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Review Article

Alternating current electrolysis for organic synthesis

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Abstract

Electrochemical organic synthesis has recently attracted much attention because of its unique reactivity and environmentally benign approach. Conventional electrosynthesis uses either constant current or constant potential, known as direct current electrolysis. However, recently, alternating current electrolysis has begun receiving more attention. The purpose of this study is to give a short overview of the history and recent advances in the field of alternating current electrolysis for organic synthesis.

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Organic electrosynthesis, Direct current, Alternating current.

Synthetic organic chemists are always searching for new techniques and methods to enhance selectivity and productivity to construct pharmaceutically essential molecules. In recent years, electrochemical organic synthesis is experiencing a renaissance, driven by the increasing demand for green chemistry and engineering in the pharmaceutical industry [1]. Electrochemical organic synthesis can cut down on the usage of chemicals, reduce waste, and offer improvements in cost, safety, and sustainability by directly using electrons from a power source to complete the redox transformations. Nearly all synthetic organic electrochemical methods use a constant voltage or current to drive chemical transformations [2–4]. Under the constant voltage or current conditions, the electric current only flows in one direction, known as direct current (DC) electrolysis. Much less attention has been paid to alternating current (AC) electrolysis, where the flow of charge changes its

direction periodically. This review provides a brief account of the history and recent advances in the field of AC electrolysis for organic synthesis.

Early explorations of AC electrolysis for organic synthesis

The early studies on AC electrolysis for organic synthesis were carried out driven by the curiosity about what products might be obtained using AC versus DC and how the use of AC would affect the nature and yield of electrolytic products. Back in the 1930s, Shipley et al. [5] conducted AC electrolysis of several organic compounds, including fatty acids and their salts (e.g. potassium acetate, potassium propionate, and potassium butyrate), alcohols, aromatic hydrocarbons (e.g. benzene, *p*-xylene, aniline, hydroquinone), thiourea, thiosulphate, acetone, thiocyanate, acetone/HCl, thymol/KI, and so on. They found that during AC electrolysis, the oxidation of substrates predominated over reduction due to hydrogen evolution reaction at the reduction potentials. They also observed that the product yields, in general, were lower than their counterparts using DC electrolysis. Later, Wilson et al. [6] followed up on Shipley's initial work with a comprehensive study of Kolbe electrosynthesis of ethane by AC electrolysis of potassium acetate. Their key finding is similar to Shipley's: the yield of ethane using AC electrolysis is typically lower than that using DC electrolysis. However, they noticed an interesting phenomenon during the AC electrolysis. Certain cations such as Cu^{2+} , Co^{2+} , and Fe^{3+} were found to inhibit the formation of ethane using DC electrolysis. These cations, however, have no appreciable effect using the AC electrolysis. The authors speculated that the periodic voltage polarity switch of AC led to a mild redox environment so that these cations could spend most of their time at a lower state of valence in which they have much less inhibition effect on the formation of ethane.

In the early studies, researchers have also noticed that the periodic voltage polarity reversal of AC could be useful for performing a sequence of redox-opposite reactions. For example, Alkire et al. [7] reported electrolysis of propylene oxide with AC. During AC electrolysis, NaBr is first oxidized to form Br_2 , which reacts with propylene by homogenous chemical reaction producing propylene bromohydrin under mild alkaline

conditions. As the polarity reverses, water is electrolyzed to hydroxide ion and hydrogen. The hydroxide ion promotes the formation of propylene oxide via the dehydrogenation of the vicinal bromohydrin. However, the same chemical transformation can also be achieved in an undivided electrolytic cell using DC electrolysis, even with a similar or higher current efficiency [8]. The advantage of AC electrolysis for propylene oxide synthesis over DC electrolysis is the energy saved by avoiding the inevitable 3–10% rectification power loss and 25% reduction of the capital investment in the electrochemical part of the plant [9].

Recent advances in AC electrolysis for organic synthesis

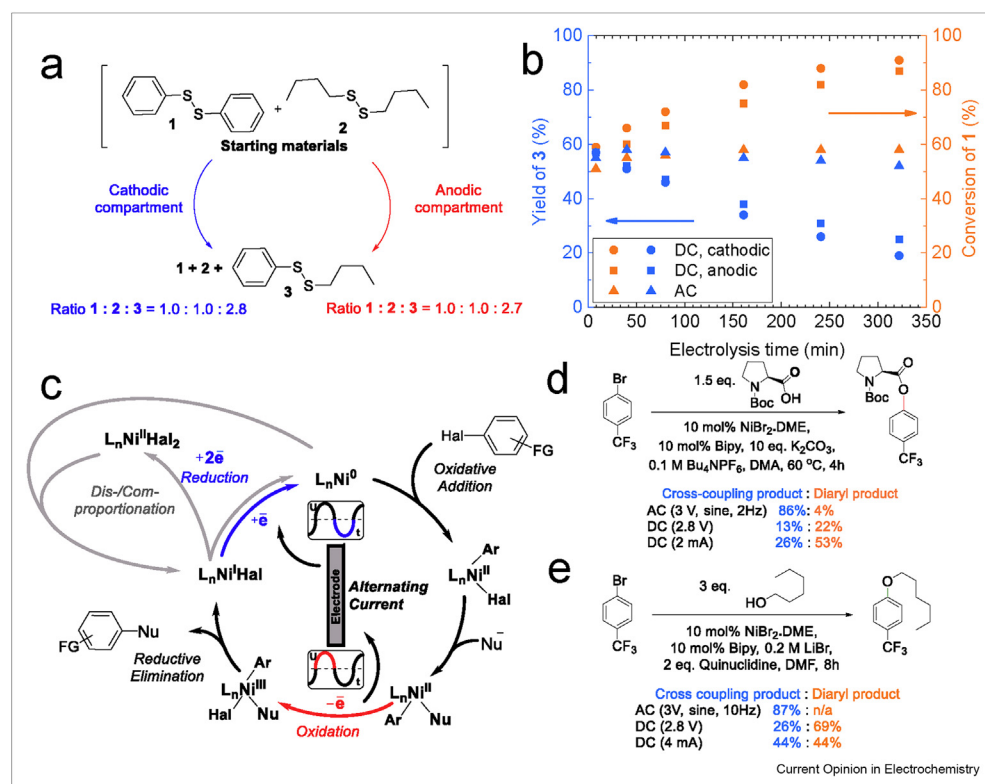
After the initial explorations of AC electrolysis for organic synthesis, the development of AC electrolysis has nearly stopped until recent years. The renaissance of electrochemical organic synthesis attracts researchers to revisit AC electrolysis and further exploit its unique reactivities.

Minimizing over-oxidation/reduction

Over-oxidation/reduction of reagents (including starting materials, catalysts, and solvents) is a common problem during DC electrolysis—especially under constant current conditions—leading to low product yield and poor product selectivity. During constant current experiments, electrode potentials are varied to maintain a fixed current throughout the experiment. When the current from the desired electrochemical reactions cannot achieve the preset current value, the system will increase the applied voltage, causing side-reactions. The over-oxidation/reduction problem is less severe under constant voltage conditions but can still occur when the redox potentials of different species are close to each other.

Sattler et al. [10] demonstrated that AC electrolysis could address the over-oxidation or reduction problem in synthesizing unsymmetrical disulfides by a sulfur–sulfur bond metathesis reaction (Figure 1a). During DC electrolysis of a 1:1 mixture of two symmetric disulfides (1 and 2), the unsymmetrical disulfide

Figure 1



Minimizing over-oxidation/reduction using AC electrolysis. (a) Results of the electrosynthesis of unsymmetrical disulfide, 3, by a sulfur–sulfur bond metathesis reaction using a constant current in a divided cell. (b) Comparison between DC and AC electrolysis in the yield of desired unsymmetrical disulfide 3 and the conversion of the starting material 1 at an extended electrolysis time. (c) The proposed mechanism underlying the coupling of AC to the nickel catalytic cycle for cross-coupling reactions. (d) and (e) Comparison of the yield and selectivity between AC and DC electrolysis for Ni-catalyzed esterification and etherification reactions. Adapted with permission from a study by Sattler et al. [10] copyright (2020) by John Wiley & Sons, Inc, and a study by Bortnikov et al. [11] copyright (2020) by the American Chemical Society.

product (**3**) was formed in both cathodic and anodic compartments because the sulfur–sulfur bond metathesis can proceed via either an oxidative intermediate $R_3S_3^+$ or a reductive intermediate RS^\bullet . A statistical mixture of **1**, **2**, and **3** with a slightly thermodynamic preference toward **3** was obtained. However, after extended electrolysis time at a constant current, the yield of **3** drastically decreased (Figure 1b) because of the over-oxidation of disulfides to oxo-species and over-reduction of disulfides to unidentified black precipitate at the cathode. This problem was entirely solved using AC electrolysis. They applied AC pulses with the same current density as the DC electrolysis condition, and the neighboring current pulses were separated by a quiet time where no current flows. The authors claimed that the quiet time allowed the diffusion of electrogenerated active species into the solution before the reversed pulse would quench these species, accelerating the reaction. The AC electrolysis results show no black precipitate, oxo-species side products, and the disulfides were not consumed or decomposed (Figure 1b). The selectivity between different disulfides is not affected as the reaction thermodynamics determines it.

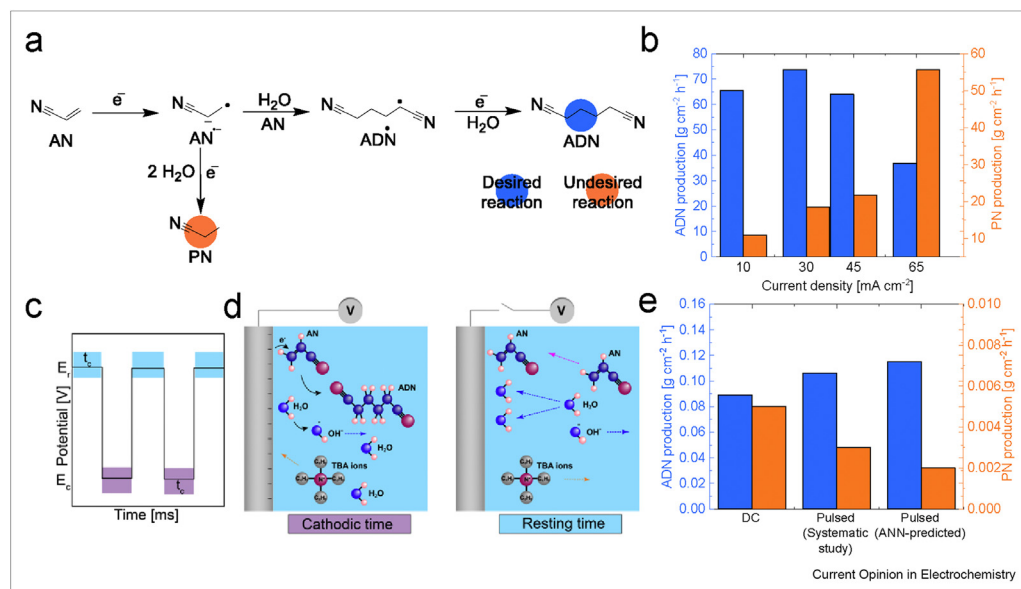
Bortnikov *et al.* [11] also observed the improved product yield and selectivity using AC electrolysis over DC electrolysis when performing Ni-catalyzed amination, esterification, and etherification reactions. In the Ni catalytic cycle, Ni(II) catalyst is first electrochemically reduced to Ni(0) for the following oxidative addition of aryl halide. The formed Ni(II) species undergoes further ligand exchange with a nucleophile and electrochemical oxidation to form Ni(III), which favors reductive elimination, yielding the cross-coupling product (Figure 1c). Under DC electrolysis using a constant current or voltage, the undesired diaryl coupling product is often the primary product for the Ni-catalyzed esterification and etherification reactions (Figure 1d and e). In contrast, a maximum product yield and high selectivity toward the cross-coupling products were obtained at an optimal AC frequency (2 Hz for esterification and 10 Hz for etherification). The authors attributed the improvement of product yield and selectivity to two possible mechanisms. First, in the DC environment on the cathode, there is a high chance to over-reduce the oxidative addition product $[NiL_n(Ar)(Nu)]$ to form Ni(I) and subsequently, a second oxidative addition, which also results in $[NiNu(Ar)_2]$ intermediates. Second $[NiL_n(Ar)(Nu)]$ has a short lifetime in AC because of the periodic voltage reversal, preventing its disproportionation reaction to form $[NiL_n(Ar)_2]$ that eventually produce diaryl products. Both mechanisms rely on suppressing the formation of $[NiNu(Ar)_2]$ intermediates by controlling the reactions of various Ni species near the electrode surface using AC electrolysis.

The reduced over-oxidation/reduction during AC electrolysis may result from the dynamic reaction environment of AC electrolysis, altering the concentration profiles of reactive species near an electrode. This mechanism is supported by a recent work by Blanco *et al.* [12] on optimizing organic electrolysis through controlled voltage dosing. In this study, they investigated the effect of voltage waveform on the yield and selectivity for electrohydrodimerization of acrylonitrile (AN) to adiponitrile (ADN). This electrohydrodimerization reaction is a cathodic reaction, where AN undergoes multi-electron/-proton transfer to form the final product ADN (Figure 2a). Propionitrile (PN) is the most common by-product in this process. PN and ADN share the same intermediate $AN^{\bullet-}$. Under the constant current conditions, PN is the favored product at high current densities (Figure 2b) because the lack of AN near the electrode surface suppresses the dimerization reaction and promotes the over-reduction of $AN^{\bullet-}$ to PN. To address the over-reduction of $AN^{\bullet-}$, they added a zero-voltage resting pulse (E_r, t_r) after each cathodic pulse (E_c, t_c) (Figure 2c). The resulting voltage allows the AN in the bulk solution to replenish the consumed AN near the electrode surface (Figure 2d), which keeps a moderate AN concentration near the electrode surface to favor ADN production and minimize the over-reduction of AN to PN. By exploring various combinations of cathodic pulse time and resting time, they successfully achieved a 20% increase in the production of ADN and a 250% increase in relative selectivity with respect to the state-of-the-art constant voltage process. They also fed the experimental data to an artificial intelligence program and discovered further improved electrosynthetic conditions, reaching improvements of 30 and 325% in ADN production rates and selectivity, respectively (Figure 2e). Although this work used a pulsed voltage waveform to avoid the over-reduction of AN, AC voltage should have a similar effect during voltage polarity reversal on the mass transfer of reactants, minimizing their over-oxidation/reduction during AC electrolysis.

Promoting effective reaction of electrogenerated intermediates in the diffusion layer

Paired electrolysis is one major reaction category for organic electrosynthesis, where two desirable half-reactions are performed simultaneously at the two electrodes. Paired electrolysis is attractive because it improves energy efficiency using both electrodes and provides a unique reaction environment where two redox-opposite reactions of substrates take place in the same pot [13]. However, the reaction scope of paired electrolysis is limited because the slow mass transfer of intermediates between two electrodes requires stable intermediates [14–22]. For reactions involving short-lived intermediates, paired electrolysis generally leads to low yields because of the loss of the intermediates

Figure 2



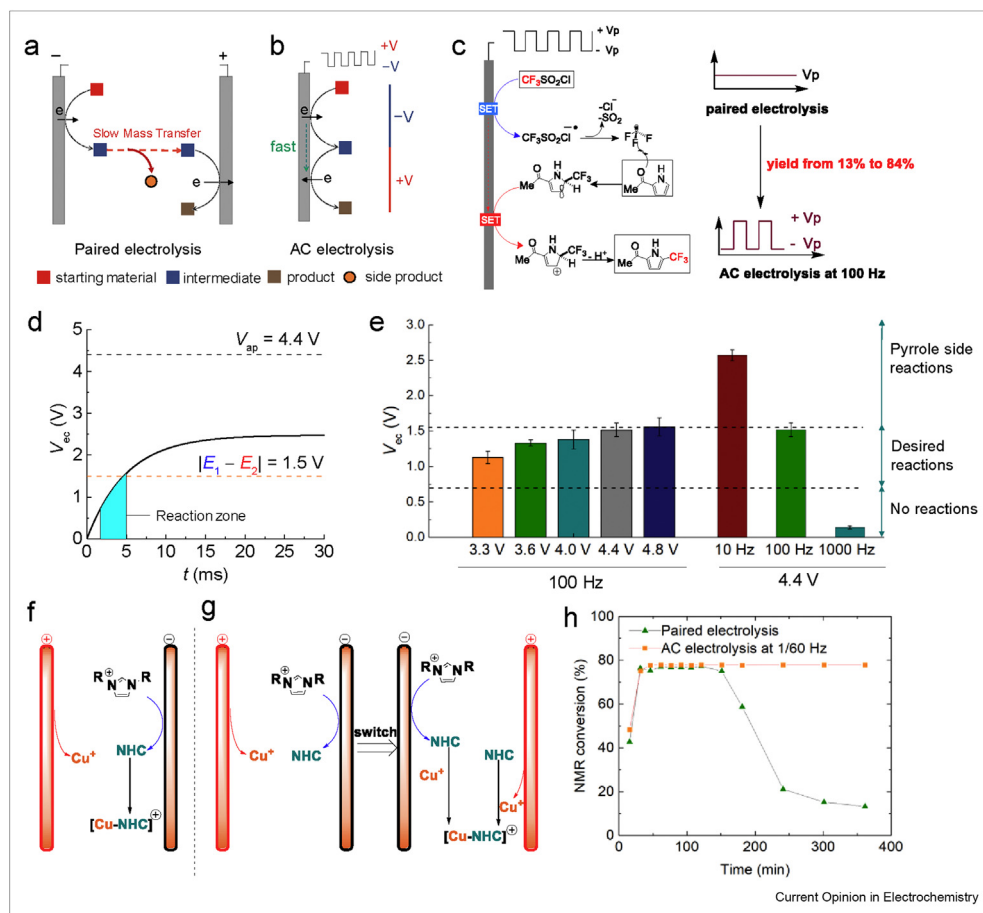
Controlling the product selectivity in electrohydrodimerization of acrylonitrile. **(a)** Cathodic reaction pathways for the electrohydrodimerization of AN to ADN. PN is the most common by-product in this process. **(b)** Under DC operation, PN becomes more favorable than ADN at high current densities. **(c)** The potential waveform highlights the resting potential (E_r), cathodic potential (E_c), resting time (t_r), and cathodic time (t_c). **(d)** The graphical representations of the effects that cathodic and resting potentials can have on the mass transport of different species in solution. **(e)** Comparison of the ADN and PN production rates obtained under best operation conditions found through DC operation optimization, a systematic study of the effect of pulsed potentials, and an artificial neural networks-predicted optimal performance prediction. Adapted with permission from a study by Blanco et al. [12] copyright (2019) by the National Academy of Sciences.

during mass transfer (Figure 3a). AC electrolysis is a solution to this inherent limitation of paired electrolysis. During AC electrolysis, an alternating voltage is applied to drive the redox transformations of the substrates sequentially at the same electrode (Figure 3b). In this case, the intermediates do not have to migrate between the two electrodes, enabling short-lived intermediates to react immediately on the electrode polarity reversal. Rodrigo et al. [23] demonstrated this advantage of AC electrolysis using trifluoromethylation of (hetero)arenes as a model reaction. The trifluoromethylation reaction proceeds via a sequential reaction mechanism: triflyl chloride is first reduced to form CF_3 radical, then the reactive CF_3 radical combines with aromatic systems, and finally the resultant radical undergoes oxidation to form the product (Figure 3c). Because the radical intermediates formed from CF_3 radical addition to (hetero)arenes lose their aromaticity, they are unstable, which ultimately causes low yields of trifluoromethylated products using the paired electrolysis approach. For the model substrate, 2-acetylpyrrole, the trifluoromethylated product yield was only 13% using a constant voltage. In contrast, the product yield increased to 84% at the optimal AC frequency of 100 Hz when the radical intermediates could be effectively oxidized to the final product. Because the charge and discharge of the electrical double layer strongly influence the AC electrolysis process at high frequencies such as 100 Hz,

they developed a numerical model to analyze the voltage available for electrochemical reaction (V_{cc}). They identified the reaction zone during each voltage pulse (Figure 3d). They also used this model to calculate the actual V_{cc} under different AC electrolysis voltage amplitudes and frequencies and to predict the possible reactions that would take place under these electrolysis conditions (Figure 3e). The predictions were in excellent agreement with the experimental results.

As the electrogenerated intermediates stay in the diffusion layer of an electrode, their reactions are also effective and reproducible. Schotten et al. [24] found a poor reproducibility in the electrosynthesis of Cu–N-heterocyclic carbene complexes ($[\text{Cu}–\text{NHC}]^+$) using a constant voltage. This reaction requires oxidation of Cu electrode to Cu^+ ions and reduction of 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride ($\text{IMes}\cdot\text{HCl}$) to NHC (Figure 3f). The poor reproducibility using paired electrolysis is caused by the electrodeposition of Cu ions onto the cathode, which forms Cu metal dendrites over time, which shorts the circuit at prolonged reaction time (Figure 3h). When they performed the reaction using AC electrolysis with a low frequency of 1/60 Hz, the reaction showed long-term stability without any loss in conversion over 7 h (Figure 3h) by avoiding metal deposition and dendrites formation. Also, the reaction rate using 1/60 Hz AC voltage was found to be

Figure 3



Schematics of (a) paired electrolysis and (b) AC electrolysis for a sequential reaction that includes two redox-opposite steps. (c) Reaction mechanism for trifluoromethylation of 2-acetylpyrrole using AC electrolysis. (d) Theoretical modeling of the voltage available for electrochemical reactions (V_{ec}) versus the voltage pulse duration, t . The region highlighted in blue indicates the reaction zone. (e) Predicted V_{ec} and possible reactions for trifluoromethylation of 2-acetylpyrrole under different AC voltage amplitudes and frequencies. Schematics of (f) paired electrolysis and (g) AC electrolysis for synthesizing Cu-N-heterocyclic carbene (Cu-NHC) complexes. (h) Comparison of the long-term reaction stability using a constant voltage and 1/60 Hz AC voltage. Adapted with permission from a study by Rodrigo *et al.* [23] copyright (2020) by the American Chemical Society and a study by Schotten *et al.* [24] copyright (2020) by the Royal Society of Chemistry.

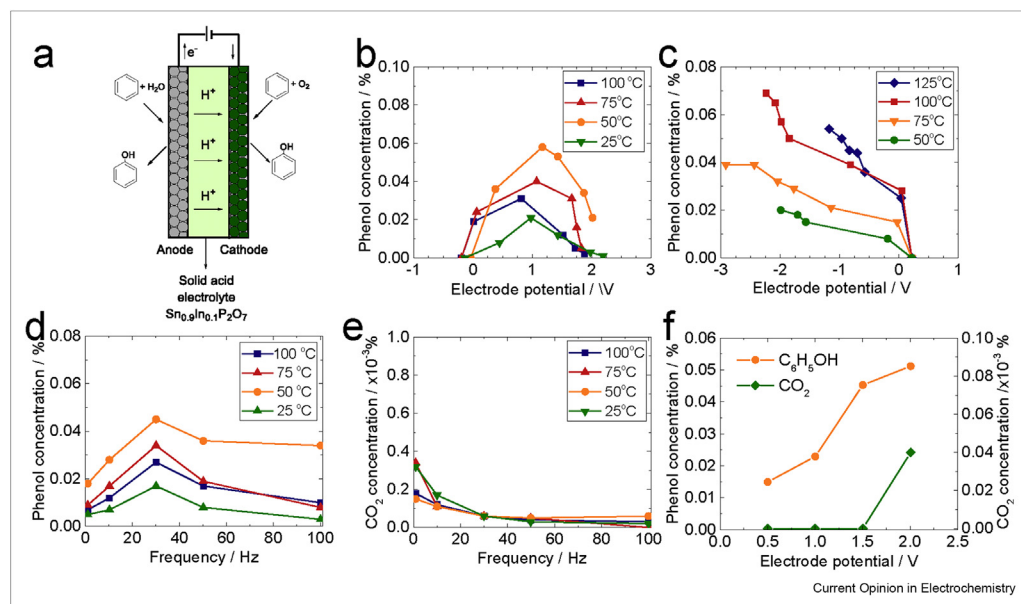
often higher than that using a constant voltage because $\text{IMes} \cdot \text{HCl}$ near the electrode surface can be constantly replenished during voltage pulses (as we have previously discussed in Figure 2d).

Controlling the reactive species on the electrode surface

All the experiments we have discussed so far used AC voltage to control the electrochemical reaction kinetics and mass transfer of reactive species in solution for efficient and selective electroorganic synthesis. AC electrolysis has also been used to control the reactive species on the electrode surface for organic synthesis. Lee *et al.* [25] discovered AC electrolysis led to higher current efficiency and selectivity than DC electrolysis for electrosynthesis of phenol from benzene. The study was conducted in the gas phase using solid acid

electrolyte $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ and vanadium oxide with mixed penta- and tetravalent vanadium (V_xO_y) as electrode material (Figure 4a). Under DC electrolysis conditions, benzene is partially oxidized to phenol by active oxygen species both on the cathode and anode. At the anode, the active oxygen species is generated by oxidizing water vapor while they are produced by reducing O_2 at the cathode. The anodically and cathodically generated active oxygen species show significant different reactivities. For the anodic phenol production, the optimal temperature is 50 °C, and the current efficiency for phenol production and selectivity toward phenol were 59% and 98%, respectively, at the maximum phenol concentration. One limitation of anodic phenol production is that the selectivity toward phenol deteriorates at large overpotentials (Figure 4b) because (1) further anodic polarization oxidizes the

Figure 4



Controlling the reactive species on the electrode surface by AC electrolysis. **(a)** Schematics of the solid-state electrochemical cell for electrolysis of phenol from benzene. Phenol concentration produced by the oxidation of benzene with electrochemically generated active oxygen species under different electrode potentials and temperatures at **(b)** the anode and **(c)** cathode. Concentrations of **(d)** phenol and **(e)** CO₂ at an AC peak voltage of 1.5 V under various temperatures as a function of the AC frequency. **(f)** Product concentrations at 50 °C and 30 Hz as a function of the AC peak voltage. Adapted with permission from a study by Lee et al. [25] copyright (2012) by John Wiley & Sons, Inc.

active oxygen species to atomic or molecular oxygen, which is assumed to be inactive toward the partial oxidation of benzene and (2) benzene is directly oxidized to CO₂. In contrast, the cathodic phenol production increases with the increasing overpotential but requires a high temperature of 100 or 125 °C (Figure 4c) and has a low current efficiency of 14% toward phenol. The *in-situ* Raman spectroscopy results suggest the active oxygen species at the anode is the HO• radical. The cathodically activated oxygen species remains unclear but is not HO• radical according to its Raman spectrum. AC electrolysis overcomes the limitations of both anodic and cathodic phenol production, generating phenol at a higher current efficiency than DC electrolysis and close to 100% selectivity toward phenol even at high overpotential under a mild temperature of 50 °C (Figure 4d). The possible mechanism for the high performance of AC electrolysis is that the continuous cycling between oxidation and reduction during AC electrolysis stabilizes the HO• radical and other radical intermediates on the electrode surface, promoting the production of phenol.

Conclusions and future directions for the field

In conclusion, this short review briefly summarizes the history and recent advances in AC electrolysis for organic synthesis. Researchers have demonstrated

several unique reactivities of AC electrolysis, including its ability to minimize over-oxidation/reduction, promote the effective reaction of electrogenerated intermediates, and control the reactive species on the electrode surface. Despite these advances, there are still many challenges in this field, especially about how to identify and understand the optimal conditions in AC electrolysis. Compared to its DC counterpart, AC electrolysis has two more parameters (i.e., AC frequency and waveform) for reaction optimization. On the one hand, additional reaction parameters provide better control over the reaction kinetics for improved reaction efficiency and product selectivity. On the other hand, a large reaction parameter space also makes the reaction optimization challenging. Most of the work in this review used the ‘trial and error’ approach in AC electrolysis condition optimization, which is inefficient and time-consuming. There are three possible solutions to this issue. The first one is to develop high-throughput methods for screening the reaction conditions, for example, by coupling an AC electrolysis setup with mass spectrometry. The second one is to establish the theories of AC electrolysis using model reactions with common reaction mechanisms and then use the theories to guide the rational design of reaction parameters. Although there have been some theoretical studies on AC electrolysis in the literature [26–31], these prior studies are purely theoretical and lack experimental

validation. More efforts are needed to close the gap between theory and experiment. The last one is to perform small-scale reaction optimization and then feed the data to an artificial intelligence program for further optimization, which has been proven successful by Blanco *et al.* [12] for electrohydrodimerization reaction of AN to ADN. This approach needs further validation using other AC electrolysis reactions. In summary, AC electrolysis for organic synthesis is undoubtedly an exciting field and addressing the current challenges in reaction optimization will attract more researchers to exploit its unique reactivities.

Declaration of competing interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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