**Electro-organic synthesis: Adding new dimensions to synthetic organic chemistry**

Partha Pratim Boruah

Department of Chemistry,

Dhakuakhana College,

Dhakuakhana, Lakhimpur, Assam-787055, India

Email: pboruah079@gmail.com

Ashitosh Baruah\*

Chemical Sciences &Techcnology Division,

CSIR- North East Institute of Science & Technology,

Jorhat, Assam-785006, India

Email: ashibarua22@gmail.com

**ABSTRACT**

Organic electro-synthesis has received great attention as a powerful green tool for synthesis, affording less waste production, less chemicals spent, and often fewer reaction steps than conventional methods. Despite the widespread advantages there remains a barrier to widespread adoption of this technology derived from the extra knowledge. This has led to a knowledge gap between experienced electrochemists and those new in the field. This chapter therefore focuses on providing a general overview of the new emerging research field and motivating researchers to investigate this topic, since it deserves more exploration in today's green movement. The authors believe that the readers will develop a keen interest of the topic after reading the chapter.

**Keywords**- Electrochemical cell, electrodes, cyclic voltametry, Single Electron Transfer (SET), current, potential.

**I. INTRODUCTION**

 The development of new and clean energy is receiving significant importance due to scarcity resources, excessive use of fossil energy, and severe environmental pollution in the current century. Electricity is considered an alternative fuel under the Energy Policy Act of 1992, therefore in most cases electricity can be considered as a greener fuel or fuel for future. However, the broader use of electricity will gain increasing influence due to sustainable transformations when electricity is obtained from renewable resources like wind-, solar-, or hydropower. Considering the vital applications of electricity in the modern era, synthetic chemists had made a progressive application in developing new methodologies for the synthesis of organic compounds using electricity. Hence, **Electro-organic synthesis** had become one of the most promising topics for research in organic synthesis. It has received a remarkable importance in last few decades due to its mild, green and atom efficient synthetic routes.It nulifies the stoichiometric use of many oxidising and reducing agents which are used widely in organic synthesis reactions. Due to its intensive advantages, electro-synthesis has gained lots of attraction in pharmaceutical science, medicinal chemistry and future industrial applications in energy storage and conversion.



 Figure 1; Comparison of conventional and electrochemical methods with an example of a coupling reaction.

 Although the process of electro-synthesis was common in inorganic transformations including production of chemicals in industrial scale, like chlor-alkali electrolysis for manufacturing basic inorganic chemicals or aluminium production by the Hall-Héroult process. The organic synthetic community was not so aware or did not accept this technique even though it was already used by Kolbe over 170 years ago. But, in the recent years, several groups across the glove have gained keen interest and explored this subject to provide sufficient knowledge for further research. However, the broad application in organic synthesis is still low although electro organic transformations enable access to novel structures due to the unique reactivity and selectivity provided. Hence, the current chapter deals on the basics concepts of electro-organic synthesis and will try to make the readers aware of the recent advances of research and development on the subject.

**II. PRINCIPLES of Electro-organic synthesis**

A simple electrochemical setup consists of a reaction vessel with an external power supply (A), a reaction solution (B) and two electrodes (C & D) which is connected to the power supply as shown in figure 2. The reaction solution or reaction mixture consists of the place in the anode (C, Red) while reduction reaction takes place on the cath lectrodes in an electrochemical reactions are also named as working or counter electrodes depending on the reaction conditions, are discussed ode (D, Blue). The arrows on the wire of the electrodes show the direction of electron flow (Figure 2). The oxidation or the reduction e in further sections.

 The versatile method of electro-organic synthesis relies on the fundamental principles of redox reactions using electric current as the starting material or substrate, suitable solvent, a supporting electrolyte and additives (if necessary). At the time of an electrochemical reaction, both the electrodes (viz. Anode & Cathode) undergoes separate electrochemical reactions. Oxidation reaction takes essential reagent. Oxidations will occur as anodic transformations, whereas reductive processes adding an electron in single electron transfers (SET) to a substrate take place at the cathode. Thus, the electrodes acts as a crucial parameter for electro- organic conversions, which take place as heterogenous chemical reactions between commonly solid electrode and a substrate in a liquid electrolyte system. This electrolyte system is comprised of a electrochemically inert solvent and supporting electrolytes to enable sufficient electrical conductivity. This supporting electrolyte can be a salt, acid, or base and will contribute to the formation of an **electrochemical double layer** (see section Electrodes) at the electrode surface. Inert ions, highly soluble in organic solvents like tetraalkylammonium, hexafluorophosphate, or tetrafluoro borate are widely used due to their excellent performance.

Figure 2; A simple electrochemical setup

**Iii. Basic concepts of electrolytic reaction**

1. **Types of Electrolytic cells**

****

 In electrolysis, there are two possibilities of operation, either in divided cell (Figure 3a) or in undivided cell (Figure 3b). In un-divided cell, both the electrodes viz. anode and cathode are placed in a same reaction vessel. In divided cells the cathode and anode chambers are separated with a semiporous membrane commonly composed membrane materials like [sintered](https://en.wikipedia.org/wiki/Sintered) glass, porous [porcelain](https://en.wikipedia.org/wiki/Porcelain),  [poly-tetrafluoroethene](https://en.wikipedia.org/wiki/Polytetrafluoroethene) or [polypropylene](https://en.wikipedia.org/wiki/Polypropylene). The purpose of the divided cell is to permit the diffusion of ions while restricting the flow of the products and reactants. This separation simplifies workup. In many of the divided cells, both the anodic compartment and cathodic compartments are separated via salt bridge (See E in figure 3a). A salt bridge or ion bridge is a laboratory device used to connect the [oxidation and reduction](https://en.wikipedia.org/wiki/Redox) [half-cells](https://en.wikipedia.org/wiki/Half_cell). It maintains electrical neutrality within the internal circuit. In the absence of salt bridge, the solution in one-half cell would accumulate a negative charge and the solution in the other half cell would accumulate a positive charge as the reaction proceeded, quickly preventing further reaction.  Considering the electrochemical process implementation, the main influence of efficiency comes from the electrochemical reactions. In divided cell, the advantage is that there is the possibility to avoid decomposition of oxidants at anode or cathode which increases the faradic yield.

Figure 3a: Divided cell

Figure 3b: Undivided Cell

****

1. **Electrodes**

 Any conducting material can be generally used as an electrode in electrochemical reactions. However, the outcome of the reaction greatly varies depending on the electrode material, size and shape. The basic role of an electrode is to transfer electrons and facilitate heterogeneous reaction. Depending on the homogeneity of the electrochemical reaction, electrodes are classified into sacrificial and non-sacrificial electrodes. Sacrificial electrodes takes part in the reaction and gets dissolved in the reaction mixture (e.g. Al, Zn, Mg, etc) while non-sacrificial electrodes are inert, highly durable and stable under oxidative conditions (e.g. Graphite, glassy carbon, RVC). Hence, favourable electrode materials are (electro-) chemically inert facilitating easy handling, and ecologically and economically beneficial use.

 In electrochemical reactions, the reactions takes place on the surface of the electrodes, therefore the surface area of electrodes which is in contact with the reaction mixture, plays an important role on the rate of an electrochemical reaction. Generally, electrode materials which are foams or meshes have a higher surface area than plates or rods and can therefore be beneficial for a reaction by increasing the reaction rate. As redox reaction takes place in an electrolytic cell, both oxidation and reduction reactions are coupled, and hence both electrode surfaces are important.

Figure 4; Helmholtz layer(Left) and Nernst diffusion layer (right)

 As discussed in earlier sections that an electrochemical reaction occurs via Single Electron Transfer (SET) to the substrate which results into a radical species that reacts further to form the desired product. During an electrochemical reaction, two layers of opposite polarities are formed when the electrode comes in contact with the electrolyte. This electrochemical double layer is called Helmholtz layer (Figure 4-left). An anodic the anodic double layer consists of a positively charged layer on the surface of the electrode and a negatively charged layer of the solvated electrolyte that covers the previous layer. The thickness of the double layer extensively depends on the applied voltage and the electrolyte concentration but is typically in a few nanometer scale. Other than the double layer, the Nernst diffusion layer (Figure 4-right) is formed which describes the substrate concentration near the electrode. As the substrate is consumed, the concentration of substrate gets lowered at the electrode compared to the bulk solution resulting in further substrate diffusion towards the electrode. If the substrate is produced, rather than consumed, the concentration is increased near the electrode. This is the general mechanism followed by nearly all the electrochemical reactions.

 **Working Electrode (WE):** The working electrode represents the most important component of an electrochemical cell. This is because, the reaction of interest takes place at the interface between the WE and the reaction solution. The success of an electrochemical reaction vitally depends upon the selection of WE. It is made up of redox inert material and it varies from experiment to experiment to provide different potential windows or to reduce/promote surface adsorption of the species of interest. It is also an important fact that the surface of the working electrode is extremely clean and its surface area well-defined. The most commonly used working electrode materials are platinum, gold, carbon, and mercury. Among these, platinum is the most favourable since it demonstrates good electrochemical inertness and could be fabricated into many forms. Although it is an expensive material to use, the huge disadvantage in using Pt electrode is that the presence of even catalytic amounts of water or acid in the electrolyte solution leads to the reduction of hydrogen ion to form hydrogen gas leading evolution of hydrogen gas at fairly modest negative potentials (E = -0.059 x pH). This reduction mask any useful analytical signal.

 **Counter Electrode (CE).** The electrochemical reactions at the electrode surfaces are intrinsically linked. When a potential is applied to the working electrode such that reduction (or oxidation) of the reaction mixture may occur, current begins to flow. The reaction occurring at the counter electrode is the counter reaction. The electrons removes at the anode are driven to the cathode by power supply ensuring a net neutral system. Thus, the fundamental purpose of the counter electrode is to complete the electrical circuit. Current is recorded as electrons flow between the WE and CE. An oxidation reaction is observed at the CE when investigating a reduction in WE. Therefore, it is necessary to select the CE to be as inert as possible. These electrodes may sometimes be separated from the rest of the system by a fritted compartment, since they can produce by-products in response to an experiment. One example is the oxidative polymerization of THF that can occur in the CE when studying the reductive process in THF (Tetrahydrofuran) at the WE.

 **Reference Electrode (RE):**  A reference electrode is generally used in addition to working and counter electrode in order to correctly measure the voltage applied at the WE . It has a well defined and stable equilibrium potential. It shall be regarded as a reference point to measure the potential for further electrodes in an electrochemistic cell. The applied potential is thus typically reported as “vs” a specific reference. There are a few commonly used (and usually commercially available) electrode assemblies that have an electrode potential independent of the electrolyte used in the cell. Some common reference electrodes used in aqueous media include the saturated calomel electrode (SCE), standard hydrogen electrode (SHE), and the AgCl/Ag electrode. These reference electrodes are generally separated from the solution by a porous frit. It is always recommended to minimize junction potentials by matching the solvent and electrolyte in the reference compartment to the one used in the experiment. In non aqueous solvents, reference electrodes based on the Ag+/Ag couple are commonly employed. These consist of a silver wire in a solution containing an Ag+ salt, typically AgNO3. However, utmost care must be taken when interconverting potentials as they can be affected by many parameters such as solvent and electrolyte concentration. The use of a reference electrode is important for reproducibility in constant potential reactions (see section Applied Current and Potential) and for the performance of cyclic voltammetry (see section Cyclic voltammetry).

1. **Electrolytes and Supporting Electrolytes**

 Resistance plays a crucial role in inhibiting the rate of an electrochemical reaction, therefore it is on the top priority of an electrochemist to stop the inhibition (resistance) and thereby enhance the rate of an electrochemical reaction. Therefore, in order to enhace the rate o an electrochemical reaction, an electrolyte is added to most of the electrochemical reactions to decrease the resistance and lower the potential of the system. The first and foremost criteria for an electrolyte is its electrochemical inertness. The supporting electrolyte used in a reaction must electrochemically inert. It must not undergo a redox process under the applied potential. It must be fully soluble in the reaction mixture. The resistance is typically lowest with short alkyl groups and increases with their length. Ammonium salts are the most preferable electrolyte for inorganic electrochemistry experiments performed in organic solvents as they fulfill all the necessary conditions of electrolyte. For reactions in dichloromethane or acetonitrile, tetrabutylammonium (+NBu4) salts are commonly used. For less polar solvents like benzene, tetrahexylammonium salts are used due to its high solubility in less polar solvents. Ammonium salts are considered as standard cation, the choice of counteranion is less standardized as anions tend to be more reactive with transition metal analytes. The most commonly used anions are [B(C6F5)4]¯, [B(C6H5)4]¯,[PF6]¯,[BF4]¯,and [ClO4]¯. The more coordinating the anion, the more likely it is to have unwanted interactions with the cation, the solvent, or the analyte. It has been found that [NBu4][PF6] salts to be ideal supporting electrolytes in acetonitrile for their stability, non-coordinating nature, ease of purification, and solubility. The purity of the electrolyte is also paramount criteria because slightest impurity can reach a concentration sufficient to interfere with the measurement, hence disturbing the overall idea of electro-organic synthesis.

In addition to the supporting electrolytes, additives can be used to enhance the reaction performance further. The main purpose of using an additive is either to promote the counter reaction or stabilise intermediates. For oxidation reactions the addition of acid can often be beneficial as it acts as a proton source for the reductive release of hydrogen as the counter reaction. Similarly, metal salts can be added since it gets reduced and get deposited on the cathode. Fluorinated alcohols, such as hexaflouroisopropanol (HFIP), can be added to stabilise radical intermediates.

**IV. MODES OF OPERATION**

 **Applied Current and Potential:** Current (I) and potential (V) are the most important parameters for an electrochemical reaction. The current describes the movement of electrons, the potential describes the energy by which they are moved. The current controls the rate at which electrons are transferred to the reaction medium and hence the reaction rate. The charge (Q) is the current in a unit time, which means that it corresponds to the amount of electrons released into the reaction medium corresponding to an analogous reagent stoichiometry. It is necessary to adjust the energy of electrons, the potential, in accordance with the desired process. It is observed that the majority of synthetic reaction occurs at 2 V, with the reaction not occurring if the potential is too small and it may lead to selectivity problems. The current and potential are related by the resistance (R) in a process. The resistance in a electrochemical cell can be offered by various components such as wiring and the electrodes but the biggest contributor is the reaction solution (discussed in supporting electrolyte section). Therefore, all the three parameters, the current, the potential and the resistance are related to each other by the Ohms law, which is given by-

 V = R .I

 V: Potential in Volt (V); R: Resistance in ohm (Ω) ; I: Current in Ampere (A)

 An electrochemical reaction can run in two modes viz. Galvanostatic mode (if it runs under constant current) and Potentiostatic mode (if it runs under constant potential). It is not practically possible to control both the current and the potential separately without changing the resistance of the setup.

 **Galvanostatic mode:** Galvanostatic setup is a simplest setup since it uses only the working electrode and counter electrode. It does not use any reference electrode for its operation and the exact stoichiometry of electrons is known. In galvanostatic mode, the system is run under constant current, which is dependent on the amount of substrate present in the reaction solution. The electrode potential decreases on the consumption of starting material. The main advantage of galvanostatic setup is that it is easy to assemble and the exact equivalents of electrons are known i.e; Fmol-1 . The only drawback of this system is that the voltage range in not under control. It is the most common mode generally employed in maximum number of electro-organic transformations.

 **Potentiostatic mode:** The energy required to move electrons from the anode into the cathode in order to create potential differences is commonly referred to as Potential, also known as voltage. The electrons may then be moved from the cathode to the reaction solution if this difference is sufficiently large. At the same time electrons shall be removed from a reaction solution at an anode, which will lead to current flow. Correspondingly, the current cannot be actively controlled under potentiostatic conditions and may vary to maintain a constant potential. Due to the fact that the current is not always constant, it is not possible to calculate the electron equivalents directly. A multimeter that records currents over time must be included in the setup if an electron equivalent is to be calculated. Therefore, a reference electrode is required in potentioststic mode (Figure 5). Hence, this setup is only used in case of highly selective reactions of for reaction mechanism clarification.

Figure 5; Electrochemical cell indicating reference electrode.

 Figure 6 shows the variation of current potentials and concentration of the substrate during the galvanostatic and potentiostatic conditions.

****

Figure 6; Graphical representation of galvanostatic(left) and potentiostatic (right) conditions.

**V. CYCLIC VOLTAMETRY**

Cyclic Voltametry (CV) is an analytical tool used in electrochemical reactions which is used to investigate the oxidation and reduction potential of a chemical species. For the measurement of CV, a CV setup is prepare which comprised of a CV working and counter electrode and a reference electrode. It must be noted that, the working electrode is different than that used in synthetic purposes. During a CV experiment the current is measured while the potential at the working electrode is scanned in a cyclic manner using a triangular waveform (Figure 7a) resulting in a cyclic voltammogram (Figure 7b). If the potential is raised and no reaction occurs, an increase in current will not be observed. If a species is present which may be oxidised or decreased within the applied voltage range, an electric current shall flow until it has depleted at the electrode surface resulting in a peak. Solvent oxidation and reduction may also be observed on the basis of the potential. The potential at which the maximum current is observed is referred to Ea and Ec for anodic and cathodic respectively. The redox potential (E1/2) of the chemical reaction is observed at the middle the peaks. Therefore CV also helps to understand the redox system and the minimum potential required for a redox reaction to occur.



Figure 7b; Cyclic Voltammogram

Figure 7a; Triangular waveform

**VI. TYPES OF ELECTROCHEMICAL REACTIONS**

There are many electro-organic transformations that are reported till-date, which can be classified into various ways. However, in this chapter a general classification few electro-organic reactions is discussed below-

1. **Transformation of Functional Groups**

 There are many electro-organic reactions known which deals in functional group inter-conversions. The general functional group transformation reaction include, NH2→NO2, NO2→NHOH, NO2→NH2, S→SO2, CH2OH→CHO, CH2OH→COOH, CHO→CH2OH, CHO→COOH, CH2NH2→CN, etc.

Reducing nitroaryles(1a) electrochemically can yield nitroso compounds (1b), hydroxylamines(1c) and anilines(1d) as products. Since the nitroso group is more easily reducible than the nitro group, obtaining nitroso derivatives by directly reducing a nitro group is difficult and it demands specific conditions like selective electrode materials. On the other hand, hydroxylamines usually form straight from the nitro reduction. It is important to mention that the hydroxylamines are very prone to oxidation and they form readily the 2 e−/2 H+ redox-pair with the corresponding nitroso system. This is one of the reasons why the final reduction to the aniline is difficult and why divided cells are often mandatory to obtain anilines or nitroso compounds on a preparative scale. Moreover, nitroso intermediates and hydroxylamines can condense to afford azoxybenzenes (**1e**), which can be subsequently electroreduced to azobenzenes (**1f**), or further to hydrazobenzenes (**1g**). Also, azobenzenes and hydrazobenzenes form reversible 2 e−/2 H+ redox-pairs. Furthermore, hydrazobenzenes can be electroreduced to anilines under acidic or basic conditions, but in the former, rearrangement to 1,1-biphenyl-4,4′-diamines competes and complicates the scenery of electroreduction. This might lead to rather complex product mixtures.



 Electrochemical alcohol oxidation methods using organic electrocatalysts ha gained considerable interest in recent years, and they provide a compelling alternative to the more-traditional chemical methods. These methods are appealing, in part, because they generate hydrogen gas as the sole byproduct of the reaction (Scheme 2). Electrochemical methods for the oxidation of primary alcohols to carboxylic acids have been investigated primarily for the conversion of mono/polysaccharides and other biomass-derived precursors.



1. **Coupling Reactions**

 Electrochemistry has long been recognized as an environmental friendly synthetic approach to various coupling reactions. Both anodic oxidation and cathodic reduction have been applied in the synthesis of complex molecules via coupling. Over the past decade, electrochemical anodic oxidation along with the cathodic proton reduction has emerged as a promising method for achieving oxidative R1–H/R2–H cross-coupling with hydrogen gas evolution (Scheme 3). In an ideal model, the overall transformation avoids the use of any sacrificial reagents and only consumes electric energy. Recent achievements have shown that carbon-carbon and carbon-heteroatom bonds can all be constructed through electrochemical dehydrogenative cross-coupling.



 Many electrochemical coupling reactions are explored in last decades which includes cross coupling of anilines and alkenes reported by Waldvogel and group at year 2000. they used Carbon electrode at the working (anode) and nickel (Cathode) as the counter electrode. The reaction used 1,4-benzoquinone as catalyst (4a). Then at 2006, the same group explored the homo coupling of phenols under oxidative condition using Boron Dopped Diamond (BDD) at the anode and simple Nickel electrode at the cathode.They also used florinated alcohols like hexafluoroisopropanol (HFIP) as solvent with supporting electrolytes(4b). Under same reaction conditions or by slight modifications, the dehydrogenative cross coupling between Phenols and arenes (4c), dehydrogenative cross coupling between two phenols (4d), etc were also studied.





1. **Cleavage**

 Electrochemical reactions resulting in cleavage of bonds are synthetically useful in many respects such as deprotonation of functional groups and generation of reactive intermediates. The electrochemical approach may be applied for the cleavage of bond, i.e. Carbon-carbon bond, carbon-hydrogen bond, carbon-sulphur bond, carbon-phosphorous bond, carbon – oxygen bond, carbon-halogen bond, oxygen-oxygen bond, sulphur-sulphur bonds, oxygen-nitrogen bonds, sulphur-nitrogen bonds and sulphur- halogen bonds. Scheme 5a shows the electrochemical C-N bond formation through C-H cleavage, scheme 5b shows the C-N bond formation through C-C bond cleavage while scheme 5c shows C-O cleavage using platinum as anode and cathode.



1. **Addition**

Anodic addition affords products, some of which are of industrial interest, such as propylene oxide, diols, and 1,4-dimethoxyfuran. To improve the selectivity, mediators like Ti3+, Pd2+, Ce4+ or Ru3+ are sometimes used. The hydrogenation of C=C bond can be achieved cathodically. Anodic additions at the double bonds may be represented as follows (Scheme 6)-

 

 Over the past few years, methoxylation of organic compounds has been one of the most highlighted anodic addition reactions. Oxazolidinones belong to a group of antimicrobial agents that are effective against gram positive pathogenic bacteria. Saravanan and coworkers reported a methoxylation of a 2oxazolidinone using boron doped diamond (BDD) or graphite as anode (Scheme 7). Higher yields were obtained for BDD, with a maximum value of 88% obtained for a current density of 50 mAcm2. Beyond that current density, yields start to decrease due to the electrochemical degradation of the starting material and the solvent oxidation.

 

**VII. ELECTRO-ORGANIC SYNTHESIS FOR INDUSTRY**

 Organic electrosynthesis, enabling the replacement of dangerous and toxic chemicals by electric current, or “clean” electrons, together with its high versatility, has attracted great attention at the laboratorial and industrial scales in areas of fine chemicals, environmental mitigation, pharmaceuticals, agrochemicals, and others. The prime parameters for an industrial scale are the yield of the desired product, rate of production and energy consumption behind the synthesis for a successful compound production. Many of the electro-organically synthesized products do not reach the official commercialization mainly due to: (a) high energy costs; (b) pollution constrains; (c) low product selectivity. In India, the Central Electrochemical Research Institute (CECRI) and other institutes has been playing an important role in developing many industrially viable products over decades, which includes p-amino benzoic acid, p-aminophenol, p-nitobenzoic acid, succinic acid, benzyl alcohol, benzaldehyde, salicylaldehyde, benzidine, saccharin and many other chemicals which have vital application in medicinal and agrochemical fields . Let us look at an example of industrial production of succinic acid in order to understand the concept of electrosynthesis as a practical application.

 Butanedioic acid also known as amber acid or succinic acid was purified for the first time in 1546 by Georgius Agricola. This dicarboxylic acid can be used in anticancer drugs, food and cosmetic products or even intermediates for the manufacture of nanomaterials due to its reactivity. Alternative sources, such as bacterial or other microbial derivative products, have become a significant focus of succinic acid production because of the limited fossil fuel resources. One of the major limitations is that large quantities of wastewater would have to be generated from bacteria sources, while there are also shortcomings in extraction efficiency and production costs. In order to overcome the disadvantages, a method of producing succinic acid via electrosynthesis has been proposed in which maleic anhydride hydrolysis is usually performed with further electroreduction under acidic conditions.(Scheme 6)

 

 Along these last few years several authors have patented the electrosynthesis methods that led to higher yields of succinic acid using different types of reactors. Gao and coworkers has disclosed a method to couple the maleic anhydride electroreduction with simultaneous oxidation of iodide ion resulting in a paired electrosynthesis process and therefore in a reduction of the overall cell voltage and cost production. By employing Ti supported RuO2TiO2 as anode and Pb alloy as cathode it was possible to obtain a current efficiency value of 95%.

**VIII. CONCLUSION**

Herein, we discussed the general overview of electro-organic synthesis which will help the readers as a guide to electrosynthesis. The use of various aspects in the electro-organic synthesis describes an exciting method that makes several discoveries but contains a great many unknown treasures, which will lead to more advanced developments. In particular, in future chemical operations the use of fluctuating and abundant electricity to produce value added chemicals is going to be a game changer. Electrochemical synthesis can generally be carried out in a benign environmental condition, at moderate or low temperature and pressures, with simple cheap facilities, it just requires the proper control of the working electrode potential, or the cell voltage (particularly in the cases of paired electrolysis), or of the cell current that is applied to the terminals of the electrolytic cell reactor vessel. In general, the galvanostatic mode is the most used in industrial synthesis and then, the potential adjusts automatically to the compound with the least positive oxidation potential (anode) or the least negative reduction potential (cathode). This allows one to study oxidation (or reduction) chemistry of a variety of different compounds, essentially under the same conditions and without the need for testing different redox reagents. The fundamental focus of the book chapter was to motivate and make the readers aware of the general concept practical applications of electrochemical pathways for organic synthesis, from bench to industrial scale. It is believed that electro-organic synthesis will occupy a more prestigious positions on the fields like science and engineering, contributing to the specific, efficient and widespread commercialization of organic electrode processes.

**IX. REFERENCES**

1. Schotten C; Nicholls T P; Bourne R A; Kapur N, Nguyen B N; Willans C E;. Making electrochemistry easily accessible to the synthetic chemist; Green Chemistry, **2020,** 22, 3358
2. Tang S; Liu Y; Lei A; Electrochemical Oxidative Cross-coupling with Hydrogen Evolution: A Green and Sustainable Way for Bond Formation; Chem Review; **2018**, 4, 27-45
3. Pollok D; Waldvogel S. R., Electro-organic Synthesis – A 21st Century Technique ;Chem. Sci., **2020**, DOI: 10.1039/D0SC01848A.
4. Zoski, C. G., Ed. Handbook of Electrochemistry; Elsevier: Amsterdam, The Netherlands, 2006.
5. Bard, A. J.; Faulkner, L. R. Electrochemical Methods: Fundamental and Applications, 2nd ed.; John Wiley & Sons: Hoboken, NJ, **2001**.
6. Saveant, J.-M. Elements of Molecular and Biomolecular Electro chemistry; John Wiley & Sons: Hoboken, NJ, **2006**.
7. Compton, R. G.; Banks, C. E. Understanding Voltammetry, 2nd ed.; Imperial College Press: London, U.K.,. **2011**
8. Graham,D.J.StandardOperating Procedures for Cyclic Voltammetry. https://sop4cv.com/index.html **(accessed July 2023).**
9. Ventura, K.; Smith, M.B.; Prat, J. R.; Echegoyen, L. E.; Villagran, D. Introducing Students to Inner Sphere Electron Transfer Concepts through Electrochemistry Studies in Diferrocene Mixed-Valence Systems. J. Chem. Educ. **2017**, 94 (4), 526−529.
10. Hendel, S. J.; Young, E. R. Introduction to Electrochemistry and the Use of Electrochemistry to Synthesize and Evaluate Catalysts for Water Oxidation and Reduction. J. Chem. Educ. **2016**, 93 (11), 1951− 1956.
11. Baca, G.; Dennis, A. L. Electrochemistry in a Nutshell A General Chemistry Experiment. J. Chem. Educ. **1978**, 55 (12), 804.
12. Faulkner, L. R. Understanding Electrochemistry: Some Distinctive Concepts. J. Chem. Educ. **1983**, 60 (4), 262.
13. Aranzaes, J. R.; Daniel, M.-C.; Astruc, D. Metallocenes as References for the Determination of Redox Potentials by Cyclic Voltammetry Permethylated Iron and Cobalt Sandwich Complexes, Inhibition by Polyamine Dendrimers, and the Role of Hydroxy Containing Ferrocenes. Can. J. Chem. **2006**, 84 (2), 288−299.
14. Elgrishi, N.; Kurtz, D. A.; Dempsey, J. L. Reaction Parameters Influencing Cobalt Hydride Formation Kinetics: Implications for Benchmarking H2-Evolution Catalysts. J. Am. Chem. Soc. **2017**, 139 (1), 239−244.
15. Myland, J. C.; Oldham, K. B. Uncompensated Resistance. 1. The Effect of Cell Geometry. Anal. Chem. **2000**, 72 (17), 3972−3980.
16. Oldham, K. B.; Stevens, N. P. C. Uncompensated Resistance. 2. The Effect of Reference Electrode Nonideality. Anal. Chem. **2000**, 72 (17), 3981−3988.
17. Elgrishi, N.; McCarthy, B. D.; Rountree, E. S.; Dempsey, J. L. Reaction Pathways of Hydrogen-Evolving Electrocatalysts: Electro chemical and Spectroscopic Studies of Proton-Coupled Electron Transfer Processes. ACS Catal. **2016**, 6 (6), 3644−3659.
18. Tojo, G.; Fernandez, M. I. Oxidation of Primary Alcohols to Carboxylic Acids: A Guide to Current Common Practice, Springer: New York, **2007**.
19. Arends, I. W. C. E.; Sheldon, R. A. Modern Oxidation of Alcohols Using Environmentally Benign Oxidants. In Modern Oxidation Methods, 2nd Ed.; Bäckvall, J.-E., Ed.; Wiley-VCH: Weinheim, **2010**; pp 147–185.
20. Lappe, P.; Schulz, E. Aliphatic Carboxylic Acids via Aldehyde Oxidation. In Applied Homogeneous Catalysis with Organometallic Compounds. Cornils, B.; Herrmann, W. A.; Eds.; Wiley-VCH: Weinheim**, 1996**; pp 424–464.
21. Caron, S.; Dugger, R. W.; Ruggeri, S. G.; Ragan, J. A.; Ripin, D. H. B. Large-Scale Oxidations in the Pharmaceutical Industry. Chem. Rev. **2006,** 106, 2943–2989
22. Zhao, M.; Li, J.; Song, Z.; Desmond, R.; Tschaen, D. M.; Grabowski, E. J. J.; Reider, P. J. A Novel Chromium Trioxide Catalyzed Oxidation of Primary Alcohols to the Carboxylic Acids. Tetrahedron Lett. **1998**, 39, 5323–5326.
23. Mahmood, A.; Robinson, G. E.; Powell, L. An Improved Oxidation of an Alcohol Using Aqueous Permanganate and Phase-Transfer Catalyst. Org. Process Res. Dev. **1999**, 3, 363–364.
24. Thottathil, J. K.; Moniot, J. L.; Mueller, R. H.; Wong, M. K. Y.; Kissick, T. P. Conversion of L Pyroglutamic Acid to 4-Alkyl-Substituted L-Prolines. The Synthesis of trans-4-Cyclohexyl-L-proline. J. Org. Chem. **1986**, 51, 3140–3143.
25. Lichtenthaler, F. W.; Peters, S. Carbohydrates as Green Raw Materials for the Chemical Industry. C. R. Chimie **2004**, 7, 65–90.
26. Mallat, T.; Baiker A. Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts. Chem. Rev. 2004, 104, 3037–3058.
27. Climent, M. J.; Corma, A.; Iborra, S. Converting Carbohydrates to Bulk Chemicals and Fine Chemicals Over Heterogeneous Catalysts. Green Chem. **2011**, 13, 520–540.
28. De, S.; Duttab, S.; Saha, B. Critical Design of Heterogeneous Catalysts for Biomass Valorization: Current Thrust and Emerging Prospects. Catal. Sci. Technol. **2016**, 6, 7364–7385.