Contact glow discharge electrolysis: a study of its chemical yields in aqueous inert-type electrolytes

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(Received 26 January 1993, in revised form 27 August 1993)

Abstract

A study of the chemical yields of contact glow discharge electrolysis (CGDE) at the anode in aqueous inert electrolytes at various quantities of electricity, applied voltages and electrolyte compositions shows that, for the passage of each mole of electrons, 0.25 mol of O₂ and more than 10 mol of both H₂ and H₂O₂ plus O₂ are produced at the anode when the glow discharges there are fully grown. Non-Faradaic yields may originate in two reaction zones: the anolyte near the plasma where liquid water molecules are broken up into H₂O₂, O₂ and H₂, and the plasma around the anode where gas phase dissociation of water molecules into H₂ and O₂ occurs. The former is important for anodic CGDE. Hickling’s radiolytic mechanism has been applied to interpret the chemical results of the liquid phase reaction zone. A comparative study of the chemical yields of anodic and cathodic CGDE indicates that the breakup of water molecules occurs entirely in the plasma during cathodic CGDE, but primarily in the liquid anolyte and partly in the plasma during the anodic phenomenon.

1. Introduction

Contact glow discharge electrolysis (CGDE) is a non-conventional electrochemical process in which a plasma is sustained by d.c. glow discharges between an electrode and the surface of the liquid electrolyte surrounding it. The phenomenon develops at either the anode or the cathode in a spontaneous transition from conventional normal electrolysis at sufficiently high voltages in aqueous, non-aqueous or molten media. A critical investigation of the growth of CGDE in aqueous media [1–3] has shown that the sequence of events leading to full or true CGDE involves normal electrolysis, solvent vaporization near an electrode by Joule heating, the onset of hydrodynamic instabilities with vapour sheathing the electrode and glow discharges across the vapour sheath. Furthermore, the electrode (i.e., anode or cathode) at which the conditions allow easier vaporization and easier onset of hydrodynamic instabilities has been found to be the location of CGDE. The critical voltage for the onset of full glow discharge at an electrode, called the mid-point voltage, is characteristically invariant to external variables. However, the mid-point voltage and the nature of the glow discharges at an anode are quite different from those at a cathode.

A remarkable characteristic of the phenomenon is the strong deviation of the chemical yield at the glow discharge electrode from that expected on the basis of Faraday’s law [2–8]. Moreover, the products obtained contain species novel for normal electrolysis. Thus the formation of H₂O₂ from H₂SO₄ and Fe³⁺ from an Fe²⁺ solution, with yields two and eight times respectively of those expected from Faraday’s law, during anodic CGDE at 450 V has been reported [2,3]. Large deviations have also been noted at a lower voltage of 220 V during cathodic CGDE of several aqueous inert-type electrolytes such as Na or K salts, which liberate cathode gases with volumes two to three times the Faraday law value and containing 15%–20% O₂ by volume [4]. However, the yields of anodic CGDE at 220 V in similar electrolytes show smaller deviations. The anode gases have volumes 1.1–1.5 times the Faraday law value and contain 7%–20% H₂ by volume [5]. In a further study on the chemical effects of CGDE, it has been found that cathodic CGDE of an I⁻ solution at 300 V can cause oxidation of I⁻ at a level of four times that expected from Faraday’s law [6]. Similar
non-Faradaic features have also been observed for the chemical effects of anodic CGDE in non-aqueous media, such as liquid ammonia [2,7], acetonitrile and dimethylformamide [8].

Such deviations from Faraday's law are also commonly observed during glow discharge electrolysis (GDE) of aqueous and non-aqueous electrolytes [2], a closely related phenomenon in which the glow discharge electrode is set up in the gas space above the liquid electrolyte. However, in the case of molten electrolytes, such deviations, although of significant magnitude in GDE [9,10], are not observed in CGDE [11].

It is usually considered that the yields in significant excess of the Faraday law value for the products of CGDE are due to reactions of the radicals generated by breakup of the solvent molecules in the glow discharges [2-8,12-18]. Indeed, the presence of H• and OH• radicals generated by GDE of aqueous solutions was confirmed by electron spin resonance (ESR) using 5,5-dimethylpyrrolidine-1-oxide as a spin trap [19]. Because of its potential for generating radicals in high local concentrations, CGDE has been used as a tool to synthesize compounds such as hydrazine [2,7], N,N-dimethylaminoacetonitrile [8] and amino acids [12-18].

The studies described above were primarily concerned with the yield of a particular product either in solution or in the gas phase. Moreover, the results were obtained for CGDE carried out at different voltages where the conditions of glow discharges vary [1]. Thus we cannot correlate the chemical yields of CGDE in solution and in the gas phase observed by different workers. Furthermore, although the solution phase yields of CGDE, such as H2O2, N2H4, Fe3+ etc., seem to originate in the solution near the plasma, it is not known whether the origin of the gas phase products, such as H2 and O2, is in the same solution near the plasma or within the plasma itself. A detailed study of the chemical yields of CGDE both in solution and in the gas phase is needed to determine the location of the reaction zones of CGDE and to elucidate the mechanisms of the reactions occurring there.

In this paper, we attempt to study systematically the formation of both gaseous products and products in solution during CGDE in aqueous media at various quantities of electricity, cell voltages and electrolyte compositions. To avoid complications from oxidation—reduction of electrolyte constituents, only inert-type electrolytes were employed. Furthermore, since CGDE is more stable when developed at an anode than at a cathode, the study concentrated on anodic CGDE rather than cathodic CGDE. The results were analysed critically to determine the location of the reaction zones of both anodic and cathodic CGDE and the mechanisms of the reactions.

2. Experimental

2.1 Cell set-up

A Corning H-type cell (height, 11 cm, diameter, 30 mm) with a bridge of length 4 cm (diameter, 15 mm), fitted with a G-5 sintered glass disc separator at a height of 1.5 cm from the base of the cell and two two-way stopcocks each fused to the base of the vertical limbs, was employed to study the chemical effects of CGDE. Into each of the vertical limbs was fitted a rubber bung carrying a platinum electrode sealed into a Corning tube (diameter, 5 mm), a thermometer and a gas exit capillary tube (internal diameter, 1 mm). The latter, in turn, was connected to a 25 ml gas burette (graduated at every 0.1 ml) containing K2SO4 solution where the gaseous products were collected and measured at atmospheric pressure and room temperature. The two-way stopcock at the base of each electrode compartment of the cell provided the outlet for the electrolysed solution as well as the inlet for filling up the cell with the electrolyte (pre-boiled to remove dissolved air) from a solution reservoir through vinyl tubing.

2.2 Cell operation

The electrode at which CGDE was carried out was a Pt wire (length, 5 mm, diameter, 0.35 mm) immersed at a depth of 3 cm from the electrolyte surface. The other electrode was a Pt foil (1 cm x 1 cm) with a thickness of 0.2 mm.

The electrode compartments were charged with 0.05 M K2SO4, the inert electrolyte of choice, however, the solution for the compartment in which CGDE was carried out was heated to approximately 80°C to ensure immediate formation of CGDE when the power was switched on at or above the mid-point voltage. Under these conditions, 420 V for anodic CGDE (mid-point voltage, 420 V [1]) and 240 V for cathodic CGDE (mid-point voltage, 160 V [1]) were found to be convenient. During CGDE, the temperature of the solution near the glow discharge electrode was self-maintained at 94 ± 1°C by the heat of the glow discharge.

The standard conditions described above for the applied voltage and electrolyte composition were varied when studying the effect of these variables on the chemical yields of CGDE.

The current was supplied from an Aplab 7322 medium voltage d.c. power supply which provided a maximum current of 1.5 A at voltages up to 600 V. The current passed through the cell and the voltage across it was measured using a Philips PM 2518X digital multimeter. During CGDE, the observed fluctuation in
current was within ±4 mA for anodic CGDE and ±15 mA for cathodic CGDE.

The quantity of electricity passed through the cell during CGDE was measured by an ESC 640 digital coulometer, the performance of which was checked against a Lingen-type H₂₋O₂ coulometer (fitted with large Pt foil electrodes and containing 0.5 M K₂SO₄).

2.3 Methods of analysis of the products of CGDE

The anodic CGDE of an aqueous inert electrolyte (K₂SO₄) was found to produce an anode gas of H₂₋O₂ and H₂O₂ in the anolyte (no H₂SO₃ or H₂S₂O₃ was detected). The cathodic CGDE also produced a liberal mixture of H₂ and O₂ at the cathode, however, it did not give rise to any product in the catholyte.

The gases produced at the glow discharge electrode were analysed using a modified form of the precision model Haldane gas analysis apparatus. The gas collected in the gas burette attached to the H-type electrolysis cell was transferred in 9 ml aliquots to a uniform bore 10 ml gas burette (thermostatically controlled in a water jacket) graduated at every 0.02 ml. O₂ was measured by absorption in alkaline pyrogallol and H₂ was analysed in the combustion unit of the apparatus after mixing with a definite volume of O₂. The volume of H₂ so determined was found to be equal to the volume of the total gas minus the volume absorbed by alkaline pyrogallol.

The H₂O₂ produced in the anolyte of anodic CGDE was estimated by titrating a 20 ml aliquot of the electrolysed solution from the anode compartment with a standardized 0.002 M KMnO₄ solution in 1M H₂SO₄.

3. Results

The chemical yields of anodic CGDE under the standard conditions showed strong deviations from Faraday’s law. The yields of both O₂ and H₂ evolved at the glow discharge anode were substantially larger than those calculated from Faraday’s law and H₂O₂ formed in the anolyte was in similarly greater yields initially. However, the yield of H₂ at the counterelectrode during anodic CGDE was as stipulated by Faraday’s law. The magnitudes of the yields of the products at the glow discharge anode were found to be influenced considerably by the quantity of electricity passed and the voltage applied.

3.1 Effect of quantity of electricity

The yield (in moles) of each of the anodic products O₂, H₂O₂ and H₂ increased with the quantity of electricity (expressed as the number of moles of electrons) passed (Figs 1, 2 and 3). The most appropriate way of expressing the yield of a product of CGDE is by quoting its differential yield which measures the instantaneous rate of formation of the product at a particular point in electrolysis when the concentration of the substances in the solution can be specified. The differential yield of a product x is conveniently represented by a dimensionless quantity, G(x), defined as the ratio of the yield (mol per mol electron) observed to the yield (mol per mol electron) stipulated by Faraday’s law. The magnitude of the yield of O₂ was as stipulated by Faraday’s law (Figs 1 and 2). The magnitudes of the yields of H₂ were considerably influenced by the quantity of electricity passed (Fig. 3).

![Graph](image-url)
day's law, the faradaic yield $G(H_2)$ is constant at 2.35 over the range of electricity passed (Fig 3) whereas $G(O_2)$ rises from an initial value of 1.8 to 3.0 (Fig 1) On the other hand, $G(H_2O_2)$ from an initial value of 1.8 continues to fall until the integral yield of $H_2O_2$ reaches a limiting value (Fig 2) However, $G([H_2O_2 + O_2]^E)$, where $O_2^E$ is the $O_2$ in excess of the Faraday law value, is constant at 2.20 (Fig 3) and interestingly quite close to $G(H_2)$, showing the maintenance of a more or less satisfactory material balance (within +5%) between the yields of $H_2$ and the sum of the yields of $H_2O_2$ and $O_2^E$ among the anodic products Thus CGDE of an aqueous inert electrolyte under the standard conditions produces, at the glow discharge anode, more than twice the Faraday law value of $H_2$ and $H_2O_2$ plus $O_2^E$ obviously by the breakup of water molecules by a certain mechanism over and above the $O_2$ produced by the normal electrolytic charge transfer mechanism

An examination of the yield curves of $O_2$ (Fig 1) and $H_2O_2$ (Fig 2) suggests strongly that, during CGDE, $H_2O_2$ forms in the anolyte initially at a rate proportional to the current passed, starts to decompose on accumulation into $O_2$ ($G(H_2O_2)$ decreasing and $G(O_2)$ increasing) and finally attains a stationary concentration when its rates of formation and decomposition become equal It is reasonable to anticipate that the precursors of $H_2O_2$ might trigger its decomposition Assuming that the rate of $H_2O_2$ decomposition is proportional to both its concentration $[H_2O_2]$ and the current passed ($I$), the rate equation for the net formation of $H_2O_2$ can be written as

$$\frac{d(H_2O_2)}{dt} = nG_0 \frac{I}{F} - nG_0 \frac{I}{F} k[H_2O_2]$$

(1)

where $(H_2O_2)$ is the integral yield, $G_0$ is the initial $G$ value, $n$ is the faradaic yield (mol per mol electron) and $k$ is a coefficient for the decomposition reaction On integration and applying the condition $(H_2O_2) = 0$ at $t = 0$, Eqn (1) becomes

$$(H_2O_2) = (1 - e^{-nG_0q/V})^k$$

(2)

where $V$ is the volume of the anolyte and $q$ is the number of moles of electrons passed Two limiting cases of the equation are as follows when $q$ is small, $(H_2O_2) = nG_0q$ and the yield increases linearly with the quantity of electricity passed, when $q$ is large, $(H_2O_2) = V/k$ or $[H_2O_2] = 1/k$ and a steady state is attained Equation (2) was tested using the experimental values of $G_0$ (from the tangent to the yield curve at the origin, Fig 2) and $V/k$ (from the steady state value of $(H_2O_2)$ in the curve) and fits the experimental results quite closely (Fig 2) Similar close matching of the experimental yield values of $H_2O_2$ by GDE of $Na_3HPO_4$ with the calculated values from eqn (2) has been reported [2] Indeed, there are similarities between the chemical effects of CGDE, GDE and spark electrolysis [2] at an anode

3.2 Effect of applied voltage

The electrolysis of 0.05 M $K_2SO_4$ at increasing voltage under otherwise standard conditions passes through normal electrolysis (up to 125 V), an unstable transition period (125-160 V), a Kellogg region (160-420 V) over which anodic CGDE originates and increases gradually to full glow discharge conditions and true CGDE at 420 V (mid-point voltage) and beyond, (although above 520 V the platinum wire anode shows signs of melting) [1-3] Furthermore, the anodic yields of $H_2$, $O_2^E$ and $H_2O_2$ are insignificant for CGDE at voltages below 250 V Thus the influence of voltage on the non-faradaic yields of anodic CGDE can be studied only over 250-520 V

The nature of the variation of these yields with voltage is remarkable The integral yield of $H_2$ or $O_2^E$ when normalized for 1 mol of electrons and expressed as $n$, is less than 0.05 at 250 V and rises very slowly up to 400 V, whereas $H_2O_2$ does not form to any substantial extent over this voltage range However, between 400 and 500 V an abrupt increase in the yield of each of the three products occurs, followed by an almost stationary yield (Fig 4) The steepest rise in the yield occurs between 410 and 420 V for all the products
This inflexion occurs more sharply when the initial differential yield \(G_0\) of \(\text{H}_2\text{O}_2\), which also measures the yield of \(\text{H}_2\text{O}_2\) plus \(\text{O}_2^F\) (from \(\text{H}_2\text{O}_2\) decomposition) at any time, is plotted versus the voltage (Fig 5). The yield of CGDE at the anode over and above the Faraday law value is therefore low over the Kellogg region and increases rapidly around the mid-point voltage (420 V). This finding is significant and supports strongly the belief that, in the Kellogg region, any glow discharge at the anode is of intermittent or partial nature, and that only at the mid-point voltage is full or true CGDE developed [1–3].

It is interesting to note that, on increasing the applied voltage from the mid-point value (420 V) to 520 V, when the electric power dissipated in the glow discharge increases considerably, the integral yields of \(\text{H}_2\) and \(\text{O}_2^F\) for a given quantity of electricity increase up to 500 V, whereas that of \(\text{H}_2\text{O}_2\) remains unchanged (Fig 4). Furthermore, the yield of \(\text{H}_2\text{O}_2\) plus \(\text{O}_2^F\) (from \(\text{H}_2\text{O}_2\) decomposition), as measured by \(G_0(\text{H}_2\text{O}_2)\), becomes stationary beyond 420 V (Fig 5). The reactions leading to \(\text{H}_2\text{O}_2\) plus \(\text{O}_2^F\) (from \(\text{H}_2\text{O}_2\) decomposition), the yields of which are unaffected by the conditions existing in the plasma sac around the anode once the full glow discharge sets in, i.e., beyond 420 V, appear to originate in the liquid phase. The yields of the liquid phase reactions consist of \(G_0(\text{H}_2\text{O}_2)\) for \(\text{H}_2\text{O}_2\) plus \(\text{O}_2^F\) and \(\text{H}_2\). In contrast, the reactions giving rise to \(\text{H}_2\) and \(\text{O}_2^F\), each in excess of \(G_0(\text{H}_2\text{O}_2)\), whose yields are significantly affected by the magnitude of the power dissipated in the plasma, seem to arise within the plasma itself. This aspect has been dealt with in detail in Section 4.

### 3.3 Chemical yields of cathodic CGDE

The chemical effects of cathodic CGDE of an inert electrolyte such as \(\text{K}_2\text{SO}_4\) are qualitatively similar to those of the anodic phenomenon. The gas evolved at the glow discharge cathode is a liberal mixture of \(\text{H}_2\) and \(\text{O}_2\) in yields greater than the Faraday law value. However, no \(\text{H}_2\text{O}_2\) could be detected in the catholyte.

The differential yields \(G(\text{H}_2)\) and \(G(\text{O}_2)\) remained constant at all points of the electrolysis with the values 2.72 and 1.84 respectively (Table 1). The material balance between \(\text{H}_2^E\) (\(\text{H}_2\) in excess of the Faraday law value) and \(\text{O}_2\) in the cathode gas was thus maintained to a satisfactory degree, the mole ratio between \(\text{H}_2^E\) and \(\text{O}_2\) being 1.9.

The yields of the novel products of full CGDE are, however, less at the cathode (1.7–1.8 each of \(\text{H}_2^E\) and \(\text{O}_2\) than at the anode (2.2–2.3 each of \(\text{H}_2\) and \(\text{O}_2^F\) plus \(\text{H}_2\text{O}_2\)). Interestingly, this is very different from

<table>
<thead>
<tr>
<th>Cathodic product</th>
<th>Differential yield</th>
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<tbody>
<tr>
<td>(\text{O}_2)</td>
<td>1.84</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>2.73</td>
</tr>
<tr>
<td>(\text{H}_2^E)</td>
<td>1.73</td>
</tr>
</tbody>
</table>

\(\text{H}_2^E\), the hydrogen in excess of the Faraday law value
the results of a previous study where the yields were much higher (about nine times) for the cathodic than for the anodic process [5]. The discrepancy is not surprising since the voltage applied in the previous study was 220 V at which CGDE, although fully grown at the cathode (mid-point voltage, 160 V [1]), would only be partial at the anode (mid-point voltage, 420 V [1]). As already observed (Section 3.2) the yields of partial CGDE are much less than those of full CGDE. Moreover, in view of the differences between the nature of the glow discharges in anodic and cathodic CGDE [1], no strict comparison between the chemical effects of the two processes should be made.

4. Discussion

In anodic CGDE of an aqueous solution, the current across the plasma can be considered to be conveyed by positive gaseous ions present in the ionized water vapour, possibly H₂O₂⁺ ions. Typical of a gas discharge phenomenon [20], most of the applied potential will drop near the cathode which is located in the vicinity of the plasma/anolyte interface for anodic CGDE. Interestingly, the critical voltage for the formation of full CGDE (420 V), the mid-point voltage, which is independent of external variables [1–3], is close to 415 V, the cathode fall measured for anodic CGDE of aqueous solutions [2,21]. As already noted, there are close similarities in the solution phase yield of H₂O₂ for anodic GDE and CGDE (Section 3.1). Furthermore, similar yields of oxidation of acidified Fe²⁺ solutions, G(Fe³⁺), by anodic CGDE (8) [2,3], anodic GDE (7–12.5, depending on the degree of oxygenation) [2], ⁶⁰Co γ-radiolysis (8.2–15.5 mol per 100 eV, depending on the concentration of dissolved oxygen) [2,22] and α-radiolysis of linear energy transfer (LET) 10 eV Å⁻¹ (4 mol per 100 eV) [2,22] have been observed. Therefore it seems reasonable to apply Hückel’s radiolytic mechanism for the chemical effects of anodic CGDE [2] to interpret the yields of anodic CGDE at and beyond 420 V.

According to this mechanism as applied to the anodic CGDE of aqueous solutions, each H₂O₂⁺ ion, after acceleration in the steep cathode fall near the plasma/anolyte interface, is driven into the anolyte solution with energies sufficient to break up several liquid water molecules into H⁺ and OH⁺ radicals by ionization and activation, in addition to the breakup of one water molecule by normal electrolytic charge transfer to produce one OH⁺ radical (H₂O₂⁺ + H₂O → H₂O + H₂O⁺ → OH⁺ + H₂O⁺). The radicals diffuse into the bulk anolyte and undergo several reactions of which the following, known to occur at high velocities from pulse radiolysis data [2,22], seem to be of importance in the CGDE of inert-type electrolytes:

\[
\begin{align*}
H^+ + OH^+ &\rightarrow H_2O, \quad k = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \\
H^+ + H^+ &\rightarrow H_2, \quad k = 1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \\
OH^+ + OH^+ &\rightarrow H_2O_2, \quad k = 5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \\
OH^+ + H_2O_2 &\rightarrow HO_2^+ + H_2O, \quad k = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \\
\end{align*}
\]

followed by

\[
\begin{align*}
OH^+ + HO_2 &\rightarrow O_2 + H_2O, \quad k = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \\
\end{align*}
\]

If the solution is sufficiently alkaline, an additional reaction

\[
\begin{align*}
OH^+ + OH^- &\rightarrow O^+ + H_2O, \quad k = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \\
\end{align*}
\]

which will inhibit H₂O₂ formation will occur, leading to the formation of an equivalent quantity of O₂.

The mechanism thus predicts the formation of more than 0.5 mol of H₂ and an equal quantity of H₂O₂ plus O₂⁻, in excess of 0.25 mol of O₂ (by normal electrolytic charge transfer), at the glow discharge anode in an inert-type aqueous electrolyte for the passage of each mole of electrons, in qualitative and partial quantitative agreement with the results obtained (Section 3.1). It predicts further that, as H₂O₂ formed by reaction (5) accumulates in the anolyte, its decomposition by reactions (6) and (7) will increase until the H₂O₂ concentration attains a stationary state, in agreement with the pattern observed for the variation of the yield of H₂O₂ with the quantity of electricity passed (Section 3.1, Fig 2). As expected, the presence of Cl⁻ in the anolyte, a potent scavenger of OH⁺ radicals, leads to a significant decrease in G₀(H₂O₂) (Table 2). Moreover, when the anolyte is alkaline, with an increase in pH, the integral yield of H₂O₂ decreases with an equivalent increase in the yield of O₂⁻, and that of H₂ remains constant (Table 3), in good agreement with the reaction scheme (eqns (3)–(8)).

However, if Hückel’s radiolytic mechanism is the only mechanism responsible for the chemical effects of

<table>
<thead>
<tr>
<th>[Cl⁻] / M</th>
<th>G₀(H₂O₂)</th>
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<tbody>
<tr>
<td>0.000</td>
<td>1.75</td>
</tr>
<tr>
<td>0.030</td>
<td>1.40</td>
</tr>
<tr>
<td>0.050</td>
<td>1.30</td>
</tr>
</tbody>
</table>
anodic CGDE, the products will form in the solution phase only and the yield of $H_2$ as well as $H_2O_2$ plus $O_2^\cdot$ (which equals $G_0(H_2O_2)$) will remain invariant to the conditions existing in the plasma sac around the anode and hence to the electric power dissipated there and to the voltage applied beyond 420 V. Although electric power or voltage independence is exhibited by $G_0(H_2O_2)$ (Fig 5) and also by the integral yield of $H_2O_2$ (Fig 4), the yields of both $H_2$ and $O_2^\cdot$ increase significantly up to 500 V (Fig 4), indicating clearly the operation of another mechanism together with that of Hickling

It is worth noting that, at voltages up to 400 V, although the solution phase yield $G_0(H_2O_2)$ is virtually zero, $H_2$ and $O_2^\cdot$ form in significant quantities, the yield rising to 0.4 at 400 V (Fig 4) This appears to arise from the dissociation of gaseous water molecules within the plasma. Similar observations were made previously for anodic CGDE at 220 V [5]. Furthermore, by examining the yields at 420 V, where full glow discharge is set up, it can be seen that the yield of $H_2$ (2.5) (Fig 4) is in considerable excess of the solution phase yield of $H_2O_2$ plus $O_2^\cdot$, i.e. $G_0(H_2O_2)$ (1.8) (Fig 5). Moreover, the yield of $H_2$ in excess of $G_0(H_2O_2)$, the limiting yield from the reactions in the solution phase, as well as the corresponding quantity of $O_2^\cdot$, increase steadily with voltage (Fig 4) and hence with electric power dissipation. Furthermore, the yield of $O_2^\cdot$, over and above that arising due to inhibition of formation of $H_2O_2$ in an alkaline anolyte (reaction (8)), remains unchanged with an increase in pH (Table 3).

The body of evidence thus favours the formation of part of the $H_2$ and $O_2^\cdot$ produced by anodic CGDE by the dissociation of gaseous water molecules within the plasma, apparently following the mechanism considered for the decomposition of water vapour in electrical discharges [20]

\[
H_2O \rightarrow H^\cdot + OH^\cdot \quad (9)
\]

\[
H^\cdot + H^\cdot \rightarrow H_2 \quad (10)
\]

\[
OH^\cdot + OH^\cdot \rightarrow O + H_2O \quad (11)
\]

\[
O + O \rightarrow O_2 \quad (12)
\]

\[
OH^\cdot + H^\cdot \rightarrow H_2O \quad (13)
\]

The scheme is in agreement with the appearance of the atomic lines of H and OH and the molecular band of OH in the emission spectra from anodic CGDE [23] It appears that, beyond 500 V, the dissociation of water molecules into the initial fragments and their recombination back into water molecules tend to occur at the same rate.

Non-faradaic yields of anodic CGDE therefore seem to originate in two reaction zones (1) the plasma around the anode where gaseous water molecules dissociate in glow discharges into $H_2$ and $O_2^\cdot$ to a degree depending on the magnitude of the electric power dissipated there, (2) the solution near the plasma anolyte interface where liquid water molecules break up into $H_2$ and $H_2O_2$ plus $O_2^\cdot$, the yields of which are unaffected by the power dissipated, by Hickling's mechanism. The relative importance of the two mechanisms depends on the magnitude of the voltage applied. Around the mid-point voltage, 420 V, the mechanism followed is principally the liquid phase Hickling's mechanism, accounting for 90% of the yield. However, with a further rise in voltage, the gas phase mechanism becomes increasingly important and at 500 V accounts for 75% of the yield.

During cathodic CGDE, most of the applied voltage (240 V) will drop in the vicinity of the cathode wire/plasma interface (cathode fall). Hence, the field near the plasma-catholyte interface will be much less than that near the plasma-anolyte interface during anodic CGDE, and insufficient to bring about the break up of liquid water molecules in the catholyte. In fact, no $H_2O_2$ could be detected in the catholyte during cathodic CGDE (Section 3.3). The entire yield of $H_2$ and $O_2^\cdot$ therefore seems to originate by dissociation of gaseous water molecules within the plasma at the cathode, following the mechanism considered for that part of the $H_2$ and $O_2^\cdot$ yield of anodic CGDE arising from reactions in the plasma (eqns (9)-(13)). The reaction scheme is consistent with the appearance of H lines and OH bands in the emission spectra of cathodic CGDE [23,24].

Therefore the chemical effects of CGDE can be considered to originate in two reaction zones the plasma near the electrode and the solution near the cathode.

### Table 3: Variation of the integral yields of $H_2$, $H_2O_2$ and $O_2^\cdot$, normalized for 1 mole of electrons in terms of the corresponding faradaic yields (mol per mol electron), with the pH of the alkaline phosphate buffer electrolyte in anodic CGDE (voltage applied, 500 V, electrolyte passed, $3 \times 10^{-4}$ mol electron, anode, Pt wire of length 5 mm and diameter 0.35 mm, cathode, 1 cm² Pt foil of thickness 0.2 mm)

<table>
<thead>
<tr>
<th>pH</th>
<th>$H_2$</th>
<th>$H_2O_2$</th>
<th>$O_2^\cdot$</th>
<th>$H_2O_2 + O_2^\cdot$</th>
<th>$(O_2^\cdot)_{corr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>7.23</td>
<td>1.01</td>
<td>6.27</td>
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<td>6.27</td>
</tr>
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<td>10</td>
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<td>0.66</td>
<td>6.75</td>
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</tr>
<tr>
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<td>Nil</td>
<td>7.49</td>
<td>7.49</td>
<td>6.48</td>
</tr>
</tbody>
</table>

*$(O_2^\cdot)_{corr}$ is the yield of $O_2^\cdot$ corrected for the amount arising due to inhibition of $H_2O_2$ formation by pH increments of the anolyte solution, and calculated as $O_2^\cdot$ minus the difference in $H_2O_2$ yield between pH 9 and another pH.*
plasma. The former is the major reaction zone of cathodic CGDE, and contributes partially, to a degree depending on the magnitude of the applied voltage, to the chemical effects of anodic CGDE. The latter contributes little to the chemical effects of cathodic CGDE, but is the reaction zone of major importance in anodic CGDE.

5. Conclusions

The following conclusions can be drawn. The chemical yields of CGDE of aqueous electrolytes show remarkable deviations from Faraday's law. However, the deviations only become appreciable when the applied voltage is beyond the midpoint voltage at which CGDE attains its full growth. Anodic CGDE of an inert electrolyte, for the passage of 1 mol of electrons, gives rise to the normal anodic yield of 0.25 mol of O₂ and leads to the dissociation of more than 2 mol of water into H₂ and H₂O₂ plus O₂, apparently by a sequence of reactions involving H* and OH* radicals primarily in the anolyte and also partly within the plasma at the anode. The nature of the yield originating in the liquid phase reaction zone bears a close resemblance to that of GDE or radiolysis of aqueous solutions. These liquid phase reactions in anodic CGDE are probably triggered by the bombardment of the liquid water molecules in the vicinity of the plasma/anolyte interface by H₂O₂ ions energized by the steep cathode fall, this proceeds via Hickling's radiolytic mechanism. The reactions within the plasma appear to follow a mechanism observed for water vapour decomposition in electrical discharges. There is a close similarity between the non-faradic yields of cathodic and anodic CGDE of inert aqueous electrolytes. However, during cathodic CGDE the reactions leading to the break up of water molecules appear to originate entirely within the plasma near the cathode.

Acknowledgment

This work was supported by a grant from the Council of Scientific and Industrial Research, New Delhi, India.

References

3. A. Hickling and M D Ingram, Trans Faraday Soc, 60 (1964) 703
15. K Harada and S Suzuki, Naturwissenschaften, 64 (1977) 484
17. K Harada, S Suzuki and H Ishida, Biostystems, 10 (1978) 247

Appendix

Definitions for expressing the yield of a product of CGDE

In line with IUPAC recommendations, the unit adopted for (i) the integral yield is mole (mol) and (ii) the quantity of electricity passed is mole of electrons (mol electron, 1 mol electron = 9.648 × 10⁴ C)

The yield of a product of CGDE (x) at a particular point in electrolysis is most appropriately expressed as its differential yield, which can be conveniently represented by a dimensionless number, G(x)

\[ G(x) = \frac{\text{yield (mol per mol electron) observed}}{\text{yield (mol per mol electron) calculated from Faraday's law (faradic yield)}} \]

The faradic yield is essentially a number being the ratio of the number of moles of the product to the number of moles of electrons.

However, when instead of the differential yield at a particular point in electrolysis, the integral yield for 1 mol electron of electricity (by dividing the yield over a period by the number of moles of electrons passed) is to be used, the dimensionless G value with the form

\[ G(x) = \frac{\text{yield (mol) computed for 1 mol electron}}{\text{faradic yield (mol per mol electron)}} \]

is used.