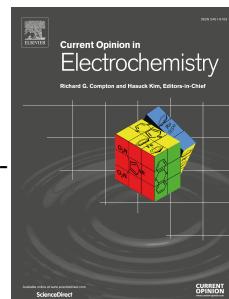


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Recent Advances in Paired Electrolysis of Biomass-derived Compounds Towards Co-generation of Value-added Chemicals and Fuels

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Abstract: Pairing the electrocatalytic hydrogenation (ECH) reaction with different anodic reactions driven by renewable electricity offers a greener way for producing value-added chemicals and fuels. In particular, replacing the sluggish water oxidation with a biomass-based upgrading reaction can reduce the overall energy cost, thus allowing for the simultaneous generation of high-value products at both electrodes. This mini-review summarized the recent progress in paired electrolysis of biomass-derived compounds, particularly the furanic chemicals. Some perspectives and outlooks were proposed for further improvements in this research area.

Keywords: Paired electrolysis, electrocatalysis, catalysis, electrocatalytic hydrogenation, biomass.

Introduction

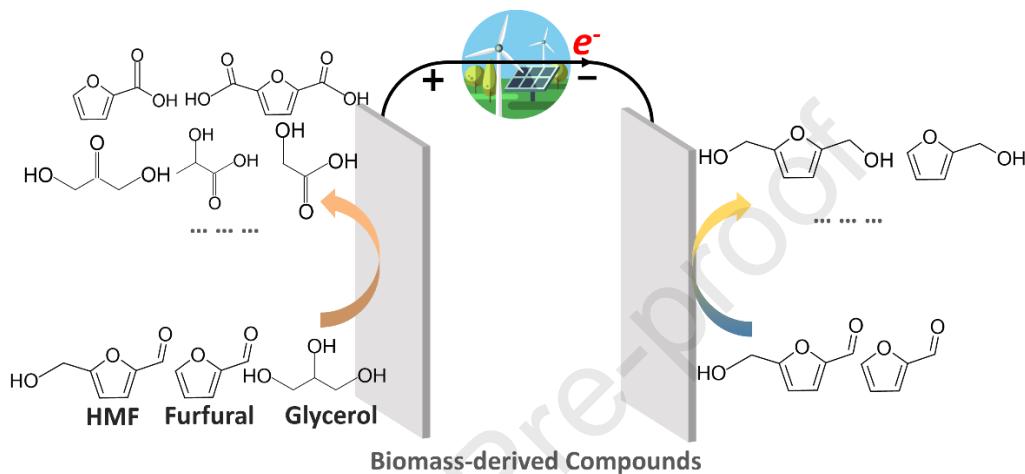
In light of the increased environmental issues caused by heavy dependence on fossil fuels, most efforts have been devoted to seeking renewable energy resources [1, 2]. Electrochemical conversions of small molecules (H_2 , formic acid, methanol, etc.) to generate electricity in fuel cells, or H_2O , CO_2 in electrolyzers to produce renewable chemicals, particularly driven by renewable electricity sources from wind and sunlight, have attracted enormous attention [3, 4]. The driving force of electrochemical reactions is the electrode potential instead of thermal energy, with “clean” electrons as the reducing and oxidizing agents rather than toxic reductants and oxidants [5].

In many circumstances, the half-reaction of interest (e.g., electrocatalytic hydrogenation, ECH), is paired with the oxygen evolution reaction (OER, $E^0 = 1.229 \text{ V}$), which is unfavorable both thermodynamically and kinetically, and produces O_2 with little value [6]. In contrast, coupling ECH with the electrochemical oxidation (ECO) of biomass-derived molecules enables the simultaneous generation of valuable chemicals at both electrodes with a theoretical charge efficiency of 200% while enhancing the overall energy efficiency (**Scheme 1**) [7-9].

Electrochemical conversion of biomass-derived feedstock to valuable chemicals and fuels is a great substitution to reduce our century-long addiction to fossil fuels for chemical manufacturing [10, 11]. Moreover, proton and oxygen sources from water avoid dealing with molecular H_2 and O_2 at an elevated temperature and pressure. Some intriguing bio-based chemicals, such as

furfural and 5-hydroxymethylfurfural (HMF), have been listed as one of the top biomass-derived compounds by the U.S. Department of Energy [12]. They hold great potential to serve as synthetic platforms for numerous value-added chemicals (*e.g.*, applied in foundry and polymer industries) [13-15].

This mini-review article summarized and discussed recent progress in paired electrolysis of biomass-based compounds, particularly furanic chemicals, and outlined some opinions for future research in this area.



Scheme 1. Schematic illustration of paired electrolysis of biomass-derived compounds powered by renewable electricity.

Thermodynamic analysis

Cathodic ECH reactions are typically coupled with a four-electron OER at the anode that is known to be thermodynamically unfavorable and kinetically sluggish. For example, thermodynamic analysis of ECH of HMF has shown that the replacement of OER by ECO of HMF significantly reduced the thermodynamic cell potentials ($|E^0|$) from 1.11 to 0.33 V, and thereby largely brought down the required energy input [16, 17]. In addition, OER has been confirmed to consume ~90% of the full cell voltage and energy consumption in a conventional CO₂ electro-reduction process [8]. These results indicated that, in most traditional electrochemical systems, the energy barrier mainly stems from the anodic OER.

Apart from ECO of HMF in substitute of the sluggish OER, oxidation of various bio-based species (such as furfural, benzyl alcohol, glucose, and glycerol) to valuable chemicals are also excellent candidates with favorable reaction energy. These paired electrolysis processes are potentially beneficial to dramatically lowering the cell voltages, highlighting the need to develop attractive paired systems with maximal atom and energy efficiencies.

Classification of the paired electrolysis systems

Paired electrolysis systems are classified into four types (**Figure 1**) as reported by Lee et al. [9]: (1) Parallel paired electrolysis simultaneously performs two unrelated reactions in a divided cell. (2) Convergent paired electrolysis produces a single product from the cathodic and anodic intermediates in an undivided electrochemical cell. (3) Divergent paired electrolysis converts a

common substrate to different products. (4) Linear paired electrolysis yields the identical product from the same reactant but through different electrochemical reactions.

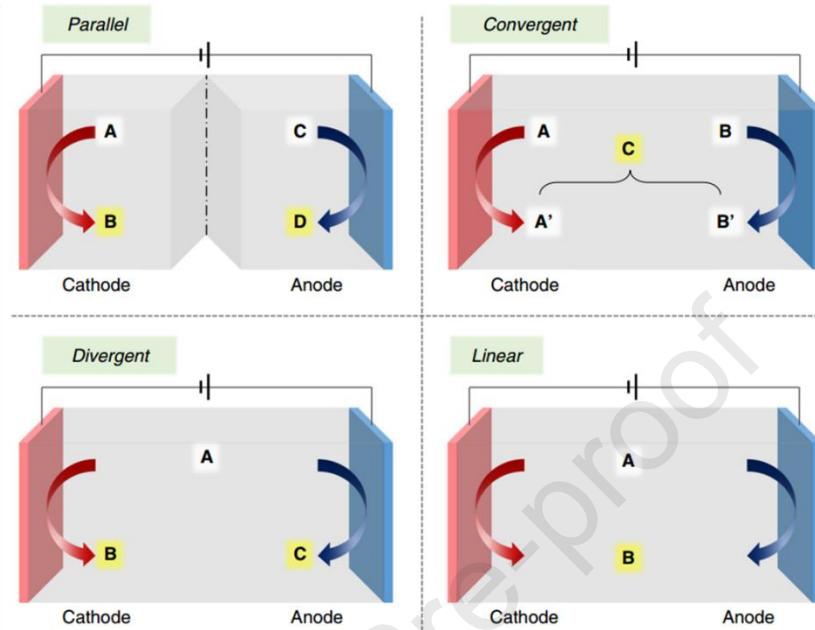


Figure 1. Schematic illustration of the electrochemical co-production system, which is divided into a parallel, convergent, divergent, and linear paired electrolysis. Adapted from ref. [21]. Copyright 2019, Nature.

Design of reactors

The simplest reactor for paired electrolysis is an un-divided, one-compartment cell (**Figure 2a**), in which the cathodic and anodic reactions are mixed in a batch reactor. High current operations can be performed in this reactor with an acceptable cell voltage exhibited. However, owing to the unseparated cathode and anode, the reduced cathodic products could be re-oxidized on the anode (and vice versa), causing largely dropped efficiency, and potentially inducing difficulties in product separation.

To avoid the interference between catholyte and anolyte, a membrane or a glass frit is placed to form a divided H-type cell (**Figure 2b**) [18, 19]. In order to accurately control the applied potential of a particular half-reaction, a suitable reference electrode is inserted to develop a three-electrode electrolytic system. As such, it is helpful to separately study the reaction mechanism (e.g., overpotential, product distribution, etc.) of a half-desired reaction. However, it is still a challenge to simultaneously control the applied potentials on both cathode and anode.

Paired electrolysis conducted in the H-type reactors in order to evaluate electrolysis performances [19, 20]; however, the high energy cost and operational inefficiencies associated with the H-cells are critical barriers to the further development of the industrial implementation of such processes [21]. In this regard, continuous operation of a flow reactor greatly reduced the ohmic loss, enhanced mass transport, and improved energy efficiency for economically feasible electrosynthesis. Adopting a similar structure of H-cell, a three-compartment flow cell was designed (**Figure 2c**) with a spacer and an inserted reference electrode to control the half-cell voltage.

Additionally, benefiting from the unique zero-gap configuration, membrane-electrode assembly (MEA)-based flow cells offered a further reduced ohmic loss (**Figure 2d**), and therefore

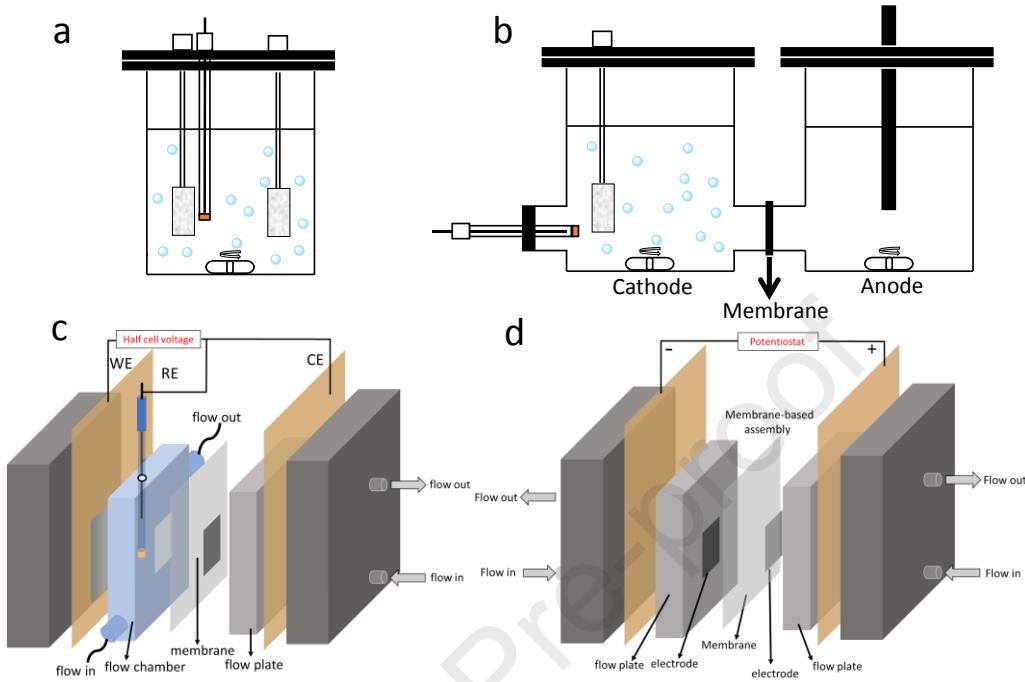


Figure 2. Schematic illustration of (a) one-compartment electrolytic cell, (b) H-type cell, (c) three-electrode flow cell with a spacer, and (d) MEA-based flow cell.

minimized cell voltage and improved energy efficiency [22, 23]. Three types of membranes are typically used in MEAs, including anion exchange membrane (AEM), cation exchange membrane (CEM), and bipolar membrane (BPM), in which anion and cation exchange layers are sandwiched together to dissociate water into H^+ and OH^- when the potential difference exceeds 0.8 V under the reverse biased mode [24, 25]. Applying CEM, such as the H^+ conductive Nafion membrane, results in a highly acidic pH on the cathode electrode and could lead to favored HER over ECH. Moreover, under some circumstances, the crossover of reaction intermediates and products is not negligible for long-term operations, particularly for the system with AEM and CEM. In contrast, the system with BPM is more stable and evitable to crossovers, and a pH-asymmetric cell design became viable due to the sandwiched anion and cation exchange layers to balance the changed pH of cathode and anode; however, BPM suffered from the high membrane resistance. To demonstrate more advanced and robust membrane is always a possible future research direction that required to devote much efforts.

Some examples of paired electrolysis systems were demonstrated in the above-mentioned reactors. Huber et al. presented a continuous-flow, MEA-based reactor in pairing ECH of furfural with hydrogen oxidation reaction (HOR), which achieved slightly higher reaction rates at a lower energy input by substituting the anodic OER with HOR [26]. In addition to the general operation parameters (i.e., gas/liquid flow rates, temperature, and humidity), the local chemical environment of the catalyst is critical in optimizing the efficiency. Taken these into account, Wood et al. reported that the addition of hydrophobic PTFE and anion exchange ionomers to the

electrocatalysts modified the protic environment of the cathode surface, resulting in the suppressed HER and increased ECH rate [27].

In addition to the normally used reactors for electrolysis, novel reactor designs are expected to be explored to maximize atom and energy efficiencies. For example, Noël et al. reported an undivided multichannel electrochemical flow reactor for ECH of furfural [28], which is equipped with flexible reactor volume and enabled both serial and parallel operation modes. They also modified the flow electrolyzer to a divided cell for paired electrolysis of furfural [29], resulting in the co-production of anodic 2(5H)-furanone, as well as cathodic furfuryl alcohol and hydrofuroin. To better address the mass transport limitation, Goetheer et al. designed a pulsating flow electrolyzer for the oxidation of 1,2-propanediol [30]. The presence of the pulsation significantly increased the Sherwood number in the system and consequently decreased the boundary layer and enhanced the mixing of reactants. Through modification of pulsation frequency, the selectivity to the desired product has increased >15% compared with the non-pulsed system.

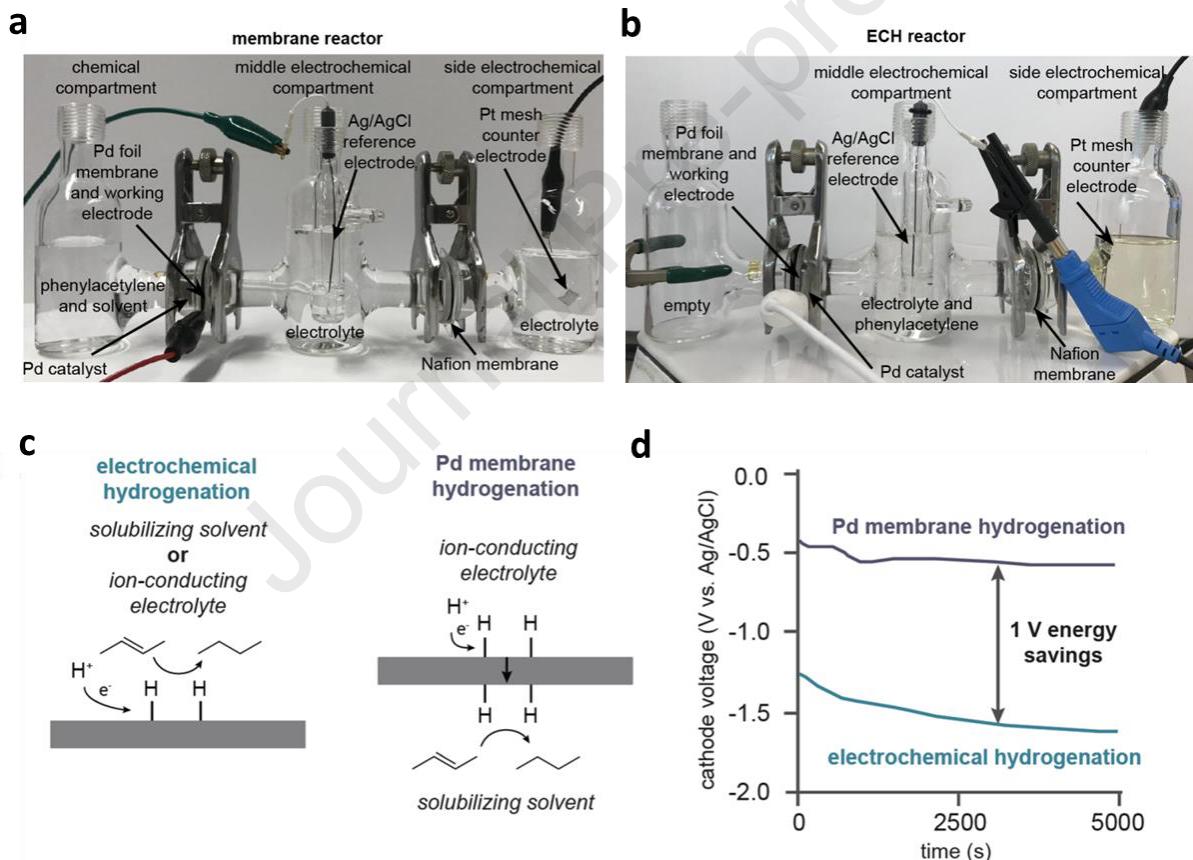


Figure 3. Photographs of the (a) membrane and (b) ECH reactors. In both cases, the cell has electrolyte in the middle and right compartments, with a Nafion membrane separating the reductive (middle compartment) and oxidative (side compartment) half-cells. A palladium membrane separates the middle and side compartments. For the membrane reactor, the organic substrate is dissolved in solvent in the chemical compartment and the Pd black catalyst faces the side electrochemical compartment. For the ECH reactor, the organic substrate is dissolved in the middle compartment and the Pd catalyst faces the middle compartment. (The chemical compartment is therefore not operative for the ECH reactor. A Pt mesh counter electrode and Ag/AgCl reference electrode are used for both setups.) (c) Protons are

reduced to surface-adsorbed hydrogen, which can permeate through a palladium membrane to react (Pd membrane hydrogenation) or react directly at the electrode surface (electrochemical hydrogenation). (d) The separation of solvent and electrolyte enables a significant voltage saving for hydrogenation. Adapted from ref. [67]. Copyright 2019, American Chemical Society.

Berlinguette group demonstrated a novel palladium membrane reactor for electrocatalytic hydrogenation or deuteration of various biobased chemicals with different functional groups, such as alkynes ($\text{C}\equiv\text{C}$), alkenes ($\text{C}=\text{C}$), aldehydes ($\text{C}=\text{O}$), and imines ($\text{C}=\text{N}$) [20, 31, 32]. As shown in **Figure 3**, the basic principle is that hydrogen atoms are generated at the electrochemical compartment, diffused to the chemical compartment in the hydrogenation of unsaturated organic substrates, stemming from the hydrogen atoms are able to adsorb and diffuse into the palladium lattice [33, 34]. The palladium membranes functioned as a separator to prevent the mixing of electrolytes between electrochemical and chemical compartments, a cathode to produce hydrogen atoms from H_2O , and a catalyst and supply of hydrogen atoms to the chemical compartment. Benefiting from this design, an over 1 V saving of cell voltage was observed, as compared with the commonly used H-type reactor. In addition, the development of palladium membranes to controllable diffuse the adsorbed H/D, and the investigation of reaction kinetics and mechanisms can be studied in this advanced reactor.

To date, most research works on the ECH of organic feedstocks suffered from low current density (*i.e.*, $<50 \text{ mA cm}^{-2}$) in order to maintain a high faradaic efficiency (FE). The competitive hydrogen evolution reaction (HER) usually outperforms ECH at higher current densities, as both processes compete for the adsorbed hydrogen (H_{ads}) as the crucial intermediate species, while the organic species for ECH are usually limited by mass transport both externally and internally [35]. As an alternative, on-site utilization of the co-generated H_2 at high current density can substantially improve the atom and energy efficiencies of the whole process [36, 37]. For instance, Moeller et al. designed an electrocatalytic-catalytic coupled reactor in synthesizing various chemicals [36]. A thermocatalytic hydrogenation (TCH) reactor in tandem was coupled with an ECH reactor that allows for the distributed chemical production using on-site generated H_2 from the ECH process at a high current density, thus avoided dealing with gaseous H_2 in the pressurized containers. These tandem electrocatalytic–catalytic systems use electricity as the only form of energy input and water as the sole source of H_2 , which is not only robust but also flexible. Depending on the scale of the TCH reactor, the production rate of H_2 can be simply controlled by the current density from the electrochemical process. To sum up, a broader range of TCH reactions and better reactor/process designs could be explored and coupled in future studies.

Development of electrocatalysts for desired half-reactions

Before demonstrating paired electrolysis in one reactor, in the past few years, many research efforts have been devoted to explore advanced electrocatalysts, and acquire fundamental mechanistic understandings of the desired half-reactions for its efficient transformations.

For ECO of HMF, Strasser et al. first demonstrated this reaction on Pt surface [38], but with a negligible yield of desired product FDCA. Li and co-workers then rereported oxidation of HMF to FDCA on PdAu_2/C in alkaline electrolytes with a yield of over 80% [39]. In this work, they observed two competitive routes for HMF-to-FDCA conversion, while its pathway was highly

dependent on the electrode potential. However, the utilization of noble metals and the required relatively higher overpotentials have brought additional cost.

In 2015, Choi group discovered 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-mediated ECO of HMF, and obtained ~100% FE and yield of FDCA [40]. The utilization of TEMPO has some distinct advantages: (1) Reaction conditions for HMF oxidation were brought down to mildly basic conditions (or near-neutral pH), where some heterogeneous electrocatalysts (e.g., Pd-catalysts) are no longer catalytically active for this reaction. (2) Metal-free and cost-effective electrodes (e.g., carbon cloth) can be used, as the oxidation of TEMPO to TEMPO⁺ shows relatively facile kinetics. (3) Apart from the oxidation of HMF, TEMPO as an efficient homogenous catalyst can potentially oxidize a wide range of organic substrates under mild conditions. However, mixing TEMPO in the anolyte introduced some separation issues that might hinder its possible future applications.

To propose a mediator-free system, the Sun group reported transition metal Co- and Ni-based electrocatalysts for HMF oxidation in 1.0 M KOH electrolyte, with all being exhibited over 90% yield of FDCA [41-45]. The feasibility of these electrocatalysts was demonstrated by extending the substrates to various biomass-derived compounds, including benzyl alcohol, furfural, and furfuryl alcohol, all showing much lower overpotentials than OER. The hierarchically porous structure with more exposed electrochemical active surface area (ECSA) enabled these high activities. To study the relation between the structure of catalysts and the oxidation activity, Poerwoprajitno et al. reported the selective expose of some specific active facet (e.g., Ni {10̄10}) was vital for its further improved activity [46]. Lu et al. introduced Cu²⁺ for the replacement of Co²⁺ in spinel oxides, which exposed relatively more degrees of Co³⁺ and enhanced the activity for ECO of HMF over four-fold. This work emphasizes the importance of regulating geometrical sites by doping other transition metals. To better understand reaction mechanisms of ECO, Barwe et al. developed *operando* electrochemistry coupled with ATR-IR spectroscopy to study HMF-to-FDCA rection on Ni_xB, and they observed the preferential pathway via 5-hydroxymethyl- 2- furancarboxylic acid rather than 2,5- diformylfuran [47].

For ECH of HMF, the Koper group screened some metals by combining voltammetry with online sample collection and offline liquid chromatography under neutral [48] and acid [49] conditions. They classified the catalysts into three groups in favoring different products. Subsequently, Choi et al. reported ECH of HMF on Ag electrodes (synthesized from sputter coating and galvanic displacement) under pH 9.2 borate buffers, showing both high selectivity and FE up to 100% under a wide potential range. The identified hydrogenation mechanism, including the adsorption and desorption of intermediates, are highly dependent on the applied potentials.

Demonstration of paired electrolysis

To carry out paired electrolysis, Li group coupled cathodic HMF-to-BHMF with anodic HMF-to-FDCA reactions in a divided H-type cell [19]. The cathodic HMF hydrogenation was performed on an Ag/C catalyst and anodic HMF oxidation on carbon felt via a 4-acetamido-TEMPO (ACT) mediator, with a combined FE of 187% to the desired BHMF and FDCA. However, the carbon support was found to interfere with the HMF reduction pathway, leading to the formation of undesirable dimeric product [5,5-bis(hydroxymethyl)hydrofuroin, BHH] at

more negative potentials. In addition, H-cell measurements suffered from high energy costs due to the considerable resistance from the cathode and anode. Subsequently, the same group developed a three-electrode flow cell and a high surface area oxide-derived Ag cathode for efficient paired electrolysis of HMF [17]. A remarkably reduced cell voltage from ~7.5 V to ~2.0 V at 10 mA was observed by transferring the electrolysis from the H-type cell to the flow cell, benefiting from the vastly reduced solution resistance between the working electrode and counter electrode from 483.2 to 39.3 Ω .

Inspired by the active Ni-based catalysts for TEMPO-free HMF-to-FDCA conversion, Wang et al. demonstrated the co-production of FDCA and 2,5-bishydroxymethyl-tetrahydrofuran (DHMTHF) from HMF on 3D vanadium nitride (VN) and Pd/VN hollow nanospheres catalysts, respectively [50]. They incorporated the paired electrolysis in a membrane-electrode assembly-

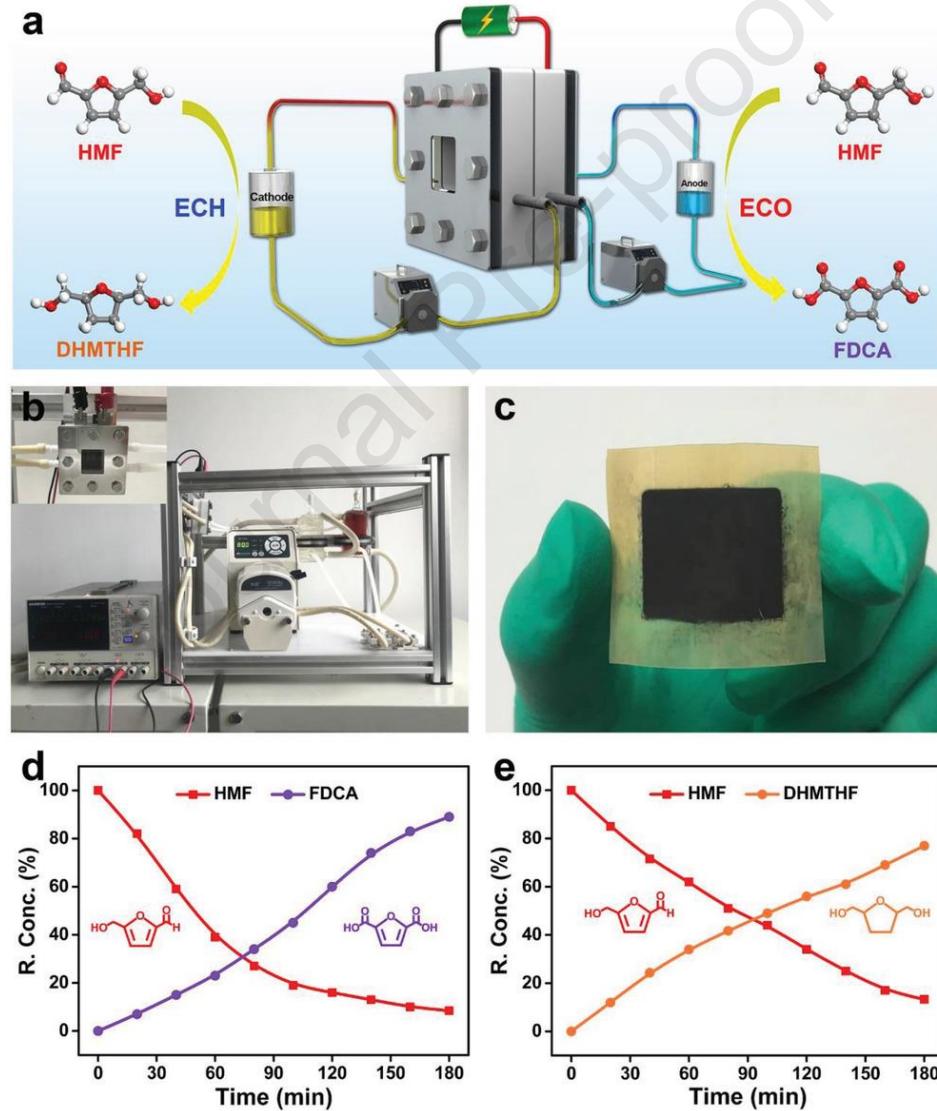


Figure 4. (a) Scheme of VN and Pd/VN paired electrolysis electrodes for ECO and ECH of HMF, respectively. (b) Photograph of the paired electrolyzer reaction system. (c) VN and Pd/VN catalyst-coated

bipolar membrane used for the electrolyzer cell. (d) Relative concentration of HMF and FDCA. (e) Relative concentration of HMF and DHMTHF. Adapted from ref. [49]. Copyright 2019, Wiley.

based flow cell (**Figure 4**). The chemisorption of HMF was improved through the modulated d-band centers in the VN catalysts. In addition, attributed to the favorable mass transport enabled by the 3D hollow nanosphere structure of catalysts, cathodic and anodic conversions were increased. Moreover, the directly deposited catalysts on the membrane favored its contact, and the zero-gap reactor design further reduced the ohmic loss and increased the transport of ions across the membrane. Sun et al. employed a NiB_x catalyst for ECO of HMF and paired it with a p-nitrophenol-to-p-aminophenol reaction [51]. Linear sweep voltammetry (LSV) and *in situ* Raman spectroscopy have confirmed the electrogenerated Ni^{3+} is the active species, which is reduced to Ni^{2+} during the ECO of HMF; meanwhile, the active Ni^{3+} species is continuously formed via the re-oxidation of Ni^{2+} under the positive potentials. The valance change of Ni during the heterogeneous catalysis process is worked as a similar fashion as that in the TEMPO-mediated homogeneous catalysis system.

Other than paired electrolysis of bio-based HMF, various other organic feedstocks acquired from different sources of biomass have been carried out and reported, including furfural [52], tertiary amines and benzonitrile derivatives [53], aldehydes (ketones) and benzylic alcohols [54], nitrobenzene (NB) derivatives and arylsulfonic acids (ASAs) [55], and benzylic C–H [56]. Similar transition metal-based electrocatalysts and reactor designs were widely used for their controllable and efficient transformations.

Alternatively, the bio-based organic oxidations are feasible to be coupled with the electrocatalytic reduction of CO_2 , a promising pathway to recycling waste carbon to generate sustainable chemicals with reduced cell voltage. For example, the methanol- CO_2 paired electrolyzer exhibited a cell voltage as low as 0.93V at 10 mA cm^{-2} to co-produce formate, significantly lower than the theoretical voltage of 1.299 V in the conventional $\text{CO}_2\text{-H}_2\text{O}$ system [57]. Similarly, the substitution of anodic OER by HMF oxidation has minimized the energy cost in the conventional electrochemical hydrogen production system [41][29][43]. Some representative paired electrolyzers with detailed information were summarized in **Table 1**.

Depending on the research targets and the practical applications requirements, pairing more promising reactions in one reactor could provide sustainable avenues towards distributed, flexible, and energy-efficient routes for chemical manufacturing.

Techno-economic analyses (TEAs) of paired electrolysis

In theory, any reactions can be paired in an electrochemical reactor with membrane-separated cathode and anode compartments. TEAs guided the selection of more valuable reactions. In a recent study, Yu et al. calculated the economic feasibility of ECO of glucose to glucaric acid on NiFe oxide (NiFeO_x) and nitride (NiFeN_x) catalysts, and the cost was estimated via a discounted cash flow analysis and simulated by ASPEN Plus [58]. The calculated minimum selling price for electrocatalytic glucose oxidation is $\$9.32 \text{ Kg}^{-1}$, much lower than $\$17.04 \text{ Kg}^{-1}$ from the chemical oxidation process. A work from Goetheer et al. performed economic viability analysis to compare paired ($\text{CO}_2\text{-1,2-propanediol}$) and unpaired ($\text{CO}_2\text{-H}_2\text{O}$) systems via the operational expenditure (OPEX) and the capital expenditure (CAPEX) [59], confirmed the paired

electrolysis system is economically more attractive, mainly attributed to the cheaper anode

Paired electrolysis	C (mM) ^a	j (mA cm ⁻²) ^b	Conditions	Cathode	Anode	Cathode FE (%)	Anode FE (%)	Ref.

materials and membrane.

From various sources of operation cost, electricity consumption is one of the majors to be considered. In a CO₂-glycerol electrolytic system [8], Verma and co-workers showed that the overall reaction is much more favorable thermodynamically and kinetically. For instance, coupling CO₂-to-C₂H₄ with glycerol-to-glyceraldehyde reactions significantly reduced the thermodynamic

Table 1. Summary of recent demonstrated biomass-derived paired electrolysis.

a. Concentration of organic feedstock. b. Current density c. 1.0 M KHCO₃ and 1.0 M KOH as the electrolyte for the cathode and anode compartment, respectively.

cell potential |E⁰| from 1.15 to 0.32 V. They experimentally observed a lowered cell potential of up to 0.85 V and energy consumption saving by up to 53%, confirming the more favorable glycerol oxidation than OER. In this regard, under a constant cell potential of 1.5 V, the production rate of CO was significantly increased, when switched from the unpaired system to the paired system (0.065 vs 0.462 kgcom⁻²h⁻¹).

HMF-HMF	10	N/A	0.5 M borate buffer (pH 9.2)	Ag/C	Carbon felt (TEMPO-mediated)	85	98	19
HMF-HMF	20	5	0.5 M borate buffer (pH 9.2)	OD-Ag	Carbon cloth (TEMPO-mediated)	80	83	17
p-nitrophenol-HMF	10	2.5	1.0 M KOH	NiBx@NF	NiBx@NF	>99	>99	51
HMF-HMF	10	25	0.2 M HClO ₄	Pd/VN	3D VN	≥86	≥84	50
Furfural-Furfural	50	10	1.0 M KOH	Cu ₃ P/CFC	Ni ₂ P/CFC	92.0–98.0	90.0–98.0	52
benzonitrile derivatives-tertiary amines	0.4	5	nBu ₄ NClO ₄ , 1,4-lutidine and DMA mixture	RVC	RVC (TEMPO-mediated)	N/A	N/A	53
ketones-benzylic alcohols	25	5.9	0.1 M nBu ₄ NOAc (CH ₃ CN/EtOAc = 3/7)	Ni	graphite	N/A	N/A	54
Nitrobenzene-aryl-sulfinic acids	1.0	0.7	0.2 M phosphate buffer (pH 3.5)	Glassy carbon	Glassy carbon	N/A	N/A	55
benzylic C–H bond convergent paired	0.6	3	0.1 M LutHClO ₄	Carbon fiber	FTO	N/A	N/A	56
CO ₂ -methanol	1000	10	1.0 M KHCO ₃ 1.0 M KOH ^c	mSnO ₂ /CC	CuONS/CF	80.5	91.3	57
CO ₂ -1,2-Propanediol	20	15	0.5 M KHCO ₃	Au/C	Carbon felt (TEMPO mediated)	76	80	59
CO ₂ -glycerol	2000	100	2.0 M KOH	Ag NPs	IrO ₂	N/A	N/A	8
H ₂ O-HMF	50	20	1.0 M KOH	Co-P/CF	Co-P/CF	~100	~90	41
H ₂ O-HMF	10	10	1.0 M KOH	Ni ₂ P NPA/NF	Ni ₂ P NPA/NF	~100	98	42
H ₂ O-HMF	10	10	1.0 M KOH	Ni ₃ S ₂ /NF	Ni ₃ S ₂ /NF	~100	98	43

Several candidate organic oxidation reactions could be selected to substitute sluggish OER, and thereby offered amounts of possible paired combinations. Lee et al. did some comprehensive work and evaluated TEAs of 295 co-production processes [9]. From their modeling and calculations, the profitability was highly dependent on the anodic organic oxidation reactions. Ideally, FDCA, 2-furoic acid, ethyl acetate, lactic acid, formic acid, glycolic acid, and oxalic acid are excellent anodic product candidates, considering the reactant costs and market value of these products.

Summary and perspectives

In summary, we have provided an overview and analysis of recent paired electrolysis systems for biomass-based compounds conversion, including reactor designs, catalyst and process developments, and TEAs of some representative systems. Replacing the sluggish OER with oxidative upgrading of biomass compounds can reduce the overall energy cost and allow for the

simultaneous generation of high-value products at both electrodes. However, some critical scientific and engineering challenges still exist that need to be considered and addressed in future research.

(1) Reaction rate

In reviewing paired electrolysis of biomass-derived compounds from recent years, realizing both high current density and high FE is still a critical challenge, yet not achieved. Most previous reports are conducted at low rates (i.e., <100 mA cm⁻², **Table 1**) in order to maximize FE to desired products, typically owing to the domination of uncontrollable side reactions (e.g., OER, HER) at large current densities. However, to cost-effectively scale up electrosynthesis at such low current densities, either high surface area of electrodes or large reactors are required, leading to an inevitable increase in capital and operation costs. In this regard, more efforts need to be devoted to designing advanced reactors and catalysts, in order to facilitate mass transport both externally and internally, and consequently increase the final delivered current density (or production rate) to desirable products.

(2) TEA

Theoretically, any reactions can be paired in a divided electrolytic cell with numerous possible combinations. It is necessary to evaluate the economic feasibilities of various candidates from different aspects: (1) Capital costs (e.g., catalysts and membranes), product management, reactor set-up, feedstock and product value, and the feasibility of pairing two reactions in one reactor. (2) Operation costs, such as electricity consumption by estimating experimental conditions (i.e., cell voltage, current density, and atom and energy efficiency), and energy utilization for separation and purification of products (downstream processing).

(3) Separation

The separation of desired products from the electrolyte is of great importance for industrial-level scale-up and application. For example, it is necessary to consider how to separate commonly used redox mediator (e.g., TEMPO) from the electrolyte after organic oxidative reactions. Moreover, supporting electrolytes is critical to completely dissolve organic reactants, keep electrochemical stability, and increase electrolyte conductivity; therefore, the cost of supporting electrolytes, and equally important, the downstream separation of product from the supporting electrolyte deserves further investigation.

(4) Advanced electrocatalysts

Many electrocatalysts (e.g., Ni, Co-based transition metal catalysts), prepared from different methods and exhibited different morphologies, have been explored to oxidize biomass-derived species in recent years. However, the critical differences among these advanced catalysts to impact reaction activity, and how to relate the structure of these catalysts with the catalytic reaction pathways are still unclear. In addition, maintaining high-performance particle size and structure for long-term operation of electrolyzers remains a challenge, especially at harsh electrochemical reaction conditions (i.e., highly acidic or basic electrolytes, large overpotentials) or in complicated mixed electrolytes. Consequently, more efforts need to be devoted to the rational design of highly efficient and robust catalysts with desired particle size and structures in enhancing reaction activities and regulating pathways.

(5) Mechanism study

A comprehensive understanding of the reaction mechanisms for the desired half-reactions should be provided before pairing them into one reactor. We should acquire deeper insights into reaction rate, product selectivity and FE, and overpotentials, and relate them well. In other words, we should know how reaction parameters regulate reaction pathways, influence adsorption/desorption of intermediates on the catalyst surfaces, and what dominated the reaction route to a desirable product. In addition, the gaps between electrocatalysis (driven by electrode potentials) and thermocatalysis (powered by temperature and pressure) should be filled. Valuable insights into the similarities and differences in mechanisms and energetics of the two systems should be provided, motivating quantitative comparisons across these two disparate reaction systems. Furthermore, efforts should be devoted to developing advanced electrochemical methods, such as *in-situ* or *operando* spectroscopic technologies, to probe the catalytic reaction occurring at the electrode/electrolyte interface. Theoretical computation (e.g., DFT) may also help offer new insights into critical mechanistic steps and further suggest promising active electrocatalysts for more efficient electrochemical conversion and transformation.

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Notes

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Topic of Contents

