

## Green electrochemistry. Examples and challenges\*

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*Abstract:* Electrochemical methods have been proposed for synthesis of organic compounds, including conversion of CO<sub>2</sub>. Such methods may provide a basis for environmentally friendly and sustainable methods for chemical production. Nevertheless, electrochemical syntheses are not widely utilized. Several examples of ongoing research are presented that illustrate both the opportunities as well as the challenges associated with the utilization of electrochemistry for green chemical manufacturing.

### INTRODUCTION

Electrochemical routes for organic synthesis must compete with more traditional industrial methods (e.g., heterogeneous and homogeneous catalysis), as well as with emerging methods (e.g., enzymatic catalysis, photocatalysis). All syntheses require application of energy to accomplish the transformation of raw materials. Electrochemical synthesis involves application of a potential, in the presence of active electrode surfaces, and the resulting flow of current drives the oxidation or reduction and subsequent recombination of reactants. Extensive reviews of electroorganic syntheses are available [1–4].

There are several features of electrosynthesis that are often cited as being environmentally favorable [5]. First, electrons flowing as current may be regarded as one of the reagents. Second, reactions may take place in a low-temperature environment, reducing the local consumption of energy, and reducing the risk of corrosion, material failure, and accidental release. Also, reactions may occur in low-volatility or no-volatility reaction media. The electrodes may be regarded as heterogeneous catalysts that are easily separated from the products. Supporting electrolyte and electrochemically active mediator species may be regenerated electrochemically and recovered.

Current research on green chemistry and engineering focuses on alternative solvents (such as supercritical carbon dioxide or ionic liquids), alternative feedstocks, and new catalyst systems, including biological catalysts. Electrochemical syntheses have been studied extensively and touted within the electrochemistry community. Yet these routes have received less widespread attention, and tools for quantitative analysis of their environmental impact are needed. Several examples will illustrate the breadth of possibilities.

### EXAMPLES

What makes a particular synthesis route “green”? As is accepted today, green engineering requires design and use of manufacturing processes that are inherently benign to human health and the environment. Green chemistry [6] encompasses utilization of new feedstocks, safer solvents, and catalysts that are more atom-efficient. Thus, the examples of electrochemical waste treatment and remediation cited

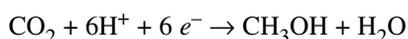
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by Pletcher and Weinberg [7,8] (possibly the first authors to use the phrase “green electrochemistry”) fall outside the scope of the current definition. Rather, here we show examples of electroorganic syntheses that use renewable raw materials, improve atom efficiency, use less toxic raw materials, or decrease emissions compared to conventional syntheses.

### Synthesis of methanol in supercritical carbon dioxide

Electrochemical reduction of CO<sub>2</sub> to methanol would allow subsequent synthesis of higher-value materials. This is one possible route for mitigation of CO<sub>2</sub> emissions, although only small amounts of CO<sub>2</sub> could be sequestered in this way [9]. Nevertheless, CO<sub>2</sub> reduction by electrochemical, as well as other means, is of considerable interest, and several recent works have appeared [9–12]. For example, Li and Prentice [12] employed a high-pressure, near-critical CO<sub>2</sub> + water + ethanol solution, with LiCl as electrolyte and a copper cathode, to synthesize methanol by direct electrochemical reduction of CO<sub>2</sub>.



Methanol was produced at 80 °C with a CO<sub>2</sub> pressure of 68 bar. The best current efficiency observed was 40%, however, which is presently too low to be commercially feasible. This synthesis uses an environmentally friendly dense-phase CO<sub>2</sub> solvent system. In addition, the CO<sub>2</sub> solvent is also the raw material for the synthesis. This aspect eliminates the mass transfer limitations that plague electrochemistry in ordinary liquids.

### Synthesis of organic carbamates via O<sub>2</sub><sup>•-</sup> and CO<sub>2</sub>

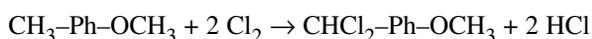
Casadei *et al.* [13–14] have recently reported an indirect synthesis of carbamides that involves electrochemically generated superoxide and CO<sub>2</sub>. Superoxide generated at the cathode subsequently converts NH protic amines to carbamides, and primary or secondary alcohols to carbonates. Organic carbamates are valuable as synthetic intermediates for chemical and biochemical applications. A representative linear carbamide synthesis is as follows:

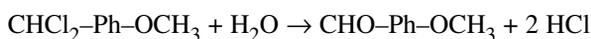


Examples cited [13,14] included R = H or CH<sub>3</sub> or Ph, and R' = PhCH<sub>2</sub> or cyclohexyl or C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>. Linear carbamides were produced by bubbling O<sub>2</sub> and CO<sub>2</sub> into a 0.1 M solution of TEAP in acetonitrile (MeCN) using a divided cell. In the cell (Hg cathode, Pt anode), O<sub>2</sub> and CO<sub>2</sub> were fed to the cathodic compartment. The superoxide generated is relatively stable in MeCN, and after electrolysis substrate was added to the solution. Alkylation was accomplished using ethyl iodide (EtI). A related synthesis produced the cyclic carbamates such as 2-oxazolidinone. The reported yields ranged from about 50% for the cyclic carbamates to 90% for the linear products. Commercial synthesis involves ammonolysis of chloroformates or addition of alcohols to isocyanates. Phosgene is frequently used in preparing these reagents, and thus a phosgene-free synthetic route appears very attractive environmentally.

### Electrochemical activation to replace chlorine

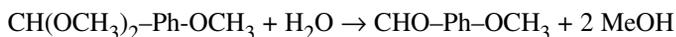
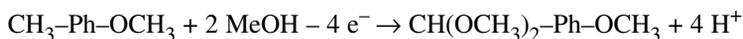
Organic intermediates are conventionally formed via activation with chlorine. The intermediates are subsequently functionalized, giving HCl as a by-product. BASF has commercialized an electrochemical alternative that appears to have less environmental impact [15]. As illustrated for the synthesis of *p*-methoxybenzaldehyde from *p*-methoxy toluene by Steckhan *et al.* [5] the conventional synthesis is as follows:





Four moles of HCl are produced per mole of product; the HCl is dilute in aqueous solution, making recovery of Cl difficult.

The BASF process takes place in methanol solvent with sodium benzene sulfonate as the supporting electrolyte.



This is a direct electrosynthesis, so the selectivity and conversion are dependent upon the electrode material. Note that methanol is also a reactant, and that it is regenerated in the electrochemical process, resulting in 100% atom efficiency. Chlorine and HCl are completely eliminated in this process.

### Other avenues of research

Recent reviews highlight other promising innovations. For example, the use of supporting electrolyte, and the accompanying liquid waste associated with the electrolyte solution, may be eliminated through the use of supported solid polymer electrolytes. In this technology, the fixed polymer electrolyte is easily removed from solution. An example is the methoxylation of tetrahydrofuran [1]. Electroenzymatic synthesis uses redox enzymes as mediators [4,5,17]. Enzymatic synthesis may improve selectivity and yield for complex and chiral compounds.

### RESEARCH AND TECHNOLOGY NEEDS

While some industrial firms such as BASF are well known for commercial utilization of electrochemical synthesis, it is not widely practiced in industry. The potential for green synthesis is real, but there are difficult technical challenges. Electrochemical processes do not scale up in the same manner as traditional petrochemical processes, primarily because of the mass transfer limitations associated with bulk electrodes. Coating, corrosion, and deactivation of electrodes are frequent problems, usually more severe than with heterogeneous catalysts. Electrochemical reactions require special reactors, and estimation of capital costs is more difficult [1].

A key rule of green engineering is to consider environmental aspects from the earliest stages of research and process development. Electrochemistry may be at a particular disadvantage in this regard because of the lack of R&D chemists and engineers trained in these methods. In addition, the reliable assessment of the life cycle and total environmental benefits are difficult; this state of affairs is common to most new technologies where sustainability is a key driver. Economic considerations, including environmental economics, dictate whether industry will adopt any process. Detailed and quantitative tools for life-cycle analyses need to be developed to support comparison of electrochemical methods to other methods. It is not possible to justify replacement of existing processes based on marginal or uncertain improvements in new technology. Prospects for adoption of electrochemical methods are improved when new products are being considered. For these and other reasons, electrochemistry is more likely to be adopted for small-scale syntheses of pharmaceuticals [18] and other high-value, low-volume specialty products [19].

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