

RECENT TRENDS IN THE SYNTHESSES OF ELECTROCHEMICALS

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This paper highlights some of the emerging technologies and trends in the production of electrochemicals-both inorganic and organic by way of a brief review. H_2O_2 by trickle bed reactor-syntheses of N_2O_5 and O_3 , paired synthesis of inorganic chemicals, indirect 'ex-cell' and in-cell processes for organic synthesis, fluoro chemicals, solid polymer electrolyte electrolyser for organic synthesis, new electrochemical route by electro reductive carboxylation for producing optically active precursor to Naproxen, Ibuprofen and Fenoprofen are dealt in this review. Apart from electrosynthesis, waste recovery by electro dialysis or electrolysis is briefly described.

Keywords: Electrochemicals, waste recovery and electro dialysis

INTRODUCTION

In recent years, the electrochemistry and electrochemical technology and especially electrosyntheses of chemicals have been experiencing an exciting period, since there is a general recognition for electrochemical synthesis due its being 'environment - friendly', as electrons are 'facile reagent' in such processes. Though the electrochemical method of manufacture has held undisputed sway in the manufacture of inorganic bulk chemicals like caustic soda-chlorine, chlorates and perchlorates, the recent publications in electroorganic chemistry reveal increased interest and awareness for electrosynthesis of different organic chemicals [1-5].

More technological innovations have been made in the production of electrochemicals-both inorganic and organic - with the twin objectives of reduction in electrical energy and pollution abatement, thanks to the availability of better materials for cell components, electrodes in general and electrocatalytic electrodes in particular, membranes and different designs of electrochemical reactors particularly to increase the space-time-yield. Furthermore assembled cells are now readily available like FM-21 electrolyser from ICI, U.K. Dished Electrode Membrane (DEM) cell, Electrosyn cell from Sweden etc. The benefits of electrochemical methods are : closer control of each reaction step; better purity, higher product selectivity, lower processing temperatures and costs, less by-product waste and in some cases safer operating conditions.

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review. Apart from electrosynthesis, waste recovery by electrolysis or electro dialysis is briefly described.

Inorganic electrochemicals

The caustic soda-chlorine industry has witnessed spectacular developments by way of anodes, cathodes and membranes leading to the establishment of high amperage membrane cells and zero gap cells. Since it has already taken a firm footing, this paper will not deal more about this except to mention that oxygen trickle bed electrode as a cathode has recently been reported [6]. Similarly for the chlorate process use of oxygen cathode has been reported [7] for the reduction in energy since hydrogen liberated in this process is not utilized at present. A novel electrochemical process for the production of perchloric acid and ammonium perchlorate of high purity developed by Olin Company [8] involves the electrolysis of chloric acid to perchloric acid and subsequent reaction with high purity ammonium hydroxide to produce ammonium perchlorate. This process involves no alkali metals, chlorides, or chromates.

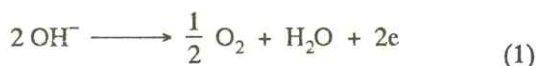
Apart from the above chemicals, other chemicals which are attracting the attention of electrochemists are : (a) 'on-site' manufacture of H_2O_2 , (b) ozone by electrolysis and (c) nitrogen pentoxide (N_2O_5).

On-site manufacture of H_2O_2 by trickle-bed reactor [9,10]

Dow Chemical Co. started scale - up stages for the production of H_2O_2 in alkaline solution using a trickle bed reactor resulting in commercial size production capable of producing over 67 kg per day per cell unit. The packed bed

cathode consisting of carbon black, Teflon and graphite chips is separated from the anode compartment by a porous diaphragm. Dilute NaOH is recirculated through the porous diaphragm onto the tickle bed ; where on the passage of current it reacts with O₂ to form peroxide. The O₂ gas from the anode and excess O₂ coming out of the cell with H₂O₂, are recycled back to the cathode oxygen feed. The alkaline H₂O₂ is recovered in a single pass through the reactor from the bottom of the cell in sufficient concentration suitable for pulp bleaching. On the commercial scale, the energy consumption is claimed at 3.3 kWh.kg⁻¹ at a current density of 7 A.dm⁻² with a current efficiency of 95% to obtain 30-50 g.l⁻¹ H₂O₂. This method is specially suitable as an on-site technique for generation of H₂O₂ for bleaching pulp and textiles. The main reactions are :

At anode



At cathode



Overall



Ozone production by electrolysis

Increasing interest in the use of ozone as an environmentally desirable alternative in waste treatment, water purification and for bleaching of pulp has led to the development of production of ozone by electrolysis. The attractive feature of the electrolytic method is that high ozone concentration can be obtained in the anodic gas stream upto 20 wt% in many cases. There are two strategies for electrolytic generation of ozone [9,11-15].

Two-dimensional carbon-based anodes

Ozone is produced in the conventional cell geometry using an aqueous electrolyte, most suitably the corrosive inorganic acid-fluoboric acid [13] with fluorocarbon impregnated carbon anode and platinum-catalysed high surface area porous cathode. In this case the ozone gas stream must be separated from the electrolyte, demisted of fluoroboric acid droplets. A current efficiency of 35% is achieved at a current density of 90 A.dm⁻² to obtain 20 wt% O₃.

At anode



and

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At cathode



Solid polymer electrolyte (SPE) technology [11-14]

Lyntech Company [11] has been involved in the development of solid polymer electrolyte in the form of proton exchange membrane (PEM) like Nafion. The acidic environment of a PEM avoids the use of an aggressive aqueous acid electrolyte. Ozone is produced directly by passing a stream of relatively pure water down the reverse side of a three dimensional porous anode consisting of polycrystalline β-PbO₂- coated porous titanium substrate in contact with PEM (Nafion); cathode is either platinum plated porous titanium substrate or platinum catalysed fuel cell grade gas diffusion electrode. The anode and cathode are placed in contact with opposite sides of PEM. Cells are operated using either hydrogen evolution or oxygen reduction cathodes. Cell voltages at a current density of 100 A.dm⁻² and at a cell temperature of 303 K are 2.3V for an oxygen cathode of 3.2 V for hydrogen cathode. The current efficiency of 20% for the production of O₃ could be achieved.

Electrosynthesis of Nitrogen Pentoxide (N₂O₅)

N₂O₅ is a strong and clean nitrating agent used in a variety of nitration media which are used to make nitro-compounds of industrial (fine chemicals, agro chemicals and pharmaceutical) and military interest. ICI had first tried the preparation of N₂O₅ [16]. Thiokom Corporation had set up a pilot plant for the production of N₂O₅ [17].

The process consists of electrolysing anhydrous HNO₃ solution saturated with N₂O₄ (20-30%) in a two compartment cell separated by Nafion membrane using platinum or titanium supported iridium oxide anodes and platinum clad cathode at temperatures between 278 and 288 K. The product formed contains 30% N₂O₅ in HNO₃ with an energy consumption of 0.3 to 0.7 kWh mole of N₂O₅. Thus the only raw materials consumed are con. HNO₃ and electricity. All other products are easily recycled and no toxic wastes are produced. The reactions are :

At anode



At cathode



Paired synthesis for inorganic electrochemicals

A novel idea of simultaneous electrosynthesis of useful products at both electrodes is being tried to make electrochemical processes more competitive. Verban and Mullinder [18] reported the simultaneous electrowinning of MnO_2 (at anode) and zinc (at cathode).

Simultaneous synthesis of H_2O_2 and $NaClO_3$

Recently simultaneous electrosynthesis and alkaline H_2O_2 (at cathode) and sodium chlorate (at anode) in the same cell was investigated [19]. The alkaline H_2O_2 was obtained by the electroreduction of O_2 in NaOH on a fixed carbon bed while the chlorate was obtained by the reaction of anodic electrogenerated hypochlorous acid and hypochlorite in an external reactor. An anion membrane, protected on the anode side with an asbestos diaphragm was used as a separator between the two chambers of the cell. It has been reported that cogeneration of peroxide and chlorate, both with current efficiency of 70% at a current density of 2.4 kA.m^{-2} at 4.2 V per cell has given an energy consumption of 9 kWh for production of 1 kg of $NaClO_3$ + 1 kg of H_2O_2 .

Simultaneous synthesis of O_3 and H_2O_2 [20, 21]

The paired synthesis of O_3 and H_2O_2 at the two electrodes separated by proton exchange membrane (PEM) (Nafion) in an electrochemical flow reactor is described [21]. Because of low current efficiencies, 4.5% for O_3 and 0.8% for H_2O_2 further improvements have to be made.

Organic electrochemicals

In the case of organic electrochemicals, it is not necessary that the entire process must be electrochemical, but some steps in the reaction can be better achieved by electrochemical route, making the process more economical, or reducing the number of steps in the reaction or avoiding handling of hazardous chemicals. Industrial scale production of organic chemicals by electrosynthesis existed earlier for chemicals like benzidine, sorbitol, mannitol, pinacol, vanillin, hydroquinone, chloroform, iodoform, anthraquinone etc. but a few have only survived eg. anthraquinone. The failure was due to the discovery of either alternative catalytic or chemical routes. Many new processes have emerged and about 120 have been piloted and out of which 60 are now commercial [4] and electrohydrodimerization of acrylonitrile to adiponitrile still remains a largest tonnage process (3×10^5 tonnes/year). Another tonnage process which had been successfully operated commercially by electrochemical route is L-cysteine (1500T/year) by reductive hydro monomerization of L-cystine [4.5] in acid solution.

Indirect electrosynthesis of organic compounds

Electrochemical oxidation or reduction can occur either directly by electron transfer from the substrate to the

electrode or vice versa or indirectly via mediator. Mediated or indirect electrosynthesis is a cyclic process involving electrochemical generation of a redox reagent and use of same to effect a chemical oxidation or reduction. This process is becoming popular in view of zero effluent and avoidance of electrode corrosion and fouling.

Ex-cell or 2-stage process

At the present time, there is a considerable industrial interest in the indirect two-stage electrochemical process for the synthesis of organic chemicals. Preparation of partially oxidised chemicals, such as aromatic aldehydes, ketones, and quinones has depended on the high selectivity of transition metal oxidants such as Cr (VI) [4], Mn (III) [22], Co (III) and Ce (IV). As a result there has been much interest recently in the electrochemical recycle of these oxidants. Of these, Cr (VI) has lower selectivity, even though it is most soluble and easiest for regeneration. Mn(III) gives good selectivity but unstable at lower acid concentrations with poor solubility of Mn (II) and Mn(III) at high acid concentrations. The powerful Co(III) is also unstable due to water oxidation. Ce(IV) is generally preferred due to higher stability and excellent selectivity. The commercialisation of use of Ce (IV) in $HClO_4$ is prevented due to explosive nature of perchloric acid in organic medium. The use of Ce(III) sulphate in H_2SO_4 medium is limited by the low solubility. Recently methane sulphonic acid or trifluoromethane sulphonic acid has been found to solubilise Ce(III)/Ce (IV) couple without the above difficulties resulting in a relatively high Ce(IV) concentration, regeneration with good current efficiency, and selective organic oxidation with high conversion. This makes the Ce-mediated electrosynthesis practical for commercial production of several carbonyl compounds. Using Ce redox couple in methane sulphonic acid, Hydroquebec in Canada had successfully operated a pilot plant (100 ton/year) for the production of anthraquinone via naphthalene to naphthaquinone route [23-27]. This system has also been employed for the synthesis of aldehydes from alkyl benzene [23].

In-cell process

The mediator is continuously regenerated at the electrode and can take up electrons or abstract hydrogen from the substrate atom and electron transfer can happen homogeneously to a mediator dissolved in the electrolyte, or heterogeneously to a mediator bound to the electrode surface.

Indirect homogeneous in-cell process Phase transfer catalysis [5]

Indirect electrosynthesis where phase transfer catalysis is used allows the chemical step to occur homogeneously in an organic solvent immiscible with the aqueous electrolyte. Electrolysis should be carried out with an emulsion of aqueous and organic phases within an undivided cell.

Oxidant generated at the electrode surface in the aqueous phase forms an ion pair in tetraalkyl ammonium cations present in the electrolyte and this leads to its transfer to the solvent (dichloromethane, CH_2Cl_2), where oxidation of the organic compound occurs. The reaction has to be fast and selective. The reduced inorganic ions reverts to the aqueous phase where it is oxidised. The organic product is readily recovered from the organic phase. Two-phase reactions are facile and efficient. It is very well illustrated (by Pletcher et al) by oxidation of alcohols to aldehydes by dichromate [5]. In addition to dichromate, systems based on hypobromite, cerium anions, and ferricyanide have been studied [5].

Ti (III) /Ti (IV) redox system for reduction

Since Ti(III) is a very powerful reducing agent, the same has been used for the reduction of aromatic nitrocompounds in H_2SO_4 medium to obtain quantitative yields [28]. The electrolyte can be recycled and thereby avoiding pollution.

Br^-/OBr^- redox system for oxidation

The Br^-/OBr^- redox system has successfully been employed for the oxidation of glucose to gluconic acid to produce calcium gluconate. A bipolar flow cell has been developed by CECRI [29] for the production of calcium gluconate, enabling a saving of 35 - 40% of energy as compared to tank cells. Based on this process, more than 500 T/year is being produced in India.

Indirect Heterogeneous in-cell process Nickel hydroxide electrode

Nickel hydroxide electrode has proved to be a versatile inexpensive and facile applicable reagent and allows easy scale-up of oxidation. It exhibits remarkable selectivity to oxidise sterically less shielded functional groups. Oxidation at the nickel hydroxide electrode is an indirect heterogeneous anodic dehydrogenation. The electrocatalyst is presumably nickel oxide hydroxide, $\text{NiO}(\text{OH})$ which is continuously formed at the electrode surface. The reactivity of NiOOH resembles that of chemical oxidant, nickel peroxide. The oxidation of primary alcohols leads to excellent yields (80-90%) to carboxylic acids [30]. The development of conversion of diacetone L-sorbose to diacetone - 2- keto L-gulonic acid - a step in vitamin C-synthesis- to an industrial scale has been achieved by Robertson et al [31]. A Swiss Roll cell will be advantageous since lower current densities will have to be applied. Oxidation of benzylic type alcohols and alkenols with the double bond more than 3-C-atoms distant from -OH group leads to unsaturated carboxylic acids with good yields. Similarly, secondary alcohols including allylic alcohols leads to corresponding ketones (70-80% yield). In steroidal alcohols, 3α or 3β - hydroxy group is selectively oxidised.

Ti/TiO₂ redox catalytic electrodes

Beck and Gabriel [32] had established that thermally coated Ti/TiO₂ electrode acts as surface - bound heterogeneous redox mediator for the reduction of nitrocompounds. A comprehensive study, covering reduction of number of nitro compounds using the above system is also being carried out at CECRI [33].

Organo fluorine compounds

Organofluorine compounds have been attracting increasing attention because of their unique nature to material and medicinal sciences. Electrochemical approach would provide a unique technique for synthetic organofluorine chemistry, otherwise, difficult by the conventional chemical methods.

Electrochemical fluorination (ECF) by Simons process [34,35]

In the electrochemical fluorination of organic compounds, all hydrogen atoms in the molecule are replaced by fluorine. However, some functional groups such as carboxylic halides, sulphonyl halides, amines are retained. The organic substance to be fluorinated is dissolved or dispersed in anhydrous HF (AHF). D.C. at voltage of 5-8V is passed through AHF containing the organic substance. The anode plates are made of nickel and cathode plates are either mild steel or nickel. Cell is operated below 283K. The fluorination is believed to occur by the fluorine adsorbed on the nickel fluoride layer formed on the anode surface.

The unique characteristic of perfluorinated compounds is the stability of fluorocarbon chain to strong acids, alkalis and oxidising agents. They are super-surfactants. Hence they find extensive applications as speciality chemicals in the field of electronics, electroplating, emulsions, fire fighting foams, blood substitutes and biomedical oxygen carriers. 3-M Company in USA and BASF in Germany are some of the companies producing perfluoro compounds by ECF on a commercial scale.

Electrochemical selective or partial fluorination

Methods for selective anodic oxidative fluorination of organic compounds have been achieved in the presence of fluoride source under mild operating conditions. Selective fluorination of aromatic side chains, naphthalene, anthracene and pyrazole derivatives has been carried out in acetonitrile medium containing tetraalkyl, ammonium polyhydrogen fluoride [36,37]. Electrochemical oxy-trifluoromethylation of butyl acrylate and electrochemical synthesis of 2-trifluoromethyl indoles have been recently reported [38].

Electrochemical carboxylation

Electroreductive carboxylation offers a very useful alternative to avoid the handling of hazardous organo-metallic and inflammable solvents or the use of HCN. It would replace a one step for a two - step synthesis. With a

consumable magnesium anode and stainless steel cathode, a wide variety of organic halides in dimethyl formamide (DMF) can be carboxylated with high faradaic and chemical yields. The reactions are run in a cylindrical diaphragm-less cell in a stream of CO_2 at constant current density and temperature ($\sim 283 \text{ K}$). Aliphatic bromides can be converted to corresponding acids in 75% yield. Allylic and benzylic halides also react efficiently giving about 80-90% of the corresponding acid. Benzylic series include many antiinflammatory drugs like naproxen, ibuprofen and fenoprofen. A wide variety of aromatic halides is also carboxylated this way. Monocarboxylation of polyhalo - aromatics is obtained quite selectively which finds application as pesticide. A pilot plant has already been operated by SNPE, France, for the production of a few tones/year of naproxen, ibuprofen, fenoprofen etc. using a 'Pencil sharpener' electrochemical cell [45, 39]. Monsanto's process for the production of naproxen makes use of the same technique [40] thereby eliminating HCN.

Koble reaction

Electrochemical generation of radicals (Koble reaction) or carbonations (non-Kolbe reaction) by anodic decarboxylation finds extensive application in the synthesis of variety of organic compounds of commercial interest. In recent times much interest has emerged in this field, in view of simple reaction conditions in an undivided cell and possibilities of easy scale up with good yields [41]. By the radical path way diacetates, diketones, -denies, -dihalides, chiral intermediates for synthesis. pheromones and unusual fatty acids are accessible in a few steps. Five membered hetero-or carbocyclic compounds can be prepared by intramolecular addition starting from unsaturated carboxylic acids. The cationic pathway allows the conversion of carboxylic acids into alcohols, ethers and acetals. The use of high surface area carbon and graphite felts has been reported [42] for Kolbe reaction with good yields instead of platinum.

Solid polymer electrolyte (SPE) method in organic preparation

Electroorganic synthesis is a prospective line of application of SPE cells, especially for fine chemicals and Ogumi et al have carried out extensive work [43]. Because of the ion-exchange properties of SPE membranes (eg. Nafion), cationic mediator can easily be introduced into SPE composite electrodes as counter ions. The incorporation of a mediator reduces the amount of mediator required and also eliminates contamination of products by the mediator [44].

Electrochemical conversion of Biomass derived raw materials

Biomass derived compounds gain increased interest as feed stock in chemical industries because of their unlimited supply. The electrochemical investigations of polymeric

constituents of biomass and their derived degradation products have opened up a new vista in the organic field. Electrochemical conversion of CO_2 , carbohydrates, fatty acids, lignins etc. has been attempted [5,45,46].

WASTE RECOVERY

Regeneration of acids and bases by electro dialysis (salt - splitting)

Recovery of H_2SO_4 and NaOH from waste Na_2SO_4 [2]

Satisfactory disposal of Na_2SO_4 waste streams is becoming increasingly problematic and expensive. The studies of the splitting of Na_2SO_4 have been carried out in a electro dialysis cell by using both anion and cation exchange membranes (IEM) in a three compartment cell with Na_2SO_4 in the middle compartment. The H_2SO_4 and NaOH are obtained in the anode and cathode compartments respectively [47]. Jorissen and Simmrock also proposed an electrolytic cell with H_2 consuming porous anodes and O_2 consuming porous cathode to bring down the electrical energy by 20-30% [48] Electrosynthesis Co in USA describes a novel approach to obtain $(\text{NH}_4)_2\text{SO}_4$ and NaOH from Na_2SO_4 waste by electro dialysis. The process is capable of making 30% NaOH and 40% $(\text{NH}_4)_2\text{SO}_4$ (used as fertilizer directly in the cell with very high efficiency [49].

Recovery of HNO_3 and NaOH from NaNO_3

Very large volume of aqueous NaNO_3 is obtained while processing reactor fuel into strategic nuclear material. Electro dialysis with three compartment cell using ion-exchange membranes has been used to separate the NaNO_3 into HNO_3 and NaOH [50].

Recovery of organic acids from their salts

Organic acids such as acetic acid, formic acid C_4 and C_{10} acids are recovered from their sodium or potassium salts by electro dialysis using a three. compartment or two compartment cell fitted with IEM.

Removal of gaseous pollutants and electrokinetic remediation of soil

Electrochemical processes have been developed for the recovery of SO_2 (acid rain) and H_2S [23]. The demand for innovative and cost effective in-situ remediation technologies in waste management of soil resulted in the development of a technique known as electrokinetic remediation, or electroreclamation or electrokinetic soil processing or electrochemical decontamination. In this process low level D.C. of the order of a few volts per cm across electrodes placed in the ground is passed in an open flow arrangement to remove chemical contaminants from soils [51,52].

CONCLUSION

Whatever its application, electrosynthesis is a viable alternative to many thermal or catalytic processes. The pressure of environmental factors will also make the electrochemical route to organic synthesis increasingly interesting. Electrochemistry is also becoming increasingly attractive in dealing with environmental problems such as effluent treatment, air-pollution abatement, recycle of waste materials in salable or reusable form and destruction of toxic chemicals. With the improved knowledge in electrochemical engineering, better designs of electrochemical reactors can be expected to handle more complex and sensitive products in future.

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