

Chemical Effects of Cathodic Glow Electrolysis in Electrolytes Containing Oxidisable Substrates: Cathodic Oxidation of Iodide to Iodine

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Cathodic glow electrolysis of an aqueous iodide solution as a catholyte affords iodine at the luminescent cathode in an amount much in excess of 1 equiv./F. To explain this novel observation, a mechanism in terms of energy transfer following collisions between electrons and water molecules in the glow discharge region around the cathode, has been proposed.

Conventional electrolysis, at sufficiently high voltages, spontaneously switches over to a new phenomenon accompanied by luminescence at either cathode or anode¹. This phenomenon variously known as contact glow discharge electrolysis, glow electrolysis, galvanoluminescence or electrode effect, depends primarily upon the difference in resistivity between the two electrode-electrolyte interfacial areas². Highly interesting are the chemical results of the process³⁻⁵. The yield at the luminescent electrode is significantly higher than that stipulated by Faraday law, and the products obtained are novel in nature. Herein, are presented our results on oxidation by cathodic glow electrolysis of iodide ions to iodine. Though this is a preliminary report, to our knowledge no report has appeared so far about oxidising action of cathodic glow process.

Cathodic glow electrolysis was carried out under nitrogen atmosphere in a H-type pyrex cell (height = 15 cm; and diam of vertical limbs = 25 mm) fitted with a fine sintered-glass disc (diam = 10 mm) separating the electrode compartment, and with two gas outlets each being connected to a gas burette; other conditions were as follows: catholyte, 0.1 N KI in 1.0 N H₃PO₄ (50 ml); anolyte, 0.2 M Na₂SO₄ (50 ml); cathode, Pt wire (diam 0.35 mm, length 8 mm); anode, Pt foil (area 1 cm × 1 cm, thickness 0.05 mm); cell voltage, 300 V; current, ca. 0.1 A; pressure, atmospheric; ambient temperature 20 °C. The solutions used were deaerated before electrolysis. The quantity of electricity passed was measured by a Lingane-type hydrogen-oxygen coulometer. The amount of iodine formed in the catholyte was estimated spectrophotometrically using starch reagent. The hydrogen in cathode

Table 1—Effect of Quantity of Electricity on the Yield of Iodine by Oxidation of Iodide

Quantity of electricity (10 ⁻⁶ F)	Yield of iodine on oxidation of iodide (10 ⁻⁵ equiv.)	Quantity of electricity (10 ⁻⁶ F)	Yield of iodine on oxidation of iodide (10 ⁻⁵ equiv.)
4	1.85	24	8.28
6	2.77	30	9.20
9	4.16	35	9.66
12	5.49	40	9.89
15	6.39	45	10.00
18	7.13	50	10.00

gas was estimated by explosion method employing a separate unit.

Data on the yield of oxidation product (iodine) of iodide at the cathode for a series of glow electrolyses as a function of increasing quantity of electricity (Table 1) show that iodine is initially formed in an amount proportional to the quantity of electricity passed, but the yield is much in excess of 1 equiv./F. However, at larger quantities of electricity, the magnitude of increase in yield is much lower and finally the yield tends to be stationary.

The results closely fit Eq. (1).

$$\text{Yield of iodine} = A[1 - \exp(-G_0Q/A)] \quad \dots (1)$$

where G_0 is the initial differential yield; Q , the quantity of electricity passed; and A , a constant. The observed value of G_0 (I_2) = 4.6 equiv./F, which is vastly in excess of any oxidation yield possible by charge transfer process, clearly indicates the involvement of some other mechanism in the oxidation reaction. The equation describing the iodine yield is typical for the occurrence of two competing reactions, seemingly initial reaction of iodide with some oxidising species yielding an amount of iodine proportional to the quantity of electricity passed and decomposition or other reactions involving the oxidising species. It has been found that the initial differential yield of iodine is substantially independent of cathode material, its length and diameter. Variation of current in the range of 0.06 A to 0.12 A has no significant effect on the yield of iodine for 1×10^{-5} faraday passed. The dominant factor which governs the yield of oxidation at the cathode seems to be the quantity of electricity passed.

The evidence gathered so far suggests that during cathodic glow electrolysis, the cathode is isolated from the catholyte by being blanketed in a sac of plasma through which current passes by some glow discharge mechanism³. The sac at the cathode is composed of

electrolyte-entrained solvent vapour plus the ions, radicals and atoms produced by discharge through it. The trend is supported by results on spectral characteristics of cathode glow⁶. Each electron from the cathode **during** its transit through the discharge section activates several water molecules by collision and at **plasma-catholyte interface breaks up one water molecule by charge-transfer mechanism producing H_2** as per Faraday's law. The activated water molecules will dissociate into H and OH radicals. The OH radicals on **entry** to the catholyte interact among themselves giving H_2 , O_2 , H_2O_2 and some H_2O , as observed with inert-type electrolytes such as potassium sulphate³. However, when iodide ions are present in the catholyte, the latter will be oxidised by OH radicals as well as by H_2O_2 to iodine. The processes envisaged above, obviously predict formation of (i) iodine in more

than 1 equiv./F, and (ii) equivalent amount of H_2 over and above the H_2 formed by charge-transfer (1 equiv./F), from the cathode zone. This is actually found to be so by the analysis of the gaseous products at the cathode. It is also observed that the excess H_2 formed is equivalent to the iodine which itself, as pointed out, is formed in excess of 1 equiv./F, indicating maintenance of a satisfactory material balance.

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