

CONTACT GLOW DISCHARGE ELECTROLYSIS AND ITS CHEMICAL
EFFECTS IN AQUEOUS ELECTROLYTES CONTAINING
INERT-TYPE AND OXIDISABLE SUBSTRATES



THESIS SUBMITTED TO THE BANARAS HINDU UNIVERSITY

FOR THE DEGREE OF

Doctor of Philosophy

IN

Chemistry

By

Rajeshwar Singh

M.Sc.

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

BANARAS HINDU UNIVERSITY

VARANASI-221 005, INDIA

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To,

The Registrar (Academic)
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Dear Sir,

In forwarding the thesis of Mr. Rajeshwar Singh entitled "Contact Glow Discharge Electrolysis and its Chemical Effects in Aqueous Electrolytes Containing Inert-Type and Oxidisable Substrates", supplicated in fulfilment of requirements for the Degree of Doctor of Philosophy in Chemistry of the Banaras Hindu University, I certify that he has completed the research work for the full period prescribed under Clause 3.1 of the Ph.D. Ordinance governing the award of the degree and the thesis embodies the results of his investigations conducted during the period he worked as a research scholar under my supervision.

Yours faithfully,

S. Sengupta
(Susanta K. Sen Gupta)

FORWARDED

R. Sengupta

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concentration, temperature and surface tension. An analysis of whether the solvent vaporization by Joule heating near an electrode, or electrolytic gas evolution there is the primary factor for the breakdown of normal electrolysis has been presented. Further, a discussion of the results on the basis of the theory of hydrodynamic instabilities for explaining the growth of a steady gaseous sheath on an electrode underneath the liquid electrolyte has been given.

Chapter 3 deals with the results of detailed analysis of the products of anodic CGDE (both gaseous and solution phases) of an inert-type buffer electrolyte under varying conditions of quantities of electricity, current, applied voltages, electrolyte concentration, pH and anode dimension. The anodic yield is 4-5 times the Faraday law value each of H_2 and H_2O_2 plus O_2^E (O_2 in excess of the Faraday law value). This chapter deals further with the chemical results of anodic CGDE of electrolytes containing OH^\bullet radical scavengers such as $Fe(CN)_6^{4-}$, Ce^{3+} and formic acid. The overall results were critically discussed in the light of a mechanism based on two reaction zones: (i) liquid near the plasma-anolyte interface where several liquid water molecules break up into H_2 and H_2O_2 plus O_2^E on being bombarded by each energetic $H_2O_{gas}^+$ ion from the plasma (Hickling's radiolytic mechanism) through H^\bullet and OH^\bullet radicals, and these radicals could undergo interaction with the suitable substrates if present in the anolyte; and

(ii) the plasma around the anode where water vapour molecules decompose into H_2 and O_2^E as in electrical discharges.

Chapter 3 is followed by "Conclusions" on the mechanisms of formation and of chemical effects of anodic CGDE from the overall findings of the study.

The thesis is concluded with a summary of the work done.

ACKNOWLEDGEMENTS

I simply fumble for words to express my debt of gratitude towards my honourable supervisor Dr. S.K. Sengupta, Reader, Department of Chemistry, Banaras Hindu University, for his valuable guidance, fruitful criticism, stimulating discussion and constant encouragement during the investigation which never allow me to forget him.

I express my sincere thanks to Prof. R.L. Gupta, Head, Dept. of Chemistry, Banaras Hindu University and Ex. Heads of the Department Prof. P.K. Srivastava and Prof. R.C. Srivastava for providing all the necessary facilities available in the department.

I express my grateful thanks to Dr. Ramji Tripathi of this Department for his constant encouragement.

It is a pleasure to record my appreciation for the nice co-operation extended by Dr. (Miss) Preeti Lahiri, Dr. O. Balasubramanian, Dr. O.P. Singh, Dr. Udai Arvind, Mr. Abbas Mohsen, Mr. A.K. Srivastava, Miss V. Radha, Miss Sangeeta Mishra and Miss Urvasi Sandhir during the entire period of the work.

I am thankful to all my friends for their willing co-operation during the tenure of the work.

I am thankful to Mr. Syama Prasad and Mr. Madan Lal Vishwakarma, both S.T.A. of the Departmental workshop. I also thank to Mr. Ambika Pd. Singh for his care in typing the thesis.

I am proud of my mother and elder brothers, for their everlasting encouragements and moral support at critical moments.

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Chapter 1

GENERAL INTRODUCTION

1.1. INTRODUCTION

Contact glow discharge electrolysis (CGDE) is a novel electrochemical phenomenon in which a gas plasma is maintained by dc glow discharges between one of the electrodes and the surrounding electrolyte in a conventional electrolysis cell set up. The phenomenon develops spontaneously in course of ordinary electrolysis whenever the voltage applied is sufficiently high. The transition from ordinary electrolysis to CGDE is marked by a significantly large drop in the current with simultaneous appearance of a luminous gaseous sheath over the cathode or the anode. CGDE can be observed in aqueous, nonaqueous or molten electrolytes whenever the conditions for its formation are favourable.

This novel electrolysis is an example of electrochemical processes across a plasma-electrolyte interface in contrast to a solid-electrolyte interface in conventional electrolysis. The chemical effects of CGDE are, not surprisingly, remarkably different from those of ordinary electrolysis. The products

are novel for ordinary electrolysis and their yields exceed significantly the Faraday law values.

The phenomenon has been reported in the literature off and on since its first reporting in 1844 [1], and described by various terms such as **anode effect** [2], **aqueous anode effect** [3], **electrode effect** [4], **glow electrolysis** [5,6], **galvanoluminescence** [7], **electrode glow** [8] besides **contact glow discharge electrolysis**.

A closely related phenomenon where electrochemical processes too occur at a plasma-electrolyte interface is '**glow discharge electrolysis (GDE)**'. As compared to CGDE, GDE has been investigated much more extensively [9]. In this technique, one of the electrodes (called the gas plasma electrode) usually the anode is placed above the liquid electrolyte and a glow discharge is passed from the electrode to the surface of the electrolyte. It is distinguished from CGDE in that one of the electrodes is located in the gas space in contrast to that both the electrodes are dipped into the liquid electrolyte during CGDE. However, there are interesting similarities in the chemical effects of CGDE and GDE. The products obtained at the glow discharge electrode in either phenomenon are novel for normal electrolysis and the yields are remarkably deviated from those stipulated by Faraday's laws.

Different aspects of CGDE have drawn the attention of many investigators. Origin, chemical effects, spectroscopy

of light emission are the principal aspects of investigation. However, there are gaps in our understanding on several important aspects such as origin and chemical effects of the phenomenon. Towards bridging a few of such gaps, the present study was undertaken. However, before specifying the objectives and scope of the work, it is worth presenting a concise review of the results of the previous researches done in this area of activity.

1.2. REVIEW OF THE WORK DONE ON GLOW DISCHARGE ELECTROLYSIS (GDE) AND CONTACT GLOW DISCHARGE ELECTROLYSIS (CGDE)

The following is a concise review of various reports on the researches done in the areas related to electrochemical processes in glow discharges at plasma-electrolyte interfaces, covered under (1) glow discharge electrolysis (GDE) and (2) contact glow discharge electrolysis (CGDE).

1.2:1. Glow Discharge Electrolysis (GDE)

In the glow discharge electrolysis (GDE) technique, a normal glow discharge is struck in a gas usually at a pressure of ~ 50 torr above the electrolyte, between a metal electrode and the surface of the electrolyte. If the electrolyte surface is the cathode of the discharge, positive ions from the discharge get accelerated in the cathode fall and enter the electrolyte with a distribution of energies having a peak at ~ 15 to 30 eV. When the electrolyte surface is the anode of discharge, electrons

are accelerated by the anode fall before entering the electrolyte. However, in this case much lower energies are involved. To trigger the discharge an application of a very high voltage pulse (~ 1000 V or more) or a momentary contact of the electrode in the gas space with the liquid electrolyte is necessary. However, once started GDE remains self-sustained at ~ 500 volt dc. The electrode placed in the gas space is referred to as the glow discharge or the gas plasma electrode. The other metallic electrode is dipped in the liquid electrolyte as in ordinary electrolysis. GDE can be anodic as well as cathodic, however, the former is significantly more productive yield-wise and more controllable operation-wise [9, 10]. The majority of the work done on GDE was thus anode centric. It is interesting to note that general features of the chemical results are similar whether GDE is anodic or cathodic. Thus, oxidation of substrates would occur whether the glow discharge electrode is the anode or the cathode.

With the gas plasma electrode as the anode, the discharge usually appears as a well-defined cone between the tip of the anode and a luminous disc on the electrolyte surface. The colour of the discharge depends upon the vapour present which may occasionally be modified by the substances present in the solution. In contrast, during cathodic GDE the discharge appears as a narrow cylindrical pencil of light to a very small glow spot on the liquid surface. Thus, the current density at the liquid surface reaches to a very high value. The metallic cathode near which most of applied potential drops, becomes very hot and the glow spreads over the

metallic surface [9]. The species formed in the discharge on entry into the electrolyte undergo two-fold reactions: (a) charge transfer reactions characteristic of ordinary electrolysis; and (b) additional reactions novel for ordinary electrolysis, by collisional energy transfer processes. However, at the counter electrode which is dipped in the electrolyte, only ordinary electrolytic charge transfer reactions occur. The situation at the gas-solution interface is thus closely similar to radiolysis by ionising radiations. However, it must be pointed out that GDE differs fundamentally from chemical decomposition brought about by electrical discharges between metallic electrodes through a gas at a low pressure. In GDE, the reactions of interest are initiated in the liquid phase and the yield of products is controlled by the quantity of electricity passed rather than by the electric power dissipated in the glow discharge unlike the situation in a conventional gas discharge phenomenon.

1.2:1A. Anodic GDE

The earliest report on anodic GDE was made by Klüpfel in 1905 who observed the formation of more than the Faraday law value of iodine from KI solutions [11]. A similar yield exceeding the Faraday law value, of H_2O_2 by anodic GDE of dilute H_2SO_4 solutions, was reported by Makowetsky in 1911 [12]. Since then, a number of systematic investigations on anodic GDE in aqueous media were undertaken. Klemenc et al. carried out extensive researches on anodic GDE using a variety of aqueous electrolytes [13].

They reported the formation of H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_8$ besides H_2O_2 from dilute H_2SO_4 (>1 M) solutions. The results from solutions of halides and oxyhalogen salts are highly complex. The yield of O_2 from NaClO_2 solutions was reported^{t₀} to be as high as 34 times the Faraday law value indicating strongly that chain reactions are involved. Oxidation yields as large 8 times the Faraday law value were obtained from the solutions of Fe^{2+} and Sn^{2+} salts. Significant yields of oxidation were observed also from aqueous solutions containing organic substrates such as methanol, ethanol, formic or acetic acid. The oxidation products were found accompanied by evolution of hydrogen and occasionally hydrocarbons.

From their results Klemenc et al. concluded that at least two types of reactions take place during GDE: (a) **polar**, corresponding to charge transfer processes characteristic of conventional electrolysis; and (b) **apolar**, the predominant one, corresponding to oxidation of electrolyte solutions accompanied by liberation of H_2 . This was thought to be due to OH^\cdot radicals which form in the steep cathode fall of the glow discharge in the vicinity of the electrolyte surface, and dissolve in the electrolyte.

A similar though somewhat different view was advocated by Hickling and his group who did fundamental researches on GDE of aqueous solutions containing inert-type electrolytes such as K_2SO_4 , H_2SO_4 , Na_2HPO_4 , NaOH , Na_2CO_3 , NaHCO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ as well as oxidisable substrates such as Fe^{2+} , Ce^{3+} , N_3^- , and $\text{Fe}(\text{CN})_6^{4-}$; liquid ammonia solutions of NH_4NO_3 , NH_4SCN , $\text{CH}_3\text{COONH}_4$ and KNO_3 ; and anhydrous as well as aqueous HCOOH and CH_3COOH [9,10,14,15].

They reported the formation of H_2O_2 in yields exceeding the Faraday law value from inert-type aqueous electrolytes, oxidation as high as 8-12 times the Faraday law value from oxidisable substrates such as Fe^{2+} , Ce^{3+} , N_3^- etc., hydrazine production to the extent of more than 2 moles per mol electron of electricity from liquid ammonia solutions, formation of oxalic acid from aqueous $HCOOH$ and of succinic, malic, tricarballic and oxalic acids from aqueous CH_3COOH ; and liberation of H_2 , CO and CO_2 from anhydrous $HCOOH$ and CH_3COOH . The reactions leading to such products were thought to originate in the liquid electrolyte phase. Interestingly, there exist a number of points of similarity between the reactions occurring during GDE and those produced by ionising radiations.

Hickling et al. concluded that the reactions in both the phenomena have a common origin [9,10,14]. According to their view point, positive gaseous (solvent vapour) ions e.g. H_2O^+ or NH_3^+ , generated in the glow discharge during GDE, are accelerated in the steep cathode fall near the liquid electrolyte surface and thus energised sufficiently to initiate chemical reactions in the liquid electrolyte. The energised positive gaseous ions on entry to the liquid electrolyte would each ionise or activate several liquid solvent molecules by collisional energy transfer processes. The energised liquid solvent molecules would in turn dissociate to reactive radicals such as OH^{\cdot} and H^{\cdot} from water or NH_2^{\cdot} and H^{\cdot} from ammonia and subsequently give rise to reactive molecules such as H_2O_2 or N_2H_4 besides producing H_2 . In addition, 1 molecule of the solvent for each bombarding (e.g. $H_2O^+_{gas}$) ion will be broken up by the charge transfer process as in ordinary electrolysis. The net

result of energy transfer from gaseous ions to liquid solvent molecules is thus the production of reactive radicals in the primary reaction zone, which would diffuse away from this zone and mutually interact among themselves or react with appropriate scavengers in the bulk solution (secondary reaction zone). In an extension of the study Denaro et al. observed a limiting oxidation yield of 7.1 moles of $\text{Fe}(\text{CN})_6^{3-}$ for each mol electron of electricity from alkaline $\text{Fe}(\text{CN})_6^{4-}$ under air, N_2 or O_2 atmosphere. The yield is lowered to 5.6 moles when the atmosphere above the electrolyte is H_2 [16]. This is very close to the yield of 5.7 moles found in neutral $\text{Fe}(\text{CN})_6^{4-}$ solution under H_2 atmosphere [15]. They further investigated the oxidation of I^- to I_2 by GDE from acidified as well as neutral solutions of KI, as a function of I^- concentration and observed a maximum in the yield of I_2 plus H_2O_2 (3.2 moles per mol electron) at low I^- concentrations [17]. This feature was attributed to the scavenging by I^- ions of radicals which attack H_2O_2 . Moreover, it was argued that the earlier treatment on chemical effects of GDE is valid above concentrations of a substrate where the substrate can penetrate effectively into the primary reaction zone. When GDE of H_2SO_4 solution at varying concentrations was carried out, H_2O_2 and H_2SO_5 were formed and a maximum in the yield of H_2O_2 (1.32 moles per mol electron) was observed [18]. It was again attributed to the scavenging by H_2SO_4 of radicals which would attack H_2O_2 . According to the mechanism proposed to interpret these chemical effects, in 0.4 M H_2SO_4 the depth of the primary reaction zone is about 400 nm and the concentration of radicals in

the zone is of the order of 10^{-5} M. Later Bullock et al. [19] identified H^{\cdot} and OH^{\cdot} radicals during GDE of aqueous solutions by electron spin resonance using 5,5-dimethylpyrroline-1-oxide (DMPO) as the spin trap. The trap was able to penetrate the primary reaction zone at the glow discharge-solution interface to scavenge for free radicals. However, no evidence for the presence of hydrated electrons was found.

The primary factor controlling the non-Faradaic yields of GDE, is the energy of the positive gaseous ions, $H_2O_{gas}^{+}$ or $NH_3_{gas}^{+}$ which are accelerated greatly in the steep cathode fall. The energy of these ions while entering the solution would be 100 eV or so. The other parameters found to influence the yields are gas pressure above the electrolyte and concentration of the substrates under going reactions in the electrolyte [14,15,20,21].

Mazzocchin et al. carried out interesting GDE experiments both anodic and cathodic in aqueous solutions of ammonia as a function of ammonia concentration, of the pressure and of the nature of supporting electrolytes. They observed formation of N_2H_4 , H_2O_2 , NO_2^{-} and NH_2OH by anodic GDE and only N_2H_4 , NO_2^{-} by cathodic GDE [20]. Formation of NO_2^{-} was accounted for by the interaction between NH^{\cdot} and O_2 and of NH_2OH by the interaction between NH_2^{\cdot} and OH^{\cdot} radicals. The yield of N_2H_4 observed in anodic GDE of aqueous ammonia, (3.5 mol per mol electron) is interestingly higher than the yield of N_2H_4 obtained from GDE of liquid NH_3 systems (2.5 mol per mol electron) [14].

A study on measurements of the electrode fall of the local discharge between a rod electrode and an electrolytic surface at varying air pressure and at varying electrolyte (KCl solution) resistivity show that electrode fall voltage remains at the high value regardless of the air pressure and increases with the resistivity of the electrolyte. It was concluded that the discharge mechanism in the local discharge between the electrode and the electrolyte surface is similar to that in glow discharges [22].

However, all these chemical effects studies were mainly centric on oxidation yields of GDE and did not pay due attention to a very fundamental aspect of GDE, the glow discharge in the gas space. Probably this is due partly to the observation that the contribution of atmospheric gases on oxidation yields was found insignificant and partly to the assumption that positively charged gaseous species which carry the current to the solution are not dependent on the nature of atmospheric gases [14]. The influence of O_2 gas on the yields of H_2O_2 and Fe^{3+} during GDE was ascribed to chemical reactions of $HO_2\cdot$ radicals (formed by the reaction of $H\cdot$ radical with O_2) in the solution bulk [14,15] and is not obviously a true gas effect. In a recent study, Matsumoto et al. could observe a true gas effect on both the discharge characteristics and the oxidation yields of GDE of aqueous H_2SO_4 solutions (H_2O_2 and H_2SO_5) as well as of redox systems of $FeSO_4$ (Fe^{3+}), $Ce_2(SO_4)_3$ (Ce^{4+}) and Tl_2SO_4 (Tl^{3+})

solutions in an oxygen-free atmosphere of N_2 , Ar, or He and at a solution temperature below $10^\circ C$ [23]. In a further study [24] they examined the connection between the oxidation yields of H_2O_2 , H_2SO_5 and $H_2S_2O_8$ by GDE of aqueous H_2SO_4 and the results of plasma diagnostics in atmospheres of H_2 , He, N_2 , and Ar above the anolyte solution. When the partial pressure of water vapour in the atmosphere was lowered to 5-8 torr (against a total of 50 torr) by preventing the solution temperature to go beyond $8^\circ C$ through intermittent electrolysis, a significant gas effect was noticed on the yield of H_2O_2 . The yield of H_2O_2 with He or H_2 atmosphere is 1.5 to 2 times higher than that with Ar or N_2 atmosphere. However, no clear gas effect was observed on the yield of H_2SO_5 or $H_2S_2O_8$. Results of diagnostics of the glow discharge by emission spectroscopy and double probe method revealed that the plasma state depends on the nature of gases when containing significant amount of water vapour. It was concluded that the radical concentration in the gas phase does not necessarily correspond to that in the solution phase. The yield of OH^\cdot radicals is much higher in Ar than in H_2 or He atmosphere as found by relative emission intensity. In contrast, the yield of H_2O_2 in H_2 or He atmosphere is much higher than in Ar. Further, atmospheres of glow discharge that contain a light-charged particle (H^+ or He^+) give rise to higher oxidation yields. Light-charged particles would gain higher acceleration energy in the cathode fall near the electrolyte surface and penetrate the solution phase transferring energy to liquid water molecules to break them into radicals over a longer spur. The primary radical formed within

the spur of the penetrated particle is the OH^\bullet radical. The yield of H_2O_2 is thus expected to be higher for lighter particles, He^+ or H^+ which have longer spurs. On the other hand the yield of H_2SO_5 or $\text{H}_2\text{S}_2\text{O}_8$ depends on bulk concentration of H_2SO_4 and is thus less sensitive to the length of the spur. However, the effect of atmospheric gases described is minor in comparison to the effect of gas pressure, solution concentration or current density.

In an extension of the study on GDE of H_2SO_4 solutions in N_2 - H_2 atmosphere, these authors [25] detected considerable quantities of NH_3 in the liquid phase along with the oxidation products of H_2SO_4 . Since NH^\bullet radical was identified in the N_2 - H_2 plasma by emissions spectroscopy and its peak head intensity corresponds to yield of NH_3 , NH^\bullet radicals produced in the glow discharge are regarded to be the precursors for the formation of NH_3 in GDE.

Among the other investigations on anodic GDE, mention must be made of the synthesis of oxamide from a solution of formamide in dilute H_2SO_4 [26], polymerisation of acrylonitrile [27] and acrylamide [9] in aqueous solution; formation of H_2SO_4 (14 mol per mol electron) and sulfur (5 g. atom per mol electron) from liquid SO_2 rendered conducting with a little water [28], oxidative decomposition of amino acids [29].

1.2:1B. Cathodic GDE

The earliest report of cathodic GDE was made by Gubkin in 1887 [5,30], who electrolysed metallic salt solutions with a glow

discharge cathode and observed reduction in some cases. Since in the cathodic GDE the discharge process corresponds to the introduction of electrons, it is expected to produce chemical reduction in the liquid phase. Thon in 1933 [5,31] though observed reduction of Ag, Au and Pt salts to the respective metals, could get only the precipitate of metallic hydroxides on the glow spot with other metallic salts. Further studies [9,10] showed that during cathodic GDE the reactions occurring are, in general, of the same type as in anodic GDE. However, the yields are much less in cathodic GDE and any reduction which occurs seems to be due to H_2O_2 which is frequently formed. Thus, with dilute H_2SO_4 , even in H_2 atmosphere a small yield of H_2O_2 (0.02 mol per mol electron) is obtained; with a FeSO_4 solution, an oxidation yield with a limiting value of about 0.28 mol per mol electron at high Fe^{2+} concentrations is observed. Both these figures get enhanced in the presence of O_2 to 0.08 and 1.9 mol per mol electron respectively. However, with Fe^{3+} solutions no definite evidence for reduction could be established. Some reduction observed with Ce^{4+} , $\text{Cr}_2\text{O}_7^{2-}$ or $\text{Fe}(\text{CN})_6^{3-}$ solutions seems to be at least partly due to H_2O_2 formed in GDE. As in anodic GDE, H_2SO_4 and S are obtained as the main products in cathodic GDE of liquid SO_2 mixed with a little water [28]. The yield of S by cathodic GDE though is the same as that in anodic GDE, the yield of H_2SO_4 is significantly less in the cathodic phenomenon.

Mazzocchin et al. showed that cathodic GDE of aqueous ammonia solutions gives rise to N_2H_4 and NO_2^- among the cathodic

products. However, no NH_2OH or H_2O_2 was observed. This was explained as due to the high rate constant of the electron capture reaction by the OH^\bullet radicals. It is to be noted that the yields of N_2H_4 and NO_2^- by cathodic GDE are much less (about 50 %) than ~~that~~ by anodic GDE [20]. The general conclusion that emerges from the study is that the reactions occurring in cathodic GDE are qualitatively similar to those in anodic GDE but that the magnitude of chemical effects is much less in the cathodic phenomenon because there is only a small potential drop near the liquid surface which serves as the anode in the cathodic glow discharge.

1.2:1C. GDE with Alternating Current

When alternating current is used in GDE, the discharge is not steady but stops and starts twice in each cycle with an appreciable gap between successive anodic and cathodic pulses; each of which shows its usual dc features. The chemical results are, as expected, of the same type qualitatively as in anodic GDE. But the yields are reduced to about half. In other words, most of the chemical reactions occur during the half cycle in which the electrode above the liquid surface is the anode and during the cathodic pulses the amount of reaction occurring is not significant. With alternating current (50 Hz), 0.4 mol of H_2O_2 per mol electron of electricity as the initial yield (as compared to 0.8 mol per mol electron in anodic GDE) from sodium phosphate solutions; and 1.3 moles of N_2H_4 per mol electron as

the initial yield (as compared to 2.5 mol per mol electron in anodic GDE) from liquid NH_3 solutions were obtained [9,10].

1.2:1D. GDE and other Forms of Electric Discharges to Solutions

A few other forms of electric discharges to solutions have been studied and the results are quite similar to those of GDE. Spark electrolysis at atmospheric pressure was investigated by de Beco [32] and its chemical effects are very closely similar to those of GDE. Silent electric discharges in an ozonizer-type apparatus to acidified solutions of Fe^{2+} and Ce^{4+} ions produce oxidation of Fe^{2+} and reduction of Ce^{4+} . The results were interpreted on the basis of radiolysis by slow electrons [33]. The chemical effects produced by driving gaseous ions formed in the gas phase by radioactive substances, into a solution under the influence of an electric field were also studied [34]. Again the results are analogous to those of GDE.

1.2:1E. GDE of Molten and Solid Electrolytes

The technique of GDE has also been applied to electrolysis of fused salts and solid ionic conductors. An important modification in the cell set-up for such electrolytes is that in several instances both the electrodes are gas plasma electrodes i.e. there is no palpable contact of the electrolyte with the metallic electrodes.

(i) GDE of fused salts

In contrast to GDE of aqueous and non-aqueous electrolytes, GDE of fused salts does not generally give rise to any novel product and the yield is in agreement with Faraday's laws as in conventional electrolysis [35]. Further, using this technique one can avoid the possibility of reaction or alloying of the product with metallic electrodes. Although in GDE of fused salts both the electrodes could be gas plasma ones, usually the cathodic product only being of importance, cathodic GDE was attempted in most experiments for obvious reasons. However, at least in one experiment, the electrolysis of molten AgCl, both the electrodes were gas plasma ones. This experiment resulted in the growth of silver dendrites, the yield of which was roughly in accord with Faraday's laws [35]. Similar metallic dendrites were reported to be formed from GDE of molten chlorides of cobalt, nickel, copper (-ous) and tin (-ous) [35]. GDE of molten $MgCl_2$ resulted in small shining crystals of Mg condensed on the cooler portion of the apparatus [35].

Ingram et al. during their studies of GDE (both anodic and cathodic) in molten electrolytes observed, however, a significant deviation from Faraday's laws. They observed NO, NO_2^- and "oxide" from anodic GDE of molten nitrates ($NaNO_3$, KNO_3 , $Ca(NO_3)_2$) [36]. The products are thus characteristically different from those of conventional electrolysis. Further, for solutions of KI in a 2:1 $KNO_3 - Ca(NO_3)_2$ melt an yield of I_2 as high as

3 times the Faraday law value was observed. These chemical effects are attributed to free radical reactions which occur in the melt following the charge transfer process. Again a close correlation between GDE and radiation chemistry was observed. During cathodic GDE of 2:1 $\text{KNO}_3 - \text{Ca}(\text{NO}_3)_2$ melt, NO , NO_2^- and "oxide" were formed as in anodic GDE. The yields of the reduction products NO_2^- and "oxide" were greater (2-3 times) than those of anodic GDE. However, the yield of the oxidation product NO is less (about 5 times) than that in anodic GDE [36].

(ii) GDE of solid ionic conductors

Under suitable conditions, a number of solid electrolytes were electrolysed between two gas plasma electrodes. GDE of silver chloride [35] is the first reported example of an electrolysis between two gas plasma electrodes. During electrolysis, the side facing the cathode became covered with silver and the material lost weight about equal to that chlorine which should have been liberated on the basis of Faraday's laws. However, the most interesting results were obtained from GDE of glass [35]. The side facing the cathode became dull and developed blisters, while the side towards the anode developed an opaque white layer which readily flaked off. The opaque material gave an X-ray pattern similar to that of the original glass and the content of silica in the material seemed to be almost the same as that in the original glass. Among other interesting reports from GDE of solid electrolytes, is the discolouration of barium titanate [35] from light yellow to black throughout its thickness.

1.2:2. Contact Glow Discharge Electrolysis (CGDE)

Contact glow discharge electrolysis (CGDE) is another novel form of electrolysis in which electrochemical processes occur in glow discharges across a gas-electrolyte interface. Here too, as in GDE, the chemical changes exceed the Faraday law value and are brought about by energy transfer besides charge transfer processes. As described already (vide Section 1.2:1 of this Chapter) during CGDE at one of the electrodes, either the anode or the cathode, a luminous electrical discharge replaces normal electrolysis. CGDE at an electrode develops whenever the power dissipated near the electrode during normal electrolysis of an electrolyte solution is high enough to vaporize the solvent locally and form a stable vapour sheath around the electrode. As a matter of fact, CGDE is a simple method for producing GDE at atmospheric pressure. CGDE has the advantage of greater simplicity as compared to GDE. The glow discharge is automatically started and can be maintained at a relatively lower applied voltage. However, it is somewhat less controllable than GDE and the experimental conditions are less precisely defined.

Since CGDE develops in a spontaneous transition from an ordinary electrolysis carried out in an dissymmetric cell allowing high enough current density at the smaller electrode, it is no surprise that this novel electrolysis has been known for a long time, although the observation might have been come across in a particular context.

In fact, since the earliest days of experiments on electrolysis of molten salts with insoluble anodes where the primary reaction is a gas evolving one, a multi-star glow phenomenon popularly known as '**anode effect**', an example of anodic CGDE has been reported [2]. The phenomenon occurs during molten salt electrolyses if the anode current density goes above a critical value ($\underline{c c d}$). Its formation is marked by a steep drop in the current, nonwettability at the anode/melt interface and arc formation between the anode and the melt. Anode effect is generally attributed to the formation of a gaseous film covering the anode through which current passes in the form of small arcs.

In aqueous electrolytes, the earliest observation of CGDE was made by Fizeau and Foucault in 1844 [1] followed by a few other workers [37-42] over the next 70 years. Fizeau and Foucault reported, in the footnote of their paper, a luminescence at the cathode during electrolysis of water with a battery of 80 voltaic couples between wire electrodes and ascribed it to some arc discharge through H_2 . The other workers [37-42] assumed ohmic heating of the electrode surface to be the origin of this electrode effect. Lagrange and Hoho in 1893 utilized these observations for the heat treatment of steel cathodes [42] and laid the basis of the technique of electrolytic heating of metals and alloys [43]. In this technological process, an aqueous solution is electrolysed using the metal to be heated as the cathode at a sufficiently high voltage when normal electrolysis breaks down and sparks with glow cover the cathode. The cathode is then encased in an insulating gaseous

shell allowing a sharp rise in the temperature of the metal. This shell effect persists for some time even after lowering the voltage. The process results in uniform heating of the metal and applies to high speed and plain C steel twist drills [44]. Another early example of CGDE is Wehnelt electrolytic circuit breaker for induction coils devised in 1899 [38]. It consisted of an electrolytic cell containing a large plate cathode and a small platinum wire anode. Humphreys showed that the interruption was associated with the growth of a high resistance and a visible glow at the small anode [40].

1.2:2A. CGDE in Aqueous and Non-Aqueous Electrolytes

The systematic study on CGDE in aqueous media, however, commenced only in 1950 when Kellogg in an attempt to simulate the anode effect phenomenon in an aqueous electrolyte investigated the current-voltage relationship of electrolysis of dilute H_2SO_4 and NaOH solutions between a platinum sheet cathode and a platinum wire anode [3]. He observed, on increasing the applied voltage, a transition from normal electrolysis through a transition region (when the electrode temperature reaches the boiling point of the electrolyte solution and the liquid near the anode becomes turbulent and emits a hissing noise) to a stable state beyond a critical voltage ~ 45 V. At this point the surface temperature of the anode rises above the boiling point of the electrolyte and the anode gets enveloped in a film of gas accompanied by a large drop in current. The phenomenon developed has

been termed by Kellogg as '**aqueous anode effect**'. During the aqueous anode effect, a dull red glow from the anode tip in dilute H_2SO_4 and a yellow glow from the anode film in NaOH solution are seen. Kellogg attempted an explanation in terms of local Joule heating of the electrolyte solution causing sheathing of the anode by water vapour through which current passes by local glow discharges where the film thickness is the least. Using the wire electrode as the cathode, Kellogg produced an '**aqueous cathode effect**' when the applied voltage was higher than some critical value (~ 110 V). During this stage a bright blue luminescence (characteristic of hydrogen emission) from the wide vapour film at the cathode in dilute H_2SO_4 and a multitude of spark discharges on the cathode surface in NaOH solution having no distinct visible film are observed. However, about the phenomenon in aqueous and in molten media, Kellogg thought different mechanisms are probably operating.

Following Kellogg's report, CGDE has become a subject of considerable interest. In fact, since 1961 many careful studies on its origin, chemical effects and spectroscopy of its emission have been reported.

Hickling et al., who first coined the term '**contact glow discharge electrolysis**', studied current-voltage characteristics (at voltages upto 600 V) of electrolysis of aqueous and liquid NH_3 electrolytes with thin wire anodes and sheet cathodes upto 600 V under a wide range of variables and found that under suitable conditions of power dissipation near the wire electrode,

local heating can produce a stable sheath of solvent vapour around the electrode through which current would flow as a glow discharge if the applied voltage is sufficiently high [9,45]. They concluded that conventional electrolysis would break down whenever the lines of flow of current converge in such a way that ohmic heating can cause local vaporization of the solvent and that the phenomenon is of quite general occurrence with any electrolyte, electrode or electrode reaction. While extending the study to electrolyses with small immersed cathodes, they observed that following the break-down of normal electrolysis no stable state was produced. The cathode became covered with an intense glow but having no stable vapour sheath and it tended to melt.

Hickling et al. showed further that something over and above normal electrolysis is involved in CGDE. They reported that during anodic CGDE of inert-type salts such as Na_2HPO_4 , H_2O_2 forms in quantities exceeding the Faraday law value. They further observed a yield of 8 moles of Fe^{3+} from Fe^{2+} solutions and more than 1 mole of hydrazine from simple liquid NH_3 systems for the passage of each mol electron of electricity. Chemical effects of anodic CGDE are thus very similar to those of anodic GDE. Moreover, for volatile substrates such as formic or acetic acid, CGDE is more advantageous than GDE since decomposition of the vapour by the electrical discharges would be minimised [9,45].

That the chemical effects of cathodic CGDE are remarkably different from those of conventional electrolysis was demonstrated by Palit [6] who while studying current-time characteristics of

electrolysis of aqueous electrolytes between wire electrodes at ~ 200 V observed a stable cathode glow (termed as **glow electrolysis**) following the breakdown of normal electrolysis. He found that the volume of the gas liberated at the luminous cathode was far in excess of the total volume of the cathode and anode gases expected on the basis of Faraday's laws and that the cathode gas was a liberal mixture of H_2 and O_2 [6]. He further noted that imposition of a magnetic field reversibly diminished the current and also the electrode glow to a considerable extent. In an extension of the study on current-time characteristics of electrolysis of various aqueous electrolytes at ~ 200 V, Sengupta et al. found that a stable form of cathodic or anodic CGDE (called by them as **galvanoluminescence**) would develop at the electrode of smaller surface area irrespective of its shape and that the colour of either the cathode glow or anode glow would depend upon the cations present in the solution [7,46]. They further studied the chemical effects of CGDE in various inert-type, non inert-type (electroactive) electrolytes, ammonium salts and inorganic acids and showed that during cathodic CGDE at ~ 220 V the volume of the cathode gas varies from 0.8 to 4 times the Faraday law value and that the percent volume of O_2 in the cathode gas varies from 4 % to as large as 92 % depending upon the nature of electrolyte used. The non-faradaic yield was found to depend on several factors such as current, voltage input, area of luminosity, intensity of luminosity and also nature/colour of the cathode glow. On the other hand, during anodic CGDE at ~ 220 V in various aqueous electrolytes, the anode gas volume varies from 1.1 to 4 times the Faraday

law value and the percent volume of H_2 in the anode gas varies from 4 % to 50 %. It was also found that the non-faradaic yield by the cathodic CGDE is 8.7 times that by the anodic one. Further, studies showed that oxidation of I^- in yields exceeding the Faraday law value occurs during its cathodic CGDE [47]. In a further study, it was demonstrated that the nature of electrolyte constituents plays a key role in deciding whether the breakdown of ordinary electrolysis would occur at the cathode or at the anode [48]. It was shown that the relative resistivity of the interfacial region between the cathode/ catholyte and the anode/ anolyte during electrolysis determines the location of breakdown of normal electrolysis.

Garbarz-Olivier et al. studied oscillographic recordings of current-time and current-voltage curves during both anodic and cathodic CGDE in various aqueous electrolyte solutions with platinum and other electrodes such as tungsten and carbon (for cathode effect) and noticed three distinct regions of activity. They correlated their findings with their results on spectroscopy of light emission during the CGDE [49,50]. They further investigated the origin of CGDE both the anodic and the cathodic in various electrolytes (both aqueous and molten) with gas evolving as well as not gas evolving electrodes on the basis of Fourier's equation. Their calculations revealed that the electrolysis time elapsed before the occurrence of CGDE at an electrode, is equal to the time necessary to bring the temperature of the electrolyte surrounding the electrode upto its boiling point.

It was concluded that CGDE originates from Joule heating of the electrolyte, whatever the experimental cell and the electrolytes are [51].

Mazza et al. on the basis of their results on electrochemical and morphological aspects of electrolytic gas evolution and the associated anomalous effects in both aqueous and molten electrolytes arrived at a general explanation of anodic and cathodic CGDE. The explanation is based on the conditions of hydrodynamic instabilities described by Helmholtz and Taylor. This was originally applied to interpret the phenomenon 'boiling crisis' or 'burn out' during boiling of a liquid in contact with a heated solid surface submerged in it. The hydrodynamic interpretation covers comprehensively the different morphological aspects of electrolytic gas evolution from an aqueous solution; accounts for the abrupt occurrence of CGDE, its dynamic characteristics, and is consistent with the results of electrochemical aspects such as electrode potential vs current density curves, dependence of critical current density (cc d) on external factors [52].

Several other workers have investigated the apparent similarity between nucleate boiling and electrolytic gas bubble evolution. To clarify the analogy between the limiting rate processes in the two phenomena, Bhattacharya et al. studied the gas removal process during an electrolysis to identify the hydrodynamic transitions at a horizontal cylindrical cathode

analogous to those occur in boiling. The transition point corresponding to the change-over from isolated bubble formation to column formation has been predicted [53]. Danby et al. who studied the dynamics of electrolytic hydrogen bubble formation on the platinum electrode in H_2SO_4 media have shown that the combination of atomic to molecular hydrogen is the rate limiting step in the bubble formation process. As there is no analogous mechanism in nucleate boiling, it is concluded that due caution should be exercised in postulating a general analogy between the two phenomena [54].

Sengupta et al. investigated ^{the influence of} the relative anode-cathode dimension, the relative anolyte-catholyte surface tension, the nature of the electrolyte constituents and the polarity of the electrode on the onset and location of CGDE in aqueous media. The mechanism of the growth of a stable vapour envelope on an electrode underneath an electrolyte during normal electrolysis has been examined in the light of the theory of hydrodynamic instabilities. The overall analysis of the results had led to the following conclusions: (a) vaporization, and not gas evolution at an electrode, is the prime requisite for the growth of CGDE in an aqueous electrolyte; (b) an electrode-electrolyte area where the conditions help both easier vaporization and easier onset of hydrodynamic instabilities would be the location of CGDE; and (c) the nature of the glow discharge at an anode is quite different from that at a cathode [55]. They studied also the

chemical yields of CGDE at the anode as well as the cathode in aqueous inert-type electrolytes under various conditions and showed that the non-faradaic yields originate in two reaction zones: the electrolyte near the plasma where liquid water molecules are broken up into H_2O_2 , O_2 and H_2 , and the plasma around the anode where gas phase dissociation of water molecules into H_2 and O_2 occurs. The former is predominant in anodic CGDE and the latter in cathodic CGDE. Hickling's radiolytic mechanism according to which non-faradaic yields originate from mutual interactions of H^\cdot and OH^\cdot radicals (identified by an ESR study [19]) generated from the bombardment of the liquid water molecules by energised $\text{H}_2\text{O}_{\text{gas}}^+$ ions from the plasma, 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 almost entirely within the plasma during the cathodic CGDE, but predominantly in the liquid anolyte and partly in the plasma during the anodic phenomenon [56].

Schiffirin et al. investigated the effect of pressure and electrolyte concentration on cathodic CGDE and concluded that the volumetric rate of gas evolution is the determining factor for the onset of glow discharges, although solvent evaporation due to Joule heating might have some influence. The discharges in cathodic CGDE, when produced at a low pressure, are very stable and appear suitable for studies of the chemistry of energetic species generated at the electrode [57].

A very interesting application of CGDE is the synthesis of bio-organic compounds. Harada et al. regarded CGDE a simulation of lightning striking on the primitive hydrosphere and explored a new possibility of synthesising amino acids under prebiotic conditions on the primordial earth. In fact, several simulated prebiotic syntheses of amino acids under anodic CGDE from saturated aliphatic carboxylic acids in aqueous ammonia [58]; from aliphatic amines (or amino acids) by direct carboxylation using formic acid (or formamide) in aqueous solutions [59]; from ammonium bicarbonate or ammonium formate in ammoniacal aqueous solutions [60]; from elemental carbon in the presence of aqueous ammonia [61]; from α,β -unsaturated carboxylic acids and aqueous ammonia [62]; from 2-pyrrolidone in aqueous formic acid [63]; from amination of aliphatic nitriles in aqueous ammonia followed by hydrolysis, and from cyanization of aliphatic amines in aqueous NaCN followed by hydrolysis [64]. The main amino acid formed is glycine. The stepwise oxidative degradation of β - and γ -amino acids [65,66]; of several hydroxy amino acids [67] and of aliphatic amines in aqueous solutions leading to amino acid formation by anodic CGDE was also studied. These results suggest that OH^\bullet radical produced by the CGDE is the key oxidising agent. CGDE, as a matter of fact, provides a clean and powerful oxidation technique without using any oxidising agent. It was further demonstrated that both H^\bullet and OH^\bullet radicals could simultaneously participate in the chemical effects of anodic CGDE of appropriate substrates. CGDE of aqueous CD_3COOH solutions has been found to give rise to both OHCD_2COOH

and CD_2HCOOH [68]. Moreover, the results from the CGDE of aqueous olefinic carboxylic acids indicate strongly the simultaneous addition of H^\cdot and OH^\cdot radicals to $\text{C}=\text{C}$ bond. Maleic and acrylic acid solutions during CGDE undergo simultaneous hydroxylation, hydration and hydrogenation giving rise to succinic acid, malic acid and tartaric acid from maleic acid; and propionic acid, β -hydroxy propionic acid, lactic acid, and glyceric acid from acrylic acid in significant quantities [69].

The study of chemical effects of anodic CGDE was extended to aprotic systems also. Results of synthetic interest such as aromatic cyanation have been obtained from the CGDE of acetonitrile containing benzene as the substrate and lithium perchlorate or tetraethylammonium bromide as the supporting electrolyte. Significant quantities of benzonitrile are formed. When mono-substituted benzene is used, three isomers of monosubstituted cyanobenzene are obtained. With *N,N*-dimethylformamide (DMF) as the solvent, significant amounts of *N,N*-dimethylaminoacetonitrile was formed. The chemical changes brought about by the CGDE appear to follow a reaction pathway involving the bond cleavage of solvent molecules caused by the bombardment of energised particles from glow discharges [70].

Besides studies on current-voltage or current-time characteristics and chemical effects, emission spectroscopy of the glow discharge during CGDE was studied in considerable details to diagnose the phenomenon.

Mergault, Valognes, Guilpin, Garbarz-Olivier and others [4,71-73] studied extensively spectral characteristics of emitted light from the vapour sheath at the glow discharge electrodes of various materials during the cathodic as well as the anodic CGDE in both aqueous and molten electrolytes. They observed that spectra of anodic CGDE contain atomic lines of H, O(II), the constituents of the electrolyte and occasionally the constituents of the anode materials; and molecular bands of OH, subhalides and oxy-subhydroxides of alkaline earths (when they are present in the solution). The spectra of the cathodic CGDE were found to consist of atomic lines of H, the constituents of the cathode, the electrolyte constituents along with the molecular bands of OH, subhalides of alkaline earths (when they are present in the solution) and the monohydride of the cathode material. The last one i.e. the hydride spectrum, is of particular interest because from a study of its fine structure thermodynamic quantities characteristic of the luminous sheath were evaluated (Similar spectrographic results were also reported in some other [8] preliminary studies). Thus, the chemical species excited in the discharge originate from the breakup of the aqueous electrolyte solution and/ or the electrode material. Further, the excitation temperature of some chemical species (Mg, Ca, O⁺) was calculated using Boltzmann plots. From a study of the H_β profile, an estimate of the electron density in the region where H emission is generated both in the anodic and the cathodic CGDE was made. Along with these spectroscopic studies, dynamic current-voltage

and current-time characteristics, and electrode temperature during CGDE were measured. Moreover, with the aid of high speed cinematography, it was found that an 'electrode effect' (the term used by these investigators for CGDE) occurs when the solution around an electrode begins to boil and an estimate of the electric discharge's size length and area ($\sim 10 \mu\text{m}$) was made. Results on electrochemical and spectroscopic studies of CGDE have been reviewed in an attempt to link the results with each other in a way to obtain a better understanding of the complex phenomenon [74]. In a recent study, Valognes *et al.* [75] investigated the calculation of theoretical line shapes for the determination of principal parameters of the electrolytic plasma produced during the occurrence of CGDE. The study referred, in particular, to the experimental line shape of the semi degenerate LiI ($4f\ 4d\ 4p \rightarrow 2p$) transition recorded during the occurrence of the anode effect in an equimolar mixture of molten LiCl and KCl. A calculation as exhaustive as possible entailed the necessity to superpose profiles corresponding to a given set of parameters. The calculation yields theoretical line shapes that link up well with the experimental ones. Further, this study provided a more precise physical interpretation of the anode effect.

CGDE of molten electrolytes: Contact glow discharge electrolysis in molten electrolytes has drawn the attention of many investigators since the earliest days of electrolysis. Anodic CGDE in molten electrolytes in the name of 'anode effect' is a well known phenomenon in molten salt electrolysis, particularly in industrial

aluminium cells of cryolite-alumina melts with a carbon anode [76, 77]. It is interesting to note that chemical yields of CGDE in molten media follow strictly Faraday's laws [78]. Since the onset of anode effect is accompanied by a considerable drop in the current there occurs an undue expenditure of electrical energy for aluminium production. Many attempts have been made for controlling as well as quenching the occurrence of the anode effect. Several theories based on ideas such as changes in wettability of the anode by the electrolyte bath; formation of surface films or solid layers with high insulating properties on the anode; formation of a gaseous film on the anode; evaporation of the electrolyte bath close to the anode; and hydrodynamic instabilities in electrolytic gas evolution [3,5,76-98] ^{have been proposed}. The last hypothesis is of much interest and is supported by both the direct evidence from cine pictures and the analysis of electrochemical investigations during anodic gas evolution in molten salts including cryolite melts [52,99-101]. The theory of hydrodynamic instabilities as described by Helmholtz and Taylor was ^{originally} applied to explain the phenomenon of 'burn out' or 'boiling crisis' which occurs due to the formation of a gaseous blanket on a hot solid surface immersed in a boiling liquid. This occurs when the specific heat flow from the hot wall to the liquid during its boiling exceeds some critical value and the growth of this phenomenon bears a close resemblance with that of 'anode effect'.

Qiu and Zhang [102] proposed a mechanism of the anode effect from the results of voltammograms and cathodic oscillograms as

well as from the results of a voltage wave with high frequency and the jet action from the anode during the anode effect. Two types of anode effects were distinguished: (i) whose initiation is due to the formation of some intermediate compounds on the anode ; and (ii) whose initiation is due to the accumulation of gas bubbles on the anode.

Conway et al. who made fundamental studies on anode effect during fluorine evolution reaction (FER) on carbon anodes in $\text{KF}\cdot 2\text{HF}$ melts traced two effects to its origin: barrier layer 'CF' film formation and the resulting large fluorine gas bubble/ $\text{KF}\cdot 2\text{HF}$ melts/carbon electrode contact angle leading to an unusual type of gas evolution through a gas film involving adherent lenticular bubbles. The F_2 bubble/film adherence effect is the main cause for the abnormally high polarisation and the anode effect for a normal unactivated carbon anode [103]. To improve the activity of a carbon anode they developed a reactivation procedure following the onset of the 'anode effect' and characterized the activated carbon anodes. The carbon anodes activated following the onset of the 'anode effect', exhibit unique exceptional polarisation behaviour e.g. high exchange current density, low Tafel slope, resistance to further anodic effects, facilitation of the detachment of the F_2 gas bubble and good electrode-life properties. ESCA studies have shown that as compared to normal non-activated carbon anodes, the activated anodes have a smaller extent of surface fluorination corresponding to thinner

'CF' films. This may lead both to a favourable contact angle and a smaller barrier layer for activated electron tunnelling at the activated carbon anodes used for the FER, than at normal non-activated carbon electrodes [104].

A number of reviews are available on the 'anode effect' in molten electrolytes [105-108].

1.3. OBJECT AND SCOPE OF THE WORK

The current work on contact glow discharge electrolysis (CGDE) was undertaken with the following two primary objectives:

(A) To sharpen the understanding on the mechanism of the growth of stable CGDE at the anode during conventional electrolysis in aqueous inert-type electrolytes; and also to examine whether electrode gas evolution or local solvent vaporization contributes more significantly to the growth of a gaseous sheath at the electrode underneath the electrolyte - a prerequisite for the formation of CGDE.

This has been attempted by studying current-voltage (I-V) characteristics of electrolysis (upto 540 V) under varying conditions of electrolyte concentration, temperature, surface tension, relative anode-to-cathode dimension and cell geometry. The results obtained and their discussion have been presented in Chapter 2.

(B) To elucidate the mechanism of non-faradaic chemical results of anodic CGDE.

This has been attempted by quantitative analysis of both the gas phase and solution phase products of anodic CGDE of inert-type aqueous electrolytes under varying conditions of the quantity of electricity, the current, the voltage applied, the presence of H_2O_2 as additive to the anolyte, the electrolyte concentration, pH, the anolyte volume and the anode dimension. The study was further extended by using anolytes containing selected potential scavengers for OH^\cdot and H^\cdot radicals (the probable initiators for the non-faradaic yield) such as $\text{Fe}(\text{CN})_6^{4-}$, Ce^{3+} and formic acid. The results obtained have been critically analysed and discussed in Chapter 3.

CGDE, as already indicated, is a potential tool for generating radicals in solutions. A few attempts have already been made to explore CGDE as a technique for synthesis. Results obtained for cyanization and amination of organic compounds, amino acid synthesis, hydrazine synthesis etc. are encouraging. Obviously the present attempt towards elucidating the mechanism of non-faradaic chemical effects of anodic CGDE would help in opening newer routes for the synthesis of useful compounds through judicious choice of substrates and solvents. Further, CGDE has the potentiality of being explored to generate energy rich gases from waste liquors containing simple organic substrates like ethanol, acetic acid etc. Results of the present study could be used as an aid towards preparation of a gaseous mixture of desirable composition.

Moreover, results of the investigation on understanding the mechanism of the growth of a stabilized gaseous sheath over the anode during electrolysis would hopefully be of aid in reducing the possibility of the occurrence of 'anode effect' in molten salt electrolyses which causes interruption of normal cell operations and significant losses of energy in industrial aluminium cells.
