on both electrodes, sometimes on one electrode of higher current density. Even with the solutions of those metallic salts (e.g. aluminium and magnesium salts) which give weak luminescence, or such luminescence as disappears in the course of time, owing to the formation of insoluble hydroxide in the electrolysis with the direct current, we can observe luminescence for a long time in electrolysis with the alternating current. The spectra are the same as in the case of the direct current.

Solutions of Ba^{++}, Sr^{++}, Mg^{++}, Al^{+++}, Cd^{++}, Zn^{++}, Hg_2^{++}, Fe^{++}, Co^{++}, Mn^{++}, Bi^{+++}, and Sn^{++} gave those lines which are observed in their arc spectra.

Summary.

If the current density at the cathode is high enough for the formation of a thin film of hydrogen in the electrolysis of the electrolyte solutions with platinum wire electrodes, considerably intense cathode luminescence takes place ; and the spectra are in most cases the same as the arc spetra (sometimes spark spectra) of the elements forming cations, and further Balmer lines of H and the molecular spectra of H_2 are often observed.

In conclusion the author wishes to express his best thanks to Mr. H. Wakesima for his kind advice and assistance and to Mr. A. Tamai and Mr. M. Nakamura for their assistance.

Taihoku Higher School.