

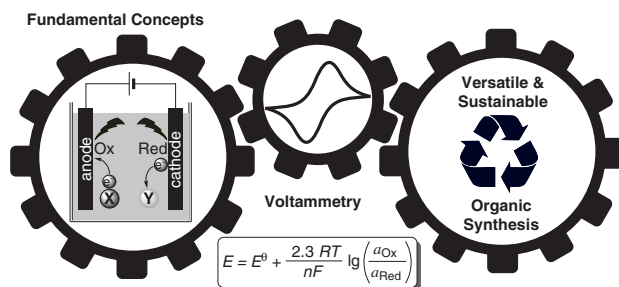
Abstracts

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2 Fundamental Principles of Organic Electrochemistry

A. Scheremetjew,¹⁶ T. H. Meyer, Z. Lin, L. Massignan, and L. Ackermann¹⁶

This chapter addresses the basic terminology of electrochemistry and its fundamental mechanisms of electron and mass transfer. The general setup and most important analytical methods are introduced to provide the reader with the theoretical prerequisites for the implementation of electrochemical transformations into organic synthesis.



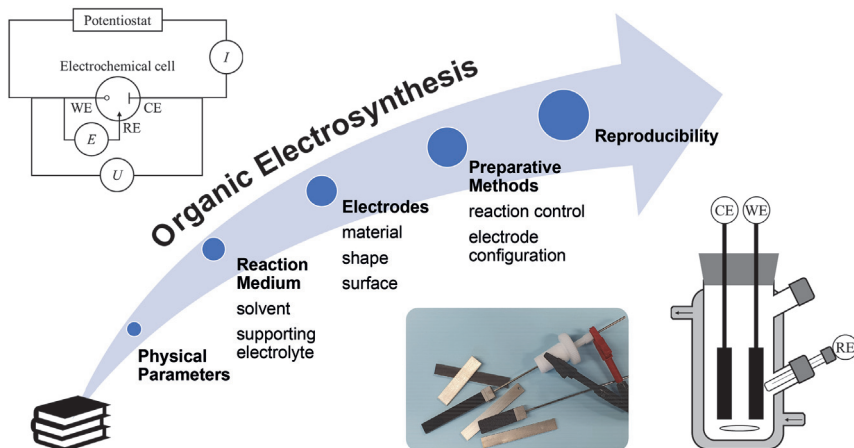
Keywords: electrosynthesis • electrochemical cell • anode • cathode • electron transfer • mass transfer • redox reaction • overpotential • cyclic voltammetry • green chemistry

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3 Methods and Materials Applied in Electrosynthesis

P. Enders and R. Francke¹⁶

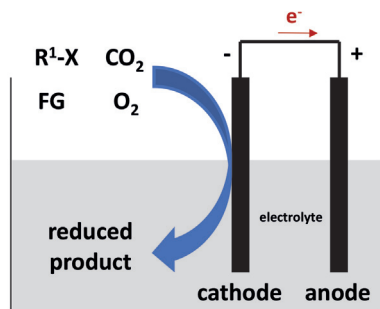
This chapter is intended as a tutorial for the organic chemist and to serve as an introductory guide to the technical and methodological aspects of electrosynthesis. The most important reaction parameters, methods, and materials are covered both from a practical point of view and in their physicochemical context.



Keywords: organic electrochemistry • electrosynthesis • reaction control • electrochemical cells • supporting electrolytes • electrodes • separators • electrocatalysts • mediators • paired electrolysis • reproducibility

4 **Electroreductive Reactions**P. Schiltz and C. Gosmini 

This review covers a variety of electroreductive reactions. A range of catalyzed electroreductive cross-coupling reactions, electroreduction of various functional groups and carbon dioxide, decarboxylation reactions, and oxygen reduction reactions are discussed.

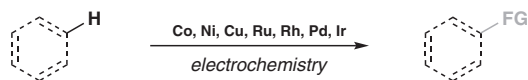
electroreductive reactions

Keywords: organic electrochemistry • electrosynthesis • nickel catalysts • cobalt catalysts • iron catalysts • electrochemical reduction • cross-coupling reactions • reductive coupling • carboxylation • decarboxylation • carbon dioxide • molecular oxygen

5 **Metal-Catalyzed C–H Activation**

Y.-K. Xing, P. Fang, Z.-H. Wang, and T.-S. Mei

Synthetic organic electrochemistry is currently experiencing a renaissance, the merger of electrochemistry with transition-metal-catalyzed C–H activation would provide not only an environmentally friendly approach, but also offer new opportunities that conventional transition-metal catalysis may not have achieved. In this chapter, we summarize the recent progress made in catalytic C–H activation reactions using organometallic electrochemistry, including C–C, C–O, C–N, C–halogen, and C–P bond-forming reactions.

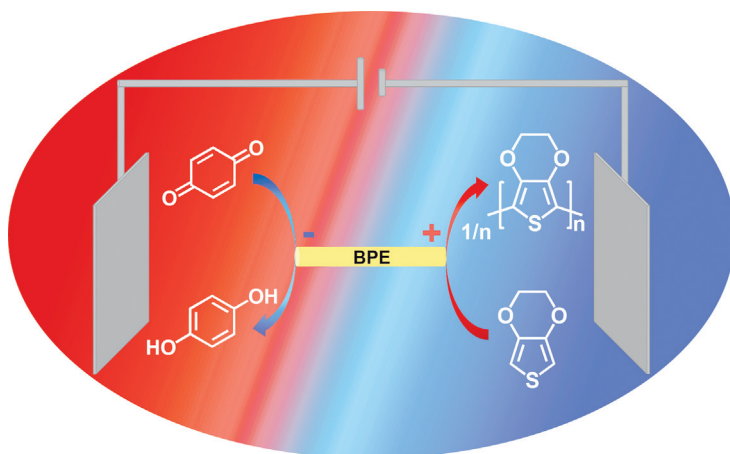


FG = functional group

Keywords: organic electrochemistry • electrosynthesis • C–H activation • organometallic electrochemistry • transition-metal catalysis • arene functionalization • cyclization

6 Bipolar Electrochemistry for Synthesis*E. Villani and S. Inagi*

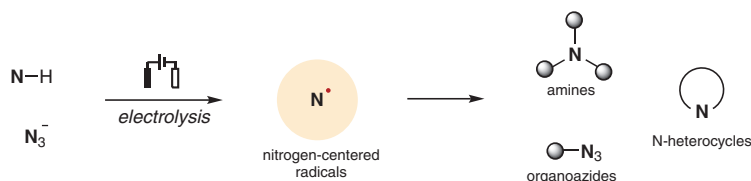
Bipolar electrochemistry has gained remarkable interest in recent years, especially in the fields of materials science and organic electrosynthesis. This is due to the interesting features of this particular electrochemical technology, such as the contactless nature of the electrochemical reactions, the use of low concentrations of supporting electrolytes, and the synergetic action of electrophoresis and electrolysis. In this chapter, the most important contributions regarding bipolar electrochemistry for the electrosynthesis of novel functional materials are reviewed. These contributions include the most traditional industrial applications and bipolar reactors for electroorganic synthesis, as well as innovative approaches for the fabrication of anisotropic materials and gradient surfaces. The peculiar characteristics of bipolar electrochemistry in these fields are emphasized.



Keywords: bipolar electrochemistry • bipolar electrodes • electroorganic synthesis • bipolar reactors • electric fields

7 Electrochemically Generated Nitrogen-Centered Radicals*Z.-W. Hou and H.-C. Xu*

Nitrogen-centered radicals are versatile reactive intermediates for organic synthesis. This chapter describes recent progress in the electrochemical generation and reactions of nitrogen-centered radicals. Under electrochemical conditions, various nitrogen-centered radicals are generated through electrolysis of readily available precursors such as N–H bonds or azides. These reactive intermediates undergo addition reactions to π -systems or hydrogen-atom abstraction to generate various nitrogen-containing compounds.



Keywords: organic electrochemistry • electrosynthesis • electrocatalysis • nitrogen-centered radicals • radical reactions • heterocycles • carbon–nitrogen bond formation • oxidation • cyclization

8 **Electrochemical Fluoroalkylation**

Z. Ruan, Z. Huang, K. Kuciński, and L. Ackermann

This chapter reviews electrochemical fluoroalkylations. Reactions covered include trifluoromethylation, difluoromethylation, monofluoromethylation, and perfluoroalkylation as well as polyfluoroalkylation through direct electrolysis and indirect electrolysis.



R^1 = arene, alkene, alkyne

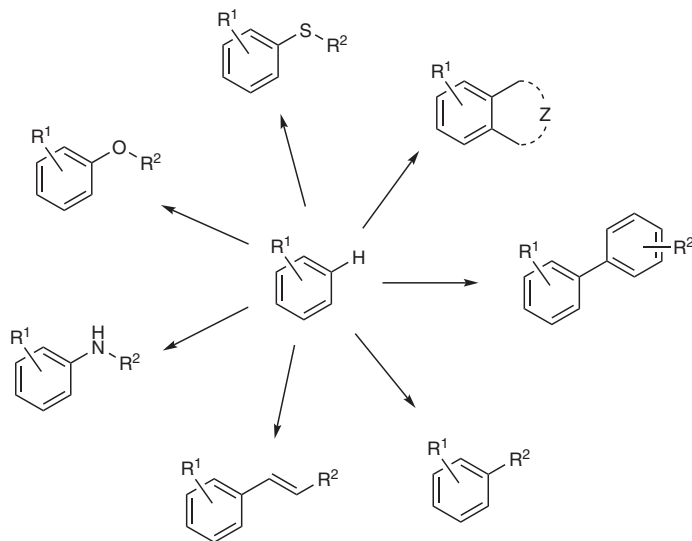
R_F = CF_3 , CF_2H , CFH_2 , perfluoroalkyl

Keywords: organic electrochemistry • electrolysis • electrochemical oxidation • fluoroalkylation • trifluoromethylation • difluoromethylation • monofluoromethylation • perfluoroalkylation • radicals • cyclization • Togni reagents • Langlois reagent

9 **Anodic Arylation Reactions**

M. Selt and S. R. Waldvogel

The arylation of organic compounds is a tremendously important tool in organic synthesis, since substituted (het)arenes are essential moieties in many applications ranging from organic intermediates to natural products, pharmaceuticals, and materials. Therefore, an effective, sustainable, and economic synthetic accesses to such compounds is of great demand. This chapter covers the arylation of carbon and heteroatom compounds via an electrooxidative pathway. Direct dehydrogenative methods without the application of a metal catalyst as well as constant-current electrolyses are emphasized. The electrochemical synthesis of biaryl compounds, arylalkanes and arylalkenes, as well as arylated nitrogen, oxygen, and sulfur compounds are described in detail. Additionally, the synthesis of heterocycles through anodic arylation reactions is discussed.



Keywords: organic electrochemistry • electrosynthesis • anodic oxidation • arylation • aromatic compounds • heteroaromatic compounds • biaryls • arylalkenes • arylalkanes •

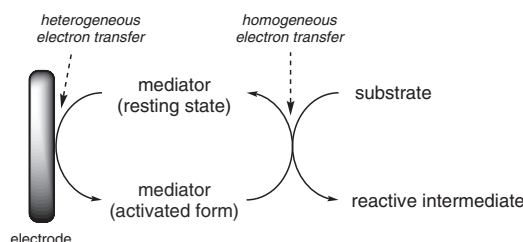
arylamines • phenols • sulfides • sulfones • sulfonates • sulfonamides • sulfonimides • benzofurans • dibenzopyranones • indoles • carbazoles • benzimidazoles • benzoxazoles • benzothiazoles • benzoxazines • phenanthridinones

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10 Redox Mediators in Organic Electrochemistry

R. Francke, A. Prudlik, and R. D. Little

This chapter is intended to serve as a mini-tutorial rather than a comprehensive review. Discussions focus upon fundamental aspects of electrochemically mediated electron transfer. Examples are provided to illustrate the major concepts and a sample procedure is provided.



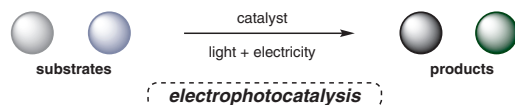
Keywords: indirect electrosynthesis • mediators • active and resting states • electron transfer • inner- and outer-sphere • follow-up reactions • catalytic current • turnover • Zeng mediators • Francke mediators • surface attachment • electrocatalysis • in-cell and ex-cell • minimizing energy waste • redox shuttle

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11 Electrophotocatalysis

J. Galczynski, H. Huang, and T. H. Lambert

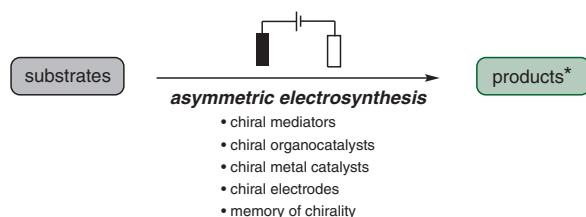
Electrocatalysis and photocatalysis have proven to be powerful strategies for molecular synthesis. Recently, methods that combine the power of light and electricity within a single catalyst have been reported. This area, termed electrophotocatalysis, offers new opportunities to promote challenging transformations. This chapter covers recent work in this area and demonstrates some of the possibilities offered by these approaches for rapidly constructing complex structures through the merger of electrochemical and photochemical energy.



Keywords: organic electrochemistry • electrosynthesis • photochemistry • catalysis • redox chemistry

12 **Asymmetric Electrosynthesis***K. Yamamoto, M. Kuriyama, and O. Onomura*

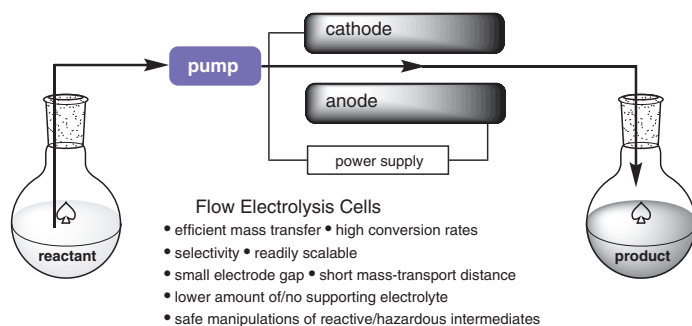
The merging of asymmetric synthesis and electrochemistry offers powerful and environmentally benign protocols for the synthesis of optically active compounds. As electrochemical reactions are performed under unique conditions compared with conventional chemical reactions, a variety of chiral sources have been investigated to achieve efficient asymmetric induction. In this review, selected examples of enantioselective electrosynthesis by using chiral mediators, organocatalysts, metal catalysts, and modified electrodes under both electrooxidative and electroreductive conditions are described. These reactions are organized according to the type of chiral source employed. Asymmetric electrosynthesis via memory of chirality is also included.



Keywords: asymmetric synthesis • electrosynthesis • anodic oxidation • cathodic reduction • mediators • organocatalysts • metal catalysts • memory of chirality • modified electrodes • *N*-oxyls • radical coupling • oxidative coupling • reductive coupling • difunctionalization of alkenes • kinetic resolution • amines • hypervalent iodine • cobalt • nickel • copper • rhodium • palladium

13 **Electrochemistry in Laboratory Flow Systems***A. A. Folqueiras-Amador, J. W. Hodgson, and R. C. D. Brown*

Organic electrosynthesis in flow reactors is an area of increasing interest, with efficient mass transport and high electrode area to reactor volume present in many flow electrolysis cell designs facilitating higher rates of production with high selectivity. The controlled reaction environment available in flow cells also offers opportunities to develop new electrochemical processes. In this chapter, various types of electrochemical flow cells are reviewed in the context of laboratory synthesis, paying particular attention to how the different reactor environments impact upon the electrochemical processes, and the factors responsible for good cell performance. Coverage includes well-established plane-parallel-plate designs, reactors with small interelectrode gaps, extended-channel electrolysis cells, and highly sophisticated designs with rapidly rotating electrodes to enhance mass transport. In each case, illustrative electrosyntheses are presented.



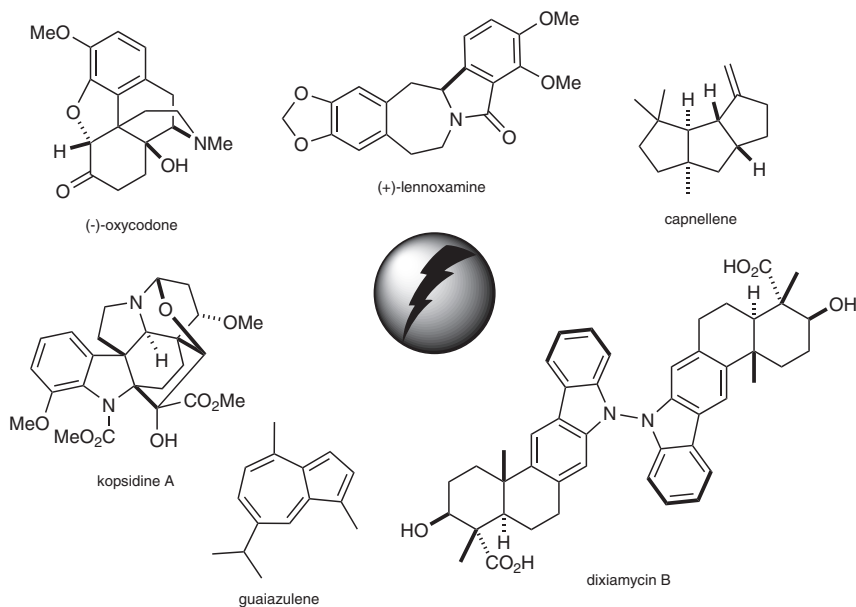
Keywords: organic electrochemistry • electrosynthesis • flow chemistry • mass transport • electrochemical cells • reactor design • anodic oxidation • cathodic reduction

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14 Electrochemistry in Natural Product Synthesis

K. Lam, M. C. Leech, and A. J. J. Lennox

The multistep synthesis of natural products has historically served as a useful and informative platform for showcasing the best, state-of-the-art synthetic methodologies and technologies. Over the last several decades, electrochemistry has proved itself to be a useful tool for conducting redox reactions. This is primarily due to its unique ability to selectively apply any oxidizing or reducing potential to a sufficiently conductive reaction solution. Electrochemical redox reactions are readily scaled and can be more sustainable than competing strategies based on conventional redox reagents. In this chapter, we summarize the examples where electrochemistry has been used in the synthesis of natural products. The chapter is organized by the reaction type of the electrochemical step and covers both oxidative and reductive reaction modes.

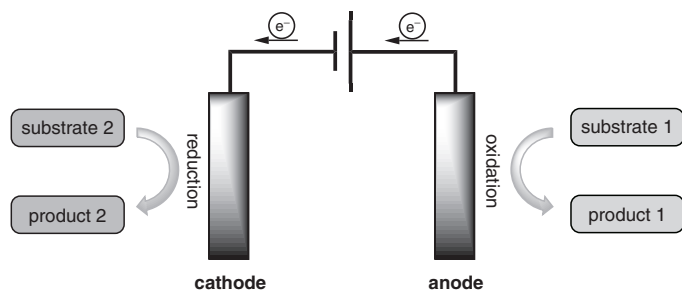


Keywords: organic electrochemistry • electrosynthesis • natural products • oxidation • reduction • total synthesis • redox • cyclization

15 Paired Electrolysis

T. Wu and K. D. Moeller 

While paired electrochemical reactions have a history that can be traced back to the 19th century and have been very effectively used for the production of commercial products, the larger synthetic community has only recently started to embrace the opportunities this approach offers to maximize the overall energy and atom efficiency of electrochemical processes. In this review, a summary of these efforts is presented in the context of four classes of paired electrochemical reactions. These classes of reaction involve parallel processing of products at the anode and cathode, divergent reactions that use a single starting material in different ways, convergent reactions that combine products made at the anode and cathode, and sequential reactions that pass a substrate between the electrodes.



Keywords: electroorganic chemistry · paired electrochemistry · anodic oxidation · cathodic reduction