

**DECENNIAL TRENDS IN ORGANIC ELECTROSYNTHESIS**

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Organic electrosynthesis, known for decades, has now gained enormous momentum and stretched its wings to other branches of chemistry, thus making it an "in-situ interdisciplinary research". This article focusses the latest trends in this area. The importance of conventional transformation of functional groups into another, paired reactions, C<sub>1</sub> chemistry, phase transfer catalysed synthesis, photoelectrosynthesis and electropolymerisation are highlighted from their basic principles to the emerging views. The trends are consolidated and futuristic prospects are predicted based on these developments.

**Key words:** Organic electrosynthesis, functional group transformation, paired reactions, C<sub>1</sub> chemistry, phase transfer catalysed synthesis, photo-electrosynthesis and electropolymerization.

**I. INTRODUCTION**

While there are ever so many methods available for organic chemists to synthesise a number of vital products (drugs, pigments, dyes, fibres, plastics), the practice of applying electrochemistry in organic synthesis is popular ever since the discovery of Kolbe electrolysis [1]. This methodology had not however been actively pursued due to the lack of interfacial understanding of both branches of chemistry as a single entity. With the advances of electrochemical techniques and engineering, newer synthetic routes have become worthwhile. Besides, this methodology helps the synthesis of a desired product selectively in pure form avoiding probable multisteps. With the expansion of traditional approach, it has indeed been possible to stretch its principles to photochemistry, catalysis and polymer chemistry.

There are a number of monographs [2-5] and reviews [6-16], but in the search for organic electrochemistry as an interdisciplinary route of synthesis, the necessity of assessing the potentialities based on the recent trends becomes imminent. With this idea, the present article focusses the recent trends (1977-1986) excluding the distant past organic electrochemical reactions.

**II. WHY AN ELECTROSYNTHESIS AT ALL?**

It is an established fact that in a chemical reaction, an external species is added to the reactant which performs either oxidation or reduction or coupling or cleaving to the desired product. This is always accompanied by unwanted side products, and the isolation of product becomes laborious. On the other hand, electrosynthesis is electron transfer dependent and offers excellent opportunities of directing many organic reactions at controlled rate and at greater product selectivity. By the control of electrode potential, discrete electrical energy is introduced into the reactants in a highly selective manner. The advantages of such electrolytically induced synthesis are: (a) it provides short-cuts in multi-stage reaction schemes; (b) it gives better yields due to strict regulation of the oxidizing and reducing power of the electrode; and (c) the isolation of the products from the reactants is easy since there is no need to remove the product from a chemical oxidant or reductant.

Any chemical that is costlier is an attractive candidate to be considered by the electrochemical route. Besides, it is free from pollution. With increase in simplicity of chemical engineering design, electrosynthetic process is not only a laboratory curiosity but also an attractive industrial proposition.

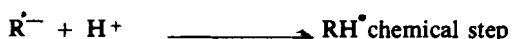
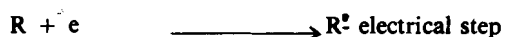
**III. CLASSIFICATION OF ORGANIC ELECTROSYNTHESIS**

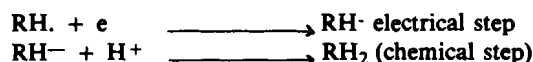
The prime factor in a given electrolysis is that one of the electrodes acts as electron sink (anode) and the other acts as an electron source (cathode), thus giving rise to respective electrode reactions simultaneously. Mostly, only half of the reactions have been taken to direct a given reaction. This is widely characterised by the occurrence of electron transfer in the electrolytic medium. Manipulation of concentration gradient, choice of electrode, electrolyte and raw material coupled with characteristic electrode potential generate various types of reactive intermediates such as ions, radicals, radicalions etc. These ensure the different possibilities of synthetic approach, thus making organic electrosynthesis as multidisciplinary. Organic electrochemical reactions based on these intermediates, can be classified as follows as per the recent trends in terms of synthetic value.

1. Cathodic reactions
2. Anodic reactions
3. Paired reactions
4. Phase transfer catalysed reactions
5. Reactions leading to C<sub>1</sub> chemistry
6. Photoelectrosynthesis
7. Electropolymerization

**III-1. Cathodic reactions**

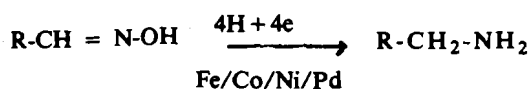
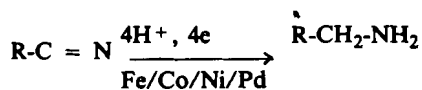
Organic compounds that are susceptible for reduction can accept electrons directly from the electrode. Such a process involves following reaction sequence:



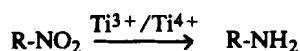


Based on this reaction sequence, it is possible to bring out reductions of carbonyl compounds, carboxylic acids, nitro compounds, unsaturated hydrocarbons, nitriles, oxime and C-Cl bond leading to useful products [2].

The choice of electrode material has been very much realised in transforming functional groups such as nitriles and oximes into primary amine. In this approach, a simpler technique which involves the combination of in situ electrochemical generation of pure hydrogen and its adsorption on thinly deposited Fe, Co, Ni, Pd black cathodes acting as catalyst has been adopted [17-28].



Another interesting development is in the preparation of amines from nitro compounds employing titanous - titanic redox couple [29-33].



The transformation of  $\text{NO}_2$  to  $\text{NH}_2$ , although very familiar, is applied to newer compounds such as conversion of 1, bromo 2, 4, 5-trimethyl - 3, 6 dinitrobenzene into 2-bromo, 3, 5, 6 - trimethyl 1, 4 phenylene diamine at mercury pool cathode [34].

The formation of amines has also been achieved cathodically from azo compounds [35] in an alkaline medium using Pb cathode which offers very high yield efficiency. There is a patent [36] claiming the crucial transformation of alcoholic hydroxyl group into chloride. Use of methylene chloride as medium has been recommended for effective transformation. Also chloride group can be removed cathodically as is seen in the reduction of 2-halo-2 nitropropane 1,3 diol into 2-nitro propane 1, 3 diol using Pt electrodes [36].

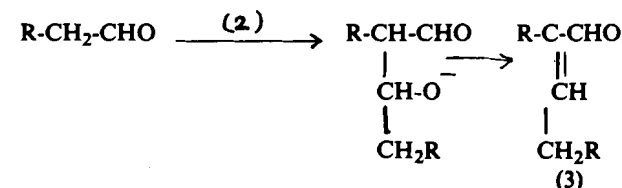
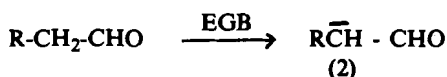
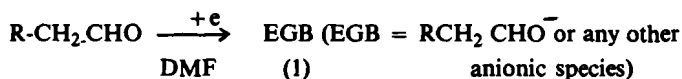
Electroreduction of double bonds has been extended to synthesise succinimide from maleimide [37] at Pb or Cu electrode in acetonitrile. A novel synthesis that is effected through this process is the introduction of acetate groups across the unsaturated chain like  $\text{C}_2\text{H}_4$  which ultimately pave the way for production of vinyl acetate, an important monomer for the preparation of useful vinyl polymers [38]. Besides, electroreduction has been found to be useful in effecting Brown-Walker synthesis [39] using dicarboxylic acid and its monoesters for the preparation of dimeric products and higher oligomers. The significant contribution of this reaction is the development of technological scheme for the industrial electroreduction of sebamic acid and sueberic acid [39]. Many patent literature stress the potentialities of electroreduction in the preparation of various compounds such as trichloromethyl carbinol

and derivatives from aldehydes [40], 1, 2 dimercapto succinic acid dinitrile from substituted 1, 2 dicyano 1, 2 dimeroapto ethenes [41], p-methoxybenzoic acid from tetraphthalic acid [42], epoxides from alkenes [43] and preparation of  $\alpha$ -hydroxy acetals and ketals [44].

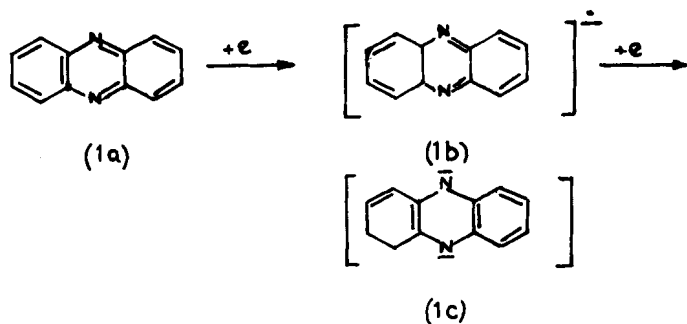
Other notable advancements in electroreduction are the effect of intentionally added inorganic salts which profoundly influence the synthesis. For example, electroreduction of deoxybenzoin, catalysed with chromium salts, in DMF has been realized at lower potential which results in product selectivity [45]. The addition of Sn(II), Tl(I) salts and the use of bismuth deposited electrodes has resulted in higher yields of p-aminophenol from nitrobenzene than from ordinary copper or monel cathodes [46].

In the electrochemical adamantylation of stilbene, the electrogenerated anion radicals of stilbene and 4-methoxy styrene are made to react with 1-bromo adamantene. This reaction in aprotic solvent proceeds via an electron transfer in solution [47].

Aldol condensations are successfully effected as per the following sequence by passing catalytic amount of electricity through dimethyl formamide solution containing aldehydes [48].



A novel electrogenerated base derived from phenazine by electroreduction is extremely helpful to carry out Darzens and Wittig-Horner type of reaction without the addition of any other base [49].



There are also studies relating to the electrochemical generation of reactive nitrogen species [50], radical species [51] and unsaturated radical cations [52].

Transesterification and amidation have been reported [53].

Alcoholysis of ester has been carried out at very high current efficiency. Amidation reactions of esters with amines have also been worked out in this class of reaction. This electrochemical technique is a novel method of preparing acid amides from esters in presence of amines.

### III-2. Anodic reactions

In the event of anode being an electron sink, the transfer of electron gives rise to a number of reactive intermediates which are responsible for reactions like oxidation of functional groups, acetoxylation, methoxylation, halogenation etc.

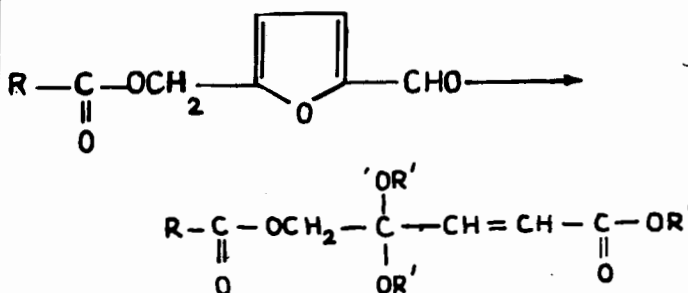
Oxidation of HCHO at Pt anode in dilute  $H_2SO_4$  to aromatic acid has been proved [34] to yield higher current efficiencies. Oxidation of aliphatic primary alcohol to an acid is another reaction, as is evident from the report [35] on the conversion of 2-ethyl-1-hexanol into 2-ethyl-1-hexanoic acid at Pt or  $PbO_2$  anodes. Conversion of 2, 3 butane diol into acetaldehyde has been made possible [36] by periodate-iodate mediated oxidation wherein maximum current efficiencies have been obtained.

Others of interest are: (i) oxidation of monochloro-substituted toluene into monochlorobenzoic acid at Pt anode [37]; (ii) conversion of benzoic acid to benzoic anhydride at Pt disk electrode in nonaqueous medium [38]; (iii) dehydrogenation of tetrahydrocarbazole to carbazole at Pt gauze electrode [39] and (iv) dimethyl sulphate at Pt anode [60].

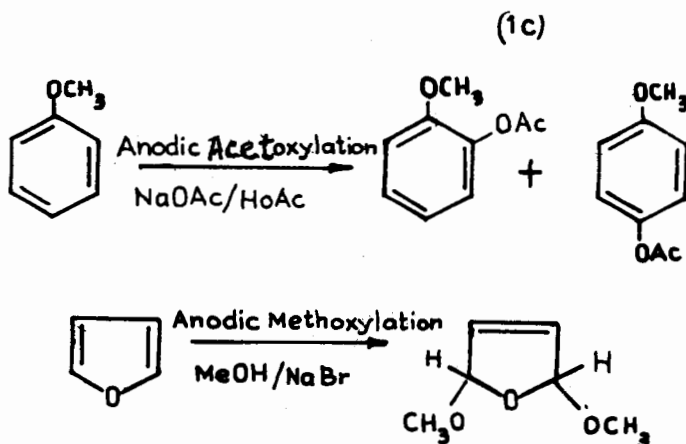
Benzene and toluene have been oxidised for industrial production of benzoquinone using  $PbO_2$  coated electrode [61] which helps to obtain higher current efficiency. The addition of salts influences the catalytically initiated synthesis of quinone compound which is quite phenomenal and  $Ce^{2+}$  helps the oxidation of naphthalene to naphthaquinone [62] and manganese ions in the synthesis of p-benzoquinone from aniline [63]. Besides the possibility of depositing anodically Ni and Co on stainless steel, graphite and titanium as oxides for the oxidation has been proved to be fruitful. Various alcohols, n-pentanol, butyl alcohol etc., have been subjected to electrochemical oxidation employing these oxide anodes.

The recent development of electrogenerative oxidation of ethanol enriched vapour is quite attractive in the industrial scale. This process employs Pt electrode in dilute  $H_2SO_4$  medium and stresses the influence of catalytic electrode. Both acetaldehyde and acetic acid can be selectively synthesised by control of electrode potential and the feed rate of ethanol vapour in the gas stream [65].

Another interesting reaction that has emerged through anodic oxidation is the opening of heterocyclic ring system [66]. A typical reaction sequence can be represented as follows:



Lewis acid catalyzed condensation [67] and acetoxylation [68] have been perfected. Furan can be methoxylated leading to useful products.



Electrohalogenation is one of the emerging anodic reactions. Both chlorination and fluorination form the very essence of vital industrial products of modern times. Electrofluorination forms a separate branch of activity which will be discussed in depth separately in this journal [69]. Hence the importance of chlorination alone is discussed here.

Electrochlorination has been fruitful in the preparation of chlorinated rubber [70] and chlorotoluene [71]. The technique is found to be quite advantageous to the conventional chemical route, as the attack of nascent chlorine on the substrate is very effective, thus leading to desired products with less cumbersome parameters. Of all the anodes employed, titanium substrate insoluble anode (TSIA) process developed at CECRI, Karaikudi) is the most potential anode due to their catalytic nature leading to high current efficiencies and yield efficiencies [72]. Synthesis of chlorinated hydrocarbons has also been successfully reported elsewhere wherein  $PbO_2$  is used as the anode. A packed type electrode with graphite plates has been recommended for the electrochlorination of butadiene using cerous chloride in acetonitrile.

The reactions so far discussed in sections III-1 and III-2 mainly centre on the transformation of traditional functional group into another which are equally well known in conventional synthetic route. On the other hand, reactions such as acetoxylation and methoxylation help to avoid the multistage reactions normally encountered in the conventional approach, thus making the electrochemical route an attractive proposition. Besides adamantlylation, aldol condensation, Lewis acid catalysed condensation etc., are highly selective and stretchable for synthesising other valuable organic compounds.

### III-3. Paired organic electrochemistry

In this type of synthesis, electron transfers occurring at both the electrodes are directed to effect useful products. By this way, both anode and cathode are simultaneously used as working electrodes. Such synthesis offers an economic advantage such as reduction of

energy consumption to just half of one single electrode reaction. Although this methodology is quite attractive, it is yet to receive greater attention. Many reactions have now started coming up in recent years, and only novel examples are quoted here: oxidation of toluene to benzaldehyde by  $Mn^{3+}$  and OH generated in the anodic and cathodic reactions respectively is a quite useful approach in this oxidation [73, 74].

Biphenols having alkyl and alkoxy substituents are converted to hydroquinone and to the corresponding benzoquinone [75].

Conversion of 2, 3 butane diol to 2-butanone [76] in an undivided flow cell using Pb/Hg or Zn/Hg cathode and graphite anode has been reported successfully. The paired electroynthesis of sorbitol and gluconic acid in an undivided flow cell using Zn/Hg cathode is carried out from glucose [77]. Co-electrolysis of ethyl acrylate and diethyl malonate in acetonitrile containing tetrabutyl ammonium iodide has led [78] to the synthesis of diethyl adipate cathodically and tetraethyl ethane tetra carboxylate anodically using graphite electrode. Yet another demonstration of the utility of the paired synthesis is in the production of ethylene glycol [79].

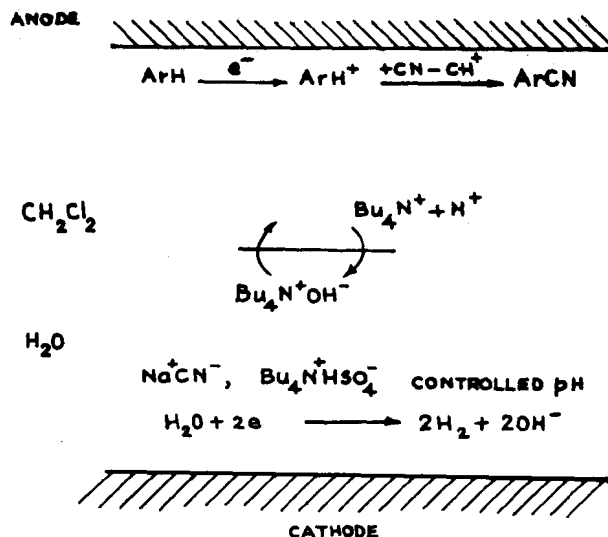
#### III-4. Phase transfer catalysed organic electroynthesis

Here, specially synthesised electroregeneratable catalyst performs the reaction more efficiently compared with conventional methodology. The prime factor is the selection of proper biphasic system as this reaction is brought about by the transfer of one reactant across the interface into the other phase where the desired reaction is effected.

In these reactions experimental procedures have been worked out for reactions like acetoxylation [80], substitution [81] and cyanation [82,83]. Of all these reactions, cyanation of naphthalene has received repeated investigations which are worth mentioning here. This is usually carried out by electrolysing in two immiscible solvents, methylene chloride containing the substrate and water containing sodium cyanide, in the presence of phase transfer catalyst namely tetrabutyl ammonium ions (in the form of the relatively cheap dilsulfate salt).

The principle of this reaction can be illustrated [84] as shown in next column.

As seen in the illustration, the anode reaction occurs in the organic solvent but the nucleophile is supplied by transfer of an ion-pair ( $Bu_4N^+ + CN^-$ ) from the aqueous solution. This reaction has further been extensively studied specially with reference to various electrochemical parameters. By judicious selection of conditions, it is proved that the yields can further be substantially improved. Similarly aromatic nuclear acyloxylation of 1, 4- dimethoxy benzene has been studied [85] in detail and also found that other substituted dimethoxy benzene can result in similar products. Conversion of 2,2, dimethyl 3-methylene bicyclo [2,2,1] -heptane (camphene) and (isoborneol) 1,7,7 trimethyl bicyclo heptane -2-ol to 1,7,7-trimethyl bicyclo heptane-2-one (camphor) has been carried out under phase transfer conditions in the presence of cetyl trimethyl ammonium chromate using  $PbO_2$  anode. Benzene/water pair is the immiscible phase in this reaction [86].

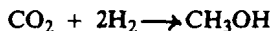


#### SCHEMATIC REPRESENTATION OF ANODIC NUCLEOPHILIC SUBSTITUTION BY TWO PHASE ELECTROLYSIS

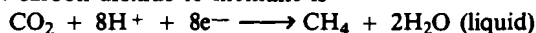
All these examples have proved the following advantages over the conventional synthesis: (a) enhanced reaction rates (b) easy work up of the solution (c) small quantities of catalyst is enough which can repeatedly be regenerated for further use (d) selectivity and (e) suppression of side reactions thus increasing the yields.

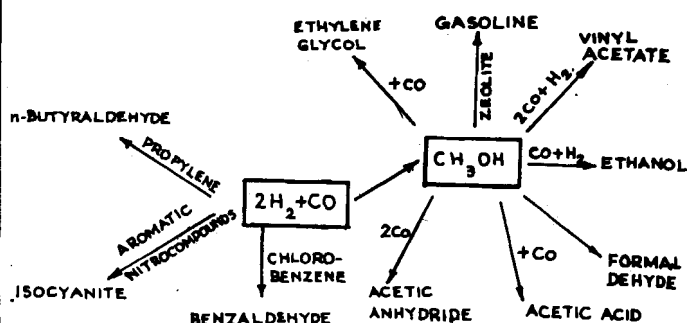
#### III-5. Organic electroynthesis on $C_1$ chemistry

In the declining trend of chemical feed stocks based on petroleum, ethylene, etc. the major direction aims at using of single carbon molecule as the building block to synthesise more complex compounds efficiently and economically [87]. The emergence of the new  $C_1$  chemistry is the versatility of methanol as a coreactant of carbon monoxide [88]. The following scheme (Fig. 1) shows the various possible products from  $C_1$  chemistry [89]. Chemical routes have been quite advancing in this area and the organic electrosynthetic route too shows an excellent promise and many industrial productionization have been realized. The following are the possible products that can be synthesised from carbon monoxide/hydrogen and methanol:(See illustration)



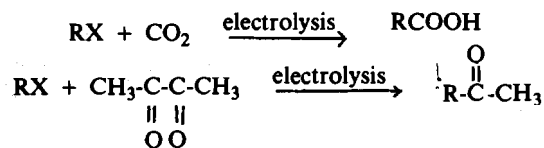
An electrochemical reduction of  $CO_2$  has been developed in aqueous medium into methanol which provides high current efficiency. Traditional reduction of  $CO_2$  to methane has been overtaken by electrochemical route as the reaction becomes very simple avoiding extreme conditions [90]. Ruthenium supported on both copper mesh and carbon rod have been used as electrodes for the production of methane [91]. The half cell reaction for the reduction of carbon dioxide to methane is





Products that can be synthesised from carbon monoxide/hydrogen and methanol

Another interesting development of industrial value is the electro synthesis of carboxylic acids [92, 93]. In this electrochemical reduction of aromatic halide in presence of  $\text{CO}_2$ , a sacrificial magnesium anode and a stainless steel cathode has been employed. A pressure of 1-5 atm, has been impressed at a low temperature of 292K to the electrolytic cell. This route has led to the synthesis of various carboxylic acids and ketones.



The production of methane and ethylene by electroreduction of  $\text{CO}_2$  in aqueous bicarbonate solution employing copper electrode, has also been reported [94]. The major event in this branch is the successful development of electrohydrodimerization of formaldehyde to ethylene glycol. Different supporting electrolytes such as NaCl, sodium sulphate, sodium formate etc. have been quite useful. Graphite is the best cathode for this reaction [95-98]. Ethylene glycol has also been obtained by reducing oxalic acid [99]. The use of porous hydrophobic gas transfer cathode has been recommended [100] for production of carboxylic acid from the electroreduction of  $\text{CO}_2$ . Methanol can be produced from electroreduction of  $\text{CO}_2$  and this can also serve as starting material to synthesise a number of compounds through photoelectrosynthesis (vide infra).

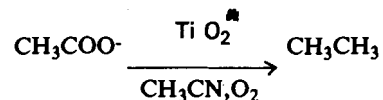
### III-6. Organic photoelectrosynthesis

Photoexcitation of electrode in a given electrolytic cell gives rise to a number of analytical, mechanical and synthetic reactions. The inherent principle of this mode of synthesis stems from the concept of electron-hole pair generation upon absorption of photon which directs the whole phenomena by establishing an electrical or chemical potential gradient at the interface. The primary requirements for facilitating such phenomena are:

- (i) Nature of semiconductor which dictates the energetics of electron exchange
- (ii) Wavelength sensitivity
- (iii) Proper flat band potential
- (iv) Surface stability of semiconductor electrode
- (v) Thickness of space charge depletion layer and
- (vi) The crystal structure of electrode surface.

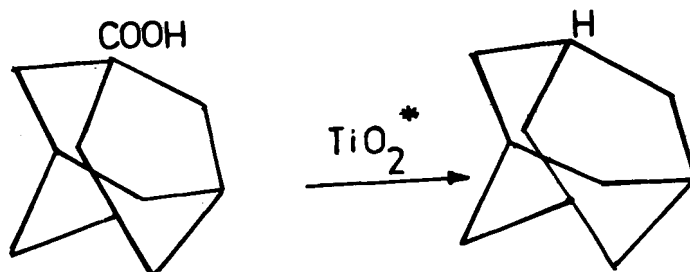
All these are very crucial before one selects the electrode material for any organic reaction to be performed on a semiconductor electrode. The nature and type of influence of these factors over photoexcitation process are well known [102-106].

Kolbe reaction of acetic acid under the influence of light irradiation on n- $\text{TiO}_2$  single crystal in  $\text{CH}_3\text{CN}$  containing tetrabutyl ammonium acetate is a typical example [107-109].



This process possesses the quantum efficiency of 65%. When the same electrode with platinisation is used for the above reaction, methane becomes the major product [110].

A number of saturated carboxylic acids have been similarly decarboxylated. The important contribution [111] in such decarboxylation studies is that even if  $\alpha$  carbon of the carboxylic acid is sterically congested, this reaction can be effected using  $\text{TiO}_2$  electrode.

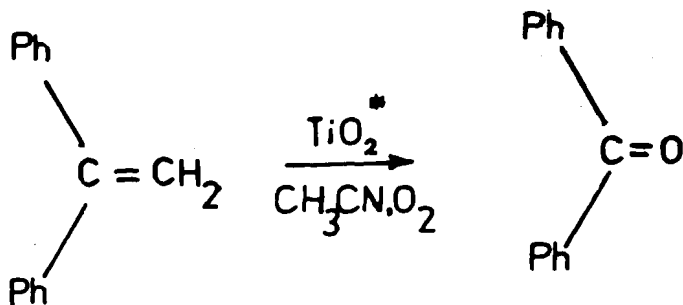


Apart from  $\text{TiO}_2$  electrode,  $\text{SnTiO}_3$  has also been found to be useful for carrying out these reactions, but it is less efficient [112]. Other semi-conducting electrodes such as modified  $\text{TiO}_2$  and  $\text{SnO}_2$  can also be fruitful particularly in olefine oxidation as indicated below [113-118].

When 1,1-diphenyl ethylene in  $\text{CH}_3\text{CN}$  is subjected to photoelectrolysis, the following reaction occurs [113-115].

(See the following illustration)

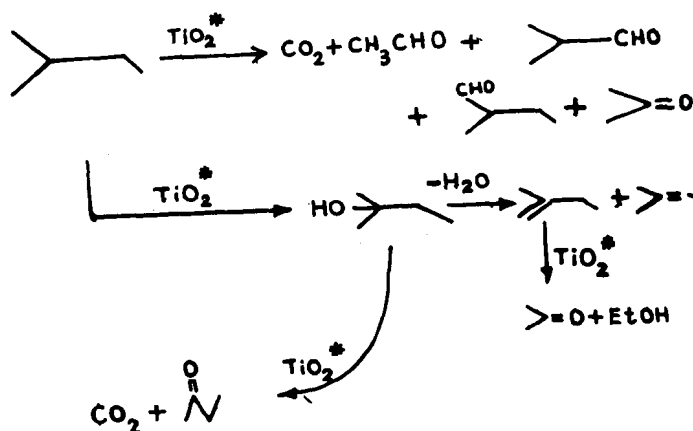
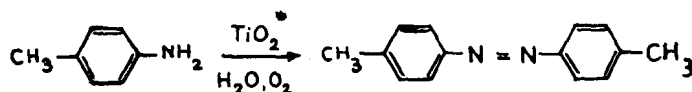
The above reaction occurs in 100% yield. A number of olefins have been oxidized and several mechanistic paths have also been proposed to account for the various products [116]. The important observation in this synthesis is that many side products are formed which can be quantitatively isolated.



Since o-substituted benzene product can be obtained in relatively high yields, it is considered as a viable alternative synthetic route. The other interesting reaction is the conversion of toluene to benzyl alcohol and benzaldehyde [121]. Aldehyde alone is resulted if the reaction is carried out in gas phase [122]. The possibility of synthesising phenol from the oxidation of benzene has also been realized but hampered by the simultaneous production of CO<sub>2</sub>. However this is a typical example of hydroxylation of aromatic ring [123].

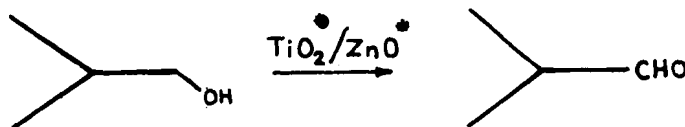
Similar considerations are extended to amine which gets cleaved. Thus toluene yields azo product [125].

Alkanes can also be oxidised leading to a variety of products as described below [119]:



A related bond cleavage has also been reported using CdS photocatalysed dealkylation of methylene blue and rhodamine B [126].

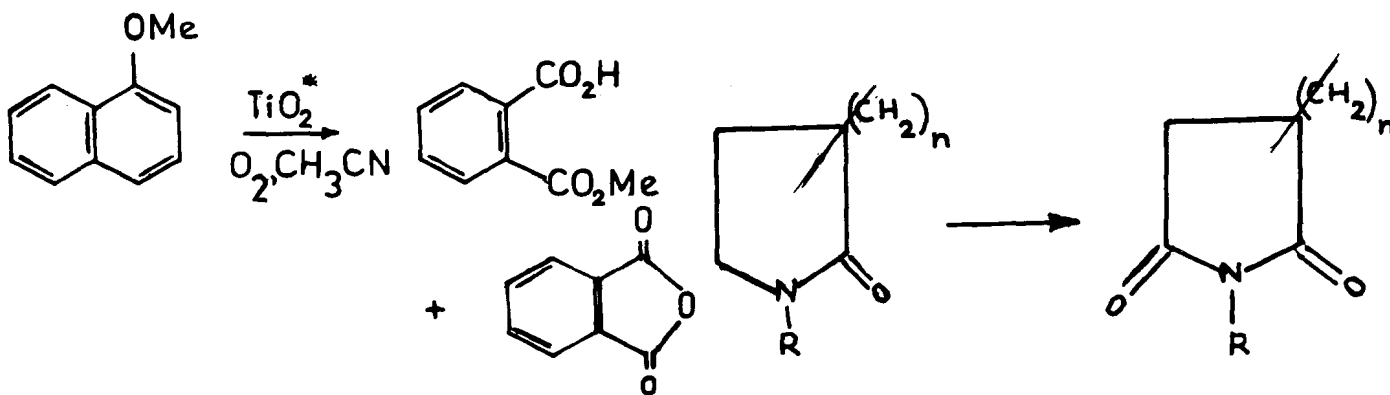
The conversion of alcohol to aldehyde or ketone has been realized in this methodology also [127].



Oxidation of arenes through this methodology is an interesting phenomenon, as the skeleton of aromatic molecule can be cleaved [120].

The efficiency of the reaction is greatly enhanced by fractional metal deposition over semiconductor electrode. The order of preference for obtaining greater efficiency is Pt > Rh > Pd > Ru > Ir > native [128].

Like this, lactams can also be converted to imides as follows: [129]



Glucose on photoelectro-oxidation at ZnO electrode yields mainly CO<sub>2</sub> [130].

Most of these reactions have employed mainly  $\text{TiO}_2$  and occasionally other metal oxides. Such oxide semiconducting electrodes are sufficiently robust for long term irradiation for photocatalysis of chemical redox transformations. Narrow-band semiconductors such as GaAs, InP etc., are yet to overcome the problem of stability in different electrolytic environments for their successful use.

Reductions have received attention only recently and a very few of them alone are known, and p-type silicon appears to be useful for electro-reduction, and  $\text{C}_1$  chemistry is being nursed to produce different products of industrial importance such as formaldehyde.

### III-7. Electropolymerization

The application of electrochemical methodology to polymerization is a young branch of research which mainly concerned in the early years in the understanding of the chemical phenomenon connected with formation of polymers in an electrolytic cell. The possibility of generating uniform polymer coating or film through electrosynthesis in the recent years has indeed activated the research on electropolymerization and this has been considered as a new synthetic tool for polymers. The major advantages of this route are the fine control of the initiation and termination steps. Basic principles of initiation, propagation and termination are excellently covered in standard books [2]. Both anodic and cathodic polymerizations exist depending on the initiating species generated. This synthetic route is characterised by following methodology of electropolymerization [131].

Two different classes exist in this synthetic approach: (i) electropolymerization in solution or bulk electropolymerization and (ii) in situ electropolymerization based on the site at which the propagation step of polymerization takes place. The product occurs in the bulk of the electrolytic solution in the former, while in the latter, at electrode surface. For both the cases, the origin of electroinitiation is the same. All types of polymerization such as free radical, ionic, coordination and ring opening are achievable in this route.

Polymerization in bulk of the electrolytic solution has been extended to a number of polymers such as polyvinyl acetate, [133,134], polyacrylamide [135], polybenzotrile [136], polyacrylonitrile [137] etc. Such synthesis of polymers are presently of academic interest and commercialisation of such synthesis is hampered by a number of difficulties. The major one is the precipitation of polymer in the bulk of the solution. Such a precipitation, as the reaction proceeds, depresses the rate of migration of electroactive species, and the process tends to become slow. Besides, synthesis of tacky polymers such as polyvinyl acetate is bound to get glued to the electrode surface haphazardly, thus hindering further electrolysis [133]. This difficulty can to some extent be overcome by the use of biphasic system [138]. Extrapolation of this, biphasic systems to large scale experiments is yet to be proved.

In situ electropolymerization, on the other hand is an advantageous route since the resultant polymer is formed either as

peelable film or adherent coating. Both insulating and conducting polymers can be synthesised in this approach and it is quite useful in electrochemical application such as device fabrications and protective surface coating. Since this methodology has been quite successful, synthesis of both these classes of polymers is highlighted below.

### Conducting Polymers

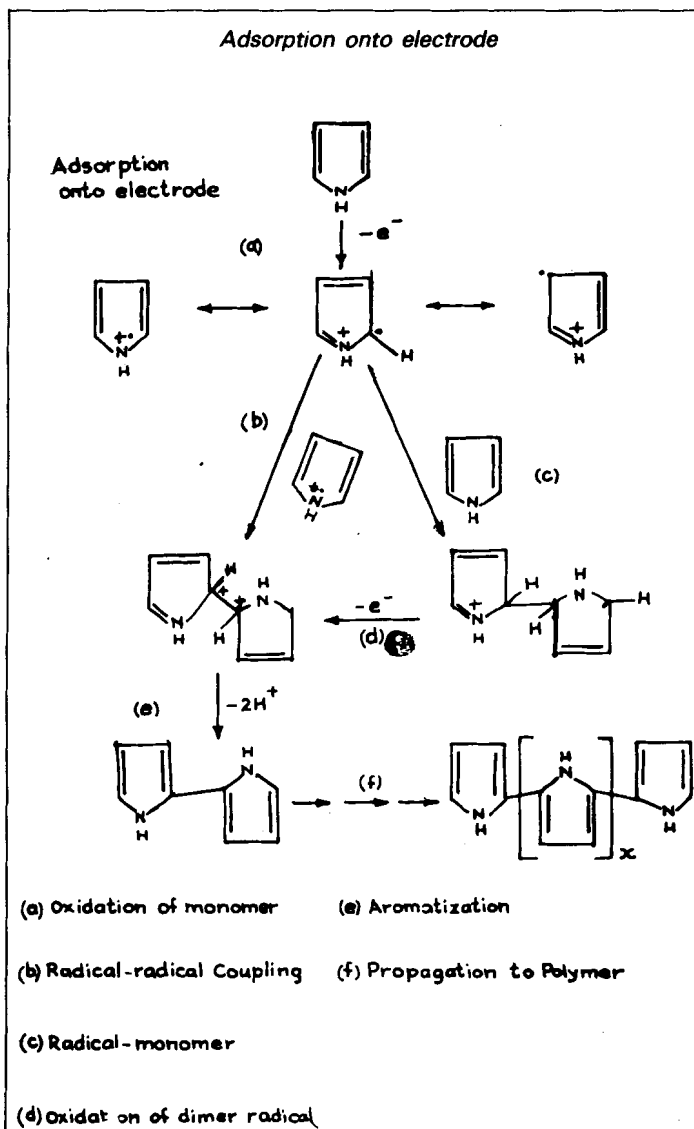
Since the polymer can be obtained as a film in this approach, conducting polymer synthesis is quite remunerative as they can directly be used in device fabrication as power sources, solar cell and electrochromic devices. Of all the monomers that give rise to conducting polymer, heterocyclic monomers are best suited. Pyrrole [139-147], thiophene [148,151-160], indole [148,149], furan [149], azulene [150] have all been polymerized through anodic oxidation. A number of anodes such as platinum, stainless steel, nickel, conducting glass etc., have been used. Besides, choice of different electrolytes such as tetra alkyl sodium, silver and copper salts give rise to a number of options in imparting counter ions to the macro molecular chain which ultimately influences the characteristics of films. Also the possibility of controlling the thickness of the film is achieved through manipulation of electropolymerization conditions. Conductivity ranges too can be varied by varying the concentration of the dopant ions in the given conducting polymer chain. With all these advantages, this particular route gives rise to different synthetic recipes for conducting polymers of preselected room temperature conductivity with the desired thickness. Hence this approach is favoured for a number of polymers.

The basic mechanistic aspects of such a growth of conducting polymer film is illustrated in the following sequence [160-161], with pyrrole polymerization as an example. (See illustration )

The important feature of this methodology is the reversibility of conducting levels and also from switching over from one type of conductivity to another type. This has been successfully accomplished for the synthesis of both n- type and p-type polythiophene containing different counter ions [162].

In recent years, modification of conducting polymers has also been achieved through copolymerization [163] and composite preparation in this synthetic route to impart flexibility [164-165] for the resultant polymeric film product. This is a major breakthrough in this area of research, thus giving rise to newer avenues of polymer modification which enhance the potentialities of these polymer systems. It has been the subject of current pursuit and a number of contributions are emerging.

The success realized in heterocyclic monomer system, as indicated above, has also been extended to other benzenoid systems which have yielded poly-p-phenylene [166-168] polyaniline [169-171], polypyridine [172], polynaphthalene [173] and polyanthracene [174] from their respective monomers, despite the availability of chemical routes for them. All these stress the importance of this route as an elegant synthetic tool in achieving the desired product. With the phenomenal growth in this class, many systems are synthesized and getting reported almost every month.



**SCHEME: MECHANISM FOR POLYPYRROLE FORMATION**

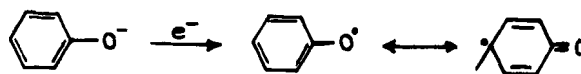
**Insulating polymers**

A class of polymers which mainly play a protective function for metallic substrates and give rise to uniform polymer coating is unique in this approach, as the formation and coating process occur simultaneously. The spreadability of polymer coating and comparatively faster rate of polymerization necessitate the use of this technique for generating a number of polymer coatings on metallic substrate, particularly for corrosion resistance. Many polymers have been attempted to coat the given metallic substrate with each having its own advantages and disadvantages [175]. Polyacrylamide and its derivatives [176,177], as well as vinyl polymers and acrylic polymers [176-181] have been constantly nursed on various metallic

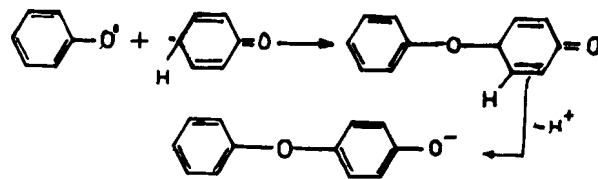
substrate such as Fe, Cu, Ni and Al, both through oxidation and reduction. Experience with different systems indicates better quality polymer coating from nonaqueous medium than from aqueous medium although the latter is preferred for economy [182]. Of all these systems, phenolic monomers are the potential sources of generating useful coating of polyphenylene oxide [183-184]. This proceeds through oxidative coupling polymerization as indicated below:

**a) Initiation**

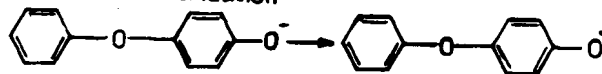
**Oxidation of Phenate ion into phenate free radicals**



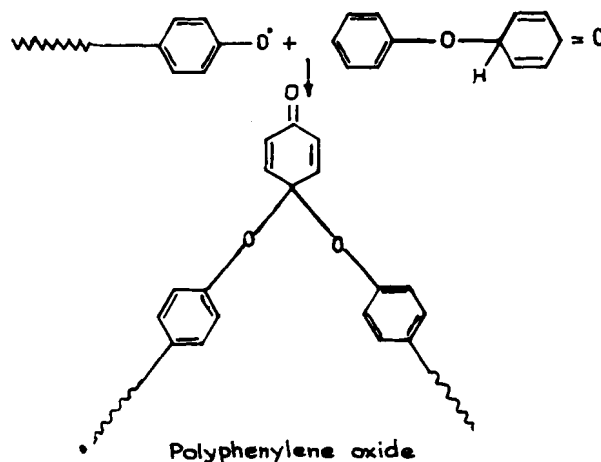
**(b) Propagation**



**and again anodic oxidation**



**(c) Termination**



Extensive studies of this polymerization over Fe, Cu, Ni etc., have been carried out [184-188]. Large scale polymerization has also been studied for possible commercial exploitation of this technique to generate polyphenylene oxide coating. The major advantages of this technology are the availability of cheaper raw materials and



repeatability of coating generation over a number of anodes from the same electrolytic bath. Attempts are under way to generate a flash coating. This has indeed encouraged to develop a number of polymer systems which are widely practised by other researchers also. Apart from this insulative polymer coating, monolayers of polymer having electroactive functional groups are being developed as the promising preparative route for development of electrocatalytic electrodes [189].

This synthetic approach is also useful in the modification of carbon and graphite fibres which are of great use in fabrication of composite material [190-191] and microelectrodes [192-193]. Polyacrylamide has been grafted to modify carbon fibres in aqueous medium for developing prepeg for composites [194]. It is the safest approach for modification of carbon fibre matrix, as this requires lesser time and the polymerization process can easily be extrapolated to large scale, similar to the continuous plating of wires. Further, efficiency of modification is as high as 70%, which can be altered as and when required through manipulation of synthetic recipes. This is indeed a modern area requiring greater attention.

#### IV. ENGINEERING ASPECTS

Electroorganic technology has been receiving enormous attention in the last twenty years or so. The successful commercialization of bench scale reactions needs an understanding of basic chemistry and electrochemistry. Engineering skills have to be coupled with the basic electrochemistry for a proper design of an electrochemical cell. For a long period, electroorganic synthesis remained only as a bench scale curiosity. It is necessary to highlight various types of cell designs that have been considered for industrial exploitation of electroorganic processes.

The following types of cells are some of the developments in the recent past for the manufacture of organic chemicals through electrosynthesis [195]:

- (i) Tank cell
- (ii) Parallel plate cell
- (iii) Swiss roll cell
- (iv) Capillary gap/disc sack cell
- (v) Pump cell
- (vi) Cylindrical cell
- (vii) Packed and fluidised monopolar cell and
- (viii) Bipolar fluidised bed cell

By thorough investigation of electrochemical processes, it is possible to arrive at the exact design for a particular reaction. For instance, electrosynthesis of ferrocene has been carried out in a special type of filter press design [196]. It has also been indicated that a tubular flow cell can also be employed for electrochemical synthesis [197]. A monopolar membrane cell has been extensively used for the electrochemical synthesis of polyols.

A bipolar electrochemical pump cell for organic synthesis has been developed [199] which has been successfully used for dimerization and hydrodimerization reactions. Propylene oxide production has also been found to be fruitful in this type [200] of bipolar electrochemical pump cell.

A bipolar narrow gap flow cell has been developed for the oxidation of reducing sugars in general and glucose in particular [201]. This cell has several advantages over the rotating electrode cell developed earlier. About 30% savings in electricity can be achieved in the bipolar narrow gap flow cell. The space time yield is more favourable.

The development of new electrochemical cell design is always directed to reduce the capital investment per unit of electrode surface area, thus reducing the cost of the product. This can well be achieved by increasing the surface area per cell volume which indirectly enhances the space time yields.

#### V. FUTURISTIC ASPECTS OF ORGANIC ELECTROSYNTHESIS

Although this area of research has been known almost for a few decades, newer approaches have also been merging for diversified applications. Even in conventional transformation of functional groups, electrosynthetic approach for reduction/oxidation of bifunctional groups is quite attractive, as is evident from the conversion of o-nitrobenzaldehyde to o-amino benzyl alcohol [202]. The major direction in this aspect is the development of sintered electrode, electrocatalytic electrodes and polymer electrodes for effecting selective reaction, which is expected to unravel many complex reactions hitherto unknown [189]. Paired synthesis is gaining importance in view of its economic gains. Many more interesting oxidation and reduction products are expected to enhance the industrial potentialities of organic electrosynthesis. Probing of newer biphasic systems such as liquid-liquid, liquid-solid, or liquid-gas with development of newer phase transfer catalysts such as crown ethers is bound to generate renewed vigour in conventional synthesis. The chemistry based on  $C_1$  through this methodology is an attractive proposition for generating useful industrial products with the success on industrial production of ethylene glycol. Further work on  $C_1$  chemistry will bring out many interesting avenues for vital products. Work on photoelectrosynthesis shows a lot of opportunities for organic synthesis, but care has to be taken for avoiding side products. Electropolymerization with increase in importance is expected to revolutionize the synthesis of polymers, especially in the development of conducting polymers. The electrosynthetic route itself appears to be quite promising in conventional polymer modifications and indeed to change the profile of polymer chemistry.

Chemical engineering aspects of electrosynthesis are yet to take full shape for different classes of reactions. Newer designs are to be developed for organic photoelectrosynthesis and electropolymerization.

Other areas requiring constant attention for electrosynthesis are the utility of magnetic field which gives rise to a new technique called magnetoelectrolysis [203]. Besides, application of ultrasonics to synthesise polymers brings about changes in the characteristics of the polymer film, as is proved in the case of polythiophene [204]. These two techniques in the application of electrosynthesis are determined to create greater impact and form an area of future study.

### CONCLUSION

The preceding section indicates the enormous potentialities of electrochemistry leading to alternative industrial routes for a number of vital products. Of all the sequences,  $C_1$  chemistry, paired synthesis, phase transfer catalyst and electropolymerization form the

present backbone of organic electrochemistry. Constant efforts towards the development of cheaper and elegant synthetic routes will certainly lead to the generation of newer compounds.

(Note: Those who are desirous of getting a copy of the references cited in this Review may contact the Editor-in-Chief.) 