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

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Abstract: Paired electrolysis enables the production of value-added chemicals and fuels at both the cathode and anode. Electrocatalytic conversion of biomass-derived feedstocks at ambient conditions would potentially integrate renewable electricity and renewable carbon for green and distributed chemical manufacturing to reduce the global carbon footprint associated with heavy use of fossil fuels. This mini-review summarized the recent progress of paired electrolysis, including biomass-biomass and biomass-small inorganics (CO_2 and H_2) paired circumstances. Some perspectives and outlooks were finally proposed for future improvement in the research area of paired electrolysis of biorenewable compounds.

Keywords: Paired electrolysis, electrocatalysis, electrocatalytic hydrogenation, biomass, CO_2 reduction.

Introduction

In light of the increased environmental issues caused by heavy dependence on fossil fuels, extensive 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 and CO_2 in electrolyzers to renewable chemicals have attracted enormous attention. Particularly, these electrolyzers can be potentially powered by renewable electricity sources from wind and solar [3, 4]. Using electrode potential as the driving force in electrochemical transformation and processes to replace conventional thermochemical processes operated at high temperature and pressure can significantly enhance reaction kinetics and pathways [5].

The electrochemical conversion of biomass feedstock to valuable chemicals and fuels can be supplemented to the current chemical industry to reduce our century-long addiction to fossil fuels for chemical manufacturing [6, 7]. Among the biomass-derived chemicals, Furfural and 5-hydroxymethylfurfural (HMF) have been listed as one of the top biomass-derived compounds by the U.S. Department of Energy [8]. They hold great potential to serve as synthetic platforms for numerous value-added chemicals [9]. In particular, the HMF hydrogenation product 2,5-bis(hydroxymethyl)furan (BHMF) is an essential precursor for polyesters and resins [10]. 2,5-furandicarboxylic acid (FDCA) derived from HMF oxidation is a feedstock to replace polyethylene terephthalate (PET) to yield renewable polymer [11]. Alternatively, furfuryl alcohol (FA) and 2-furoic acid, the hydrogenation and oxidation product of furfural, have been applied in the foundry [12] and polymer [13] industry, respectively.

Electrochemical half-reactions accommodate in paired circumstances may achieve simultaneous production of chemicals and fuels powered by renewable energy. Traditionally, in most electrolyzers, the reaction that occurred at the counter electrode yields a waste product [14]. For instance, the four-electron oxygen evolution reaction (OER) at the anode has sluggish kinetics (consumed ~90% of the full cell voltage) and produced O_2 directly releases back to the atmosphere with low value [15]. As a comparison, pairing anodic oxidation of a biomass compound can significantly reduce the full cell potential and have a theoretical 200% charge efficiency with economic feasibility [16, 17]. Besides, a few other advantages include [6, 18-20]: (1) Water serves as oxygen and proton sources for electrolysis instead of dealing with large amounts of O_2 and high-cost H_2. (2) Processes can be operated at ambient conditions to reduce the capital cost and energy input. (3) Reaction rate and product selectivity can be controlled by potentials or currents.

Paired electrolysis can be classified into four types as reported by Lee et al. (Figure 1) [21]: (1) Parallel paired electrolysis simultaneously performs two unrelated reactions in a divided cell. (2) Convergent paired electrolysis produces a single product from the intermediates of cathode and anode in an undivided electrochemical cell. (3) Divergent paired electrolysis operates to convert a common substrate to different products. (4) Linear paired electrolysis yields the same product from the same reactant generated through different electrochemical reactions.

In this mini-review, we reviewed recent progress on paired electrolysis, which can potentially integrate renewable electricity and renewable carbon (biomass) for green, resilient, and distributed chemical production.

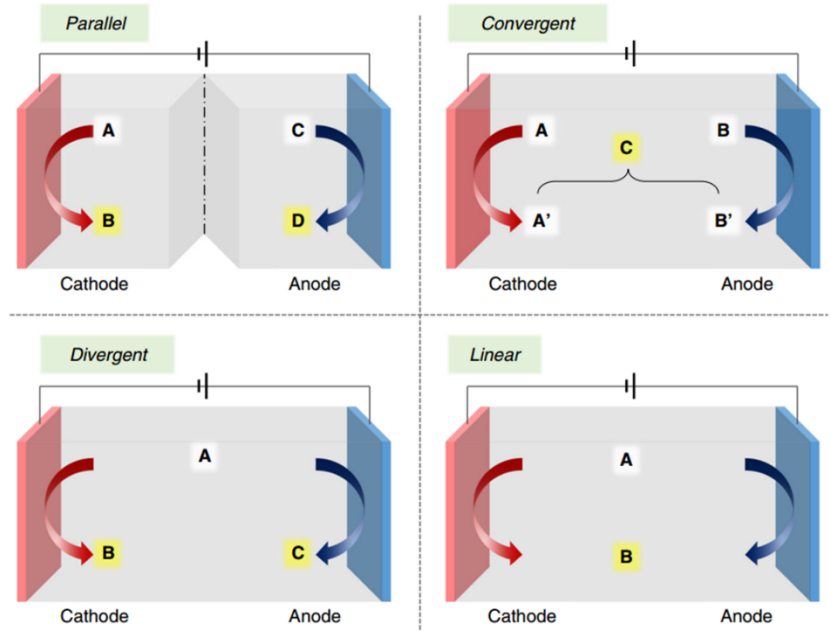

Figure 1. Schematic illustration of the electrochemical coproduction system. a parallel, convergent, divergent, and linear paired electrolysis. Adapted from ref. [21]. Copyright 2019, Nature.

Paired electrolysis of biomass-derived chemicals

In 2012, Strasser et al. reported electro-oxidation of HMF on Pt surface [22], with an only negligible yield of desired product FDCA. Li and co-workers further found HMF oxidation to FDCA with over 80% yield on $PdAu_2$/C in alkaline electrolytes [23]. In 2015, Choi group discovered electro-oxidation of HMF to FDCA by a 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) mediator and attained ~100% FE and yield in pH 9.2 buffer [24]. For electrocatalytic hydrogenation (ECH) of HMF, Koper group screened some metals by combining voltammetry with on-line sample collection offline liquid chromatography under neutral [25] and acid [26] conditions. They classified the catalysts into three groups in favoring different products. Choi et al. reported ECH of HMF on Ag electrodes (synthesized from sputter coating and galvanic displacement) under pH 9.2 borate buffers, with both highest selectivity and FE up to 100%.

Recently, Li group demonstrated HMF-to-BHMF and HMF-to-FDCA paired electrolyzer in a divided H-type cell [27]. The cathodic HMF hydrogenation was performed on an Ag/C catalyst, and anodic HMF oxidation was conducted on carbon felt via a 4-acetamido-TEMPO (ACT)-mediated process. ACT was oxidized to ACT^+ and served as a mediator that oxidized HMF to FDCA. They obtained a combined faradaic efficiency (FE) to BHMF and FDCA of 187%, almost doubled the unpaired cell.

Sun group discovered different transition metal-based electrocatalysts for direct HMF oxidation in alkaline solution without TEMPO mediator. They first reported electrodeposited Co-P as electrocatalysts for HMF oxidation in 1.0 M KOH electrolyte and obtained a ~90% yield of FDCA [28]. They then reported different Co and Ni-based electrocatalysts in catalyzing biomass-derived substrates (such as benzyl alcohol, furfural, furfuryl alcohol, and HMF) to value-added-chemicals with a much lower overpotential than OER [29-32]. Very recently, many advanced transition metal-based nanomaterials (Ni, Co, Fe, Cu) have been demonstrated to be able to improve the HMF oxidation activity and selectivity to desired FDCA [33-47].

Inspired by the active Ni-based catalysts for HMF-to-FDCA conversion, Sun et al. employed a NiB_x catalyst for HMF oxidation paired with p-nitrophenol-to-p-aminophenol reaction [48]. High conversion, selectivity, and FE of >99% on both compartments were observed. Wang et al. further demonstrated 3D vanadium nitride (VN) and Pd/VN hollow nanospheres for coproduction of FDCA and 2,5-bishydroxymethyl-tetrahydrofuran (DHMTHF) from HMF [49].

Various organic feedstocks were conducted for paired electrolysis, including furfural [50], tertiary amines and benzonitrile derivatives [51], aldehydes (ketones) and benzylic alcohols [52], nitrobenzene (NB) derivatives and arylsulfinic acids (ASAs) [53], and benzylic C–H [54]. More detailed information and some other paired electrolyzers were summarized in Table 1.

Paired electrolysis of biomass-derived chemicals and small inorganic molecules

Importantly, eletcroreduction of CO_2 to value-added chemicals or fuels is a promising strategy to reduce greenhouse gas emissions [55]. Nam et al. constructed HMF-CO_2 paired electrolysis using NiO NP_s anode and BiO_x cathode, respectively, for simultaneous generation of high value-added FDCA and formate [56]. A combined FE of 36% for HMF oxidation and 81% for CO_2 reduction to formate was achieved, respectively. Replacing the anodic feedstock to methanol, Shi et al.

reported methanol-CO_2 paired electrolyzer, and both convert to formate [57]. The assembled paired electrolysis exhibited a cell voltage as low as 0.93V at 10 mA cm^{-2}, significantly lower than the theoretical voltage of 1.299 V for electroreduction of CO_2 only.

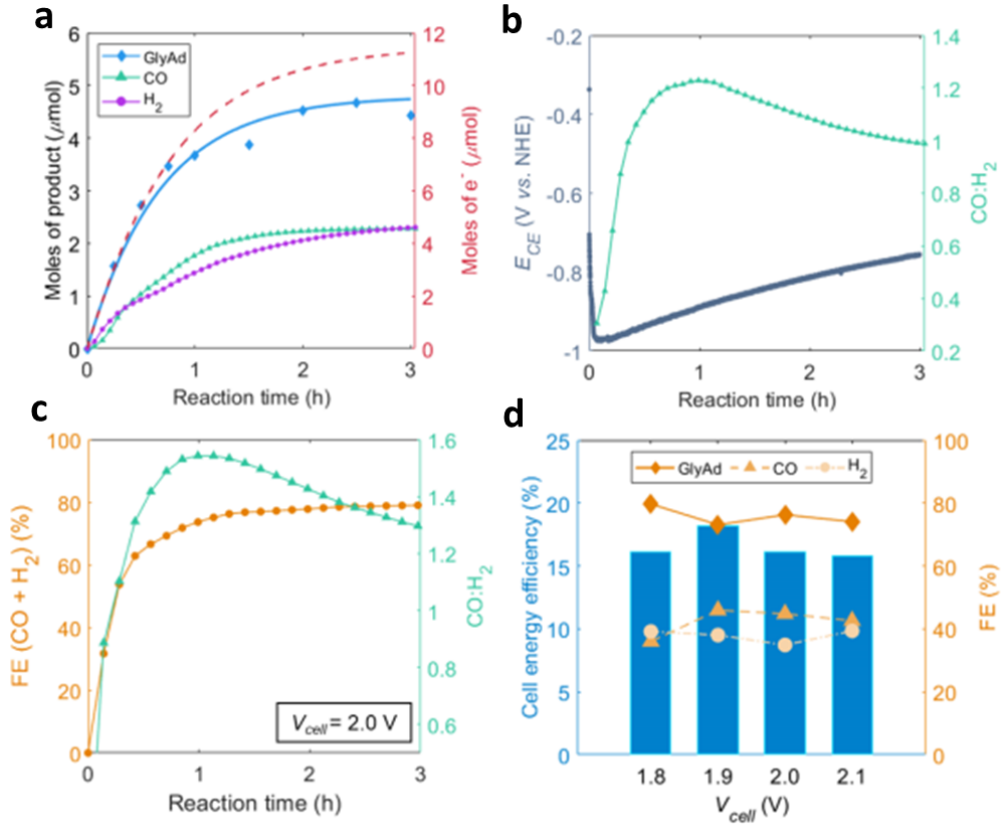

Figure 2. (a) Coupled electrolyzer, showing product (liquid and gaseous) and charge passed (red trace, as recorded by the potentiostat, where 1 mol of e = 96,485 C or 1 faraday) over reaction time. (b) Trend in the CO:H_2 ratio and CE (i.e., CP|CNT-CoPPc) potential (ECE) over reaction time. (c) Combined FE for CO and H_2, and CO:H_2 ratio for the two-electrode configuration employing glycerol as the substrate (applied cell potential= 2.0 V). (d) Cell energy efficiency and FE plotted as a function of V_{cell} in the same two-electrode setup. Conditions: for both the three-electrode (plots (a) and (b)), and two electrode (plots (c) and (d)) configurations, a two-compartment cell (fitted with anion-exchange membrane) was used; anode compartment: N_2 saturated pH 8.3 aq. HCO_3^-/CO_3^{2-} (0.5 M); cathode compartment: CO_2 saturated pH 7.3 aq. HCO_3^-/CO_3^- (0.5 M); glycerol substrate (50 mM) present in anodic compartment, t_{CPE}= 3 h, r.t. Glycerol oxidation and gaseous products were quantified by HPLC and continuous flow GC analysis, respectively. Adapted from ref. [58]. Copyright 2019, Wiley.

Reisner et al. showed a glycerol-CO_2 paired electrolysis ($AlcO_x$–CO2R) [58]. They modified TEMPO with a silatrane anchor (giving STEMPO), immobilized it on a mesoITO scaffold (giving mesoITO/ STEMPO), and served as the anode electrode to oxidize alcohols. The superior activity of STEMPO was attributed to the caged silatrane unit that increased the anchoring stability to metal oxide under alkaline conditions. It was then coupled with a cobalt phthalocyanine (CoPc)-based electrocatalyst for CO_2 reduction (Figure 2). They versatility of mesoITO/STEMPO was

tested by extending the substrate to oxidize HMF and lignin model compound 2-phenoxy-1-phenylethanol.

A study by Meyer et al. paired electrochemical reduction of CO_2 to syngas with the oxidation of benzyl alcohol to benzaldehyde and achieved the highest energy efficiency of 17.6% [59]. The onset potential for electrocatalytic benzyl alcohol oxidation appeared at ~1.1 V, which prevented the single-site Ru catalyst self-oxidation from $Ru^{III}–OH^{2+}$ to $RuI^{V}=O^{2+}$. Besides, CO_2-to-CO can be coupled with other alcohol oxidation reactions, as demonstrated by other researchers [60, 61].

In addition, HMF can replace H_2O oxidation to perform HMF-hydrogen evolution reaction (HER) paired electrolysis, as HMF oxidation is more favorable thermodynamically and kinetically than OER. Sun et al. proposed the HMF-HER paired electrolysis through earth-abundant OER electrocatalysts, including CoP [28], Ni_2P [29], and Ni_3S_2/NF [30]. The selected organics at the anode should satisfy the following criteria: (1) Reactant and products are both soluble in aqueous media. (2) They have more facile kinetics and more valuable than OER. (3) Substrate and its oxidized products do not compete with HER.

Reactor design for paired electrolysis

The most frequently used reactor for paired electrolysis is the two-compartment divided H-type cell separated by a membrane or a glass frit [27, 36]. For two-electrode cells, paired electrolysis is usually operated at constant current conditions. If the potential of one reaction needs to be accurately controlled, a three-electrode system need be set up by inserting a suitable reference electrode (RE). However, it is hard to control the applied potential for both the anode and cathode simultaneously.

If paired electrolysis needs to be scaled up to perform continuously to minimize mass transport limitations, a flow reactor must be demonstrated. The frequently used flow reactor is the membrane electrode assembly (MEA)-based cell with a membrane separated anode and cathode compartments, with a peristaltic pump controlling the flow rate. An example of the flow reactor applied for paired electrolysis was demonstrated by Huber et al. [62]. They presented a continuously flow membrane reactor for furfural hydrogenation paired with a hydrogen oxidation reaction (HOR). When replaced OER at the anode compartment, slightly higher reaction rates were obtained at a lower energy input. Wood et al. also reported an anion exchange membrane (AEM)-based MEA for ECH of furfural [63]. They found the addition of hydrophobic PTFE and anion exchange ionomers to the electrocatalysts could modify the protic environment of the cathode surface, which suppressed HER and increased the ECH rate.

Noël et al. designed an undivided multichannel electrochemical flow reactor to hydrogenate furfural [64]. This reactor had 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 [65], with 2(5*H*)-furanone, and furfuryl alcohol and hydrofuroin coproduced. Goetheer et al. designed a pulsating flow electrolyzer that increased mass transfer and enhanced the performance for oxidation of 1,2-propanediol [66]. The pulsation frequency can be adjusted in the range of 0-3 HZ by a pulsation pump. In comparison with the un-pulsed case, the desired product selectivity has increased >15%.

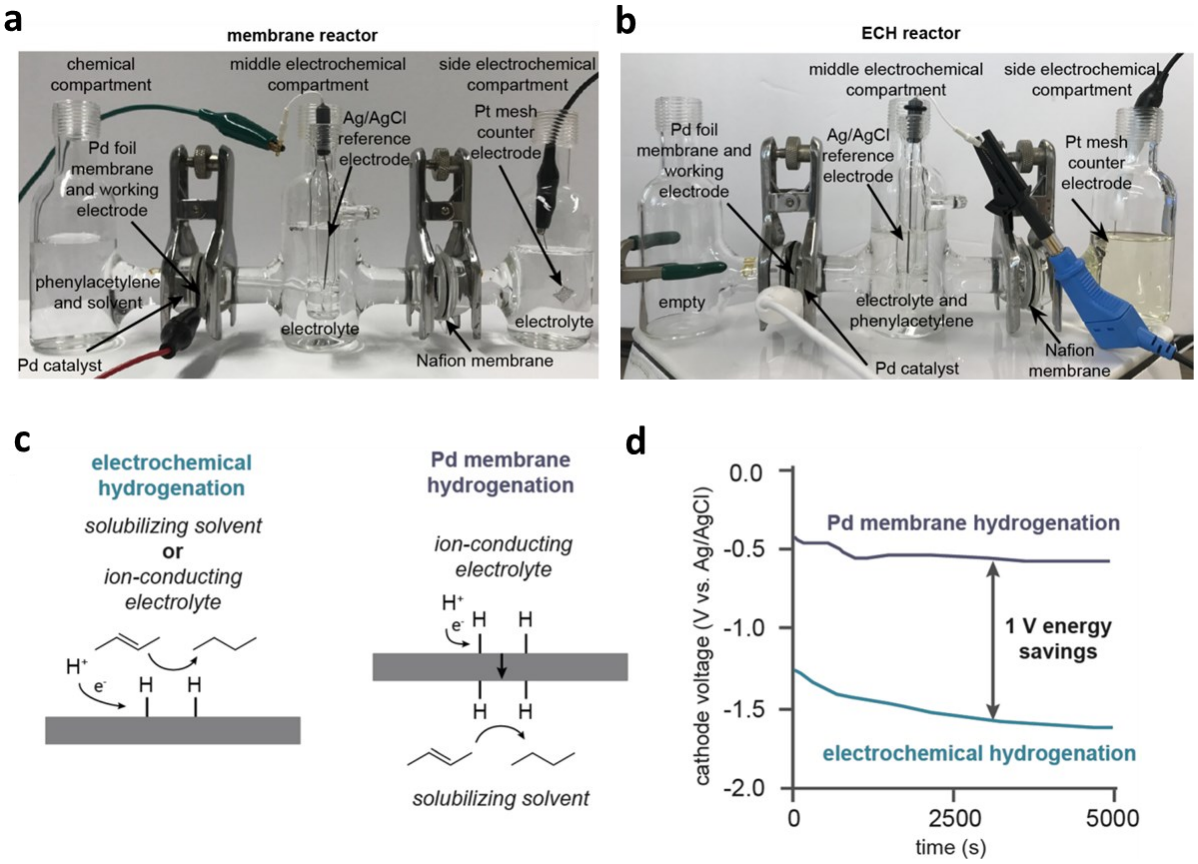

Figure 3. Photographs of the (a) membrane and (b) ECH reactors. In both cases, the cell has electrolyte in the middle and right compartments, with a Nafion membrane separating the reductive (middle compartment) and oxidative (side compartment) half-cells. A palladium membrane separates the middle and 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 palladium membrane reactor for electrocatalytic hydrogenation or deuteration of various functional groups, including alkynes (C≡C), alkenes (C=C), aldehydes (C=O), and imines (C=N) [67-69]. As shown in Figure 3, the membrane reactor saved 1 V cell voltage more than the commonly used H-type reactor. The basic principle is that hydrogen atoms are generated at the electrochemical compartment and diffused to the chemical compartment to hydrogenate unsaturated organic substrates, as hydrogen atoms can adsorb and diffuse into the

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

Paired electrolysis	C (mM)[a]	Conditions	Cathode	Anode	Cathode FE (%)	Anode FE (%)	ε (%)[b]	Ref.
HMF-HMF	10	0.5 M borate buffer (pH 9.2)	Ag/C	Carbon felt (TEMPO-mediated)	85	98	N/A	27
p-nitrophenol-HMF	10	1.0 M KOH	NiBx@NF	NiBx@NF	>99	>99	N/A	48
HMF-HMF	10	0.2 M $HClO_4$	Pd/VN	3D VN	≥86	≥84	N/A	49
Furfural-Furfural	50	1.0 M KOH	Cu_3P/CFC	Ni_2P/CFC	92.0–98.0	90.0–98.0	N/A	50
benzonitrile derivatives-tertiary amines	0.4	nBu_4NClO_4, 1,4-lutidine and DMA mixture	RVC	RVC (TEMPO-mediated)	N/A	N/A	N/A	51
ketones-benzylic alcohols	25	0.1 M nBu_4NOAc (CH_3CN/EtOAc = 3/7)	Ni	graphite	N/A	N/A	N/A	52
Nitrobenzene-aryl-sulfinic acids	1.0	0.2 M phosphate buffer (pH 3.5)	Glassy carbon	Glassy carbon	N/A	N/A	N/A	53
benzylic C–H bond convergent paired	0.6	0.1 M $LutHClO_4$	Carbon fiber	FTO	N/A	N/A	N/A	54
CO_2-HMF	10	0.5 M $KHCO_3$	NiO NP_s	BiO_x	81	36	N/A	56
CO_2-methanol	1000	1.0 M $KHCO_3$ 1.0 M KOH[c]	$mSnO_2$/CC	CuONS/CF	80.5	91.3	N/A	57
CO_2-glycerol	50	0.5 M $KHCO_3$	CP|CNT-CoPPc	mesoITO/ STEMPO	82	83	18	58
CO_2-benzyl alcohol	100	0.5 M Na_2SO_4 (pH 7.2) 0.5 M acetate buffer (pH 5)[d]	Ru-based	Ru-based	30-40	~70	17.6	59
CO_2-1,2-Propanediol	20	0.5 M $KHCO_3$	Au/C	Carbon felt (TEMPO mediated)	76	80	N/A	60
CO_2-alcohols	0.25	0.5 M $NaHCO_3$	Cu-In film	Pt mesh (TEMPO mediated)	>70	>75	N/A	61
CO_2-glycerol	2000	2.0 M KOH	Ag NPs	IrO_2	N/A	N/A	N/A	15
H_2O-HMF	50	1.0 M KOH	Co–P/CF	Co–P/CF	~100	~90	N/A	28
H_2O-HMF	10	1.0 M KOH	Ni_2P NPA/NF	Ni_2P NPA/NF	~100	98	N/A	29
H_2O-HMF	10	1.0 M KOH	Ni_3S_2/NF	Ni_3S_2/NF	~100	98	N/A	30

a. concentration of organic feedstock. b. energy efficiency c. 1.0 M $KHCO_3$ and 1.0 M KOH as the electrolyte for the cathode and cathode compartment, respectively. d. 0.5 M Na_2SO_4 (pH 7.2) and 0.5 M acetate buffer (pH 5) as electrolyte for the cathode and cathode compartment, respectively.

palladium lattice [70, 71]. 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.

Moeller et al. designed an electrocatalytic-catalytic coupled reactor in synthesizing various chemicals [72]. This reactor is worked via on-site electrochemical generated H_2 directly supplied to drive Pd-catalyzed hydrogenation or hydrogenolysis reactions. In such a design, the whole synthetic process can be positioned in a renewable electricity scenario, therefore, avoid purchasing and shipping hydrogen gas from a remote location.

Techno-economic analyses (TEAs) for paired electrolysis

Theoretically, any reactions can be paired in a divided electrolyzer, and TEAs provided rationale why specific reactions are chosen to pair in one reactor. In a recent study by Yu et al. [73], they assembled electro-oxidation of glucose to glucaric acid on NiFe oxide ($NiFeO_x$) and nitride ($NiFeN_x$) catalysts and achieved the highest glucaric acid yield of 83% at a current density of 100 mA cm^{-2}. The economic feasibility was estimated via a discounted cash flow analysis and simulated by ASPEN Plus. The calculated minimum selling price for electrocatalytic glucose oxidation is \$9.32 Kg^{-1}, much lower than \$17.04 Kg^{-1} from the chemical oxidation process. A work from Goetheer et al. performed economic viability analysis to compare paired (CO_2-1,2-propanediol paired) and non-paired (CO_2 reduction only) reactions via the operational expenditure (OPEX) and the capital expenditure (CAPEX) [60].

Verma and co-workers demonstrated electroreduction of CO_2 combined with anodic electro-oxidation of glycerol [15], which lowered the cell potential of up to 0.85 V and resulted in energy consumption saving by up to 53%. CO_2 reduction can be converted to several products, with much lower thermodynamic cell potentials ($|E^0|$) were obtained by utilizing organic oxidation reactions at the anode to replace OER. For instance, coupling CO_2-to-C_2H_4 with glycerol-to-glyceraldehyde significantly reduced $|E^0|$ from 1.15 to 0.32 V. When demonstrated in a constant cell potential of −1.5 V, CO production was much larger for paired cell compared with the unpaired one (0.462 vs. 0.065 $kg_{CO}m^{-2}h^{-1}$). Qiu et al. reported an A-Ni-Co-H/NF electrocatalyst for benzyl alcohol oxidation with 0.024 Wh lower electric energy input [74].

Lee et al. have evaluated several TEAs of CO_2-organic paired electrolysis [21], and found the profitability was highly dependent on the anodic organic oxidation. They analyzed 16 CO_2 reduction reactions and 18 anodic reactions, with 295 coproduction processes in total. FDCA, 2-furoic acid, ethyl acetate, lactic acid, formic acid, glycolic acid, and oxalic acid are excellent candidates to be paired with CO_2 reduction.

Summary and perspectives

In summary, we have provided an overview of electrochemical paired electrolysis processes in recent years, frequently used reactor systems, and TEAs of some representatives. Ideally, paired electrolysis can achieve coproduction of valuable chemicals or fuels in both anode and cathode

compartments, with a theoretical FE of 200% and more facile kinetics than OER. However, there still are some critical challenges that need to be considered and addressed in future research.

(1) Reaction rates

In reviewing biomass paired electrolysis from recent years, high current density and FE are still critical challenges yet not achieved. Large current densities are necessary for industry-relevant operations, but it will inevitably lead to uncontrolled side products, such as O_2 and CO_2, along with electro-oxidation of biorenewable compounds. Therefore, the previously reported electrolysis of HMF or furfural, alcohol, and glycerol is usually conducted at low rates (i.e., <100 mA cm^{-2}) to maximize FE to target products. To satisfy industrial requirements, the high surface area of electrodes or large reactors is in need, leading to high capital costs. Therefore, more efforts need to be devoted to designing advanced reactors and catalysts to increase delivered current density by facilitating external and internal mass transport to boost the specific reaction rate.

(2) TEA

Although theoretically any reactions can be paired in a divided electrolytic cell, leading to numerous possible combinations, it is necessary to evaluate the economic feasibility of performing the candidate paired electrolysis from different perspectives, including the capital cost of reactors, the easiness of paired reactions, electricity and separation costs, and market needs and value for the products. Besides, various experimental parameters should be estimated for analysis, such as FE, cell potential, current density, and atom economy and energy efficiency.

(3) Product separation

The separation of desired products from the electrolyte is of great importance for industrial-level applications. For example, the frequently used redox mediators (e.g., TEMPO) for organic oxidations introduced separation issues that need to be considered. Some factors, such as solubilities and pH, need to be examined in separations.

(4) Advanced electrocatalysts

Many electrocatalysts have been explored, i.e., transition metals (e.g., Ni, Co)-based catalysts were prepared from different methods and applied for HMF oxidation. The critical differences among these advanced catalysts to influence the reaction activity and how to relate the structure of the catalysts with reaction pathways are still unclear. Moreover, catalysts should be stable in long-term operations, especially at harsh electrochemical reaction conditions (highly acidic or basic, highly overpotentials) or in complicated mixed electrolytes along with reaction occurrence. Ideally, rational design and accurate synthesis of catalysts with desired particle size and structures are anticipated to regulate reaction activities and pathways.

(5) Electrochemical reaction mechanisms

More fundamental studies need to be conducted to half-reactions before they are applied for paired electrolysis, including understanding the reaction mechanisms and enhancing the reaction rate, selectivity, and FE, minimizing the overpotentials, clarifying how reaction parameters regulate reaction pathways and adsorption/desorption of intermediates on the catalyst surfaces, comparing the ECH and traditional thermocatalytic hydrogenation (TCH) to understand their similar mechanisms. ECH and TCH gaps might be mitigated by understanding how electrode potential and H_2 activation (temperature and pressure-driven) affect reaction activity differently. Combining

advanced electrochemical methods, in-situ spectroscopy study of electrochemical reactions with theoretical computation (e.g., DFT) may provide new insights into critical mechanistic steps of biomass compounds conversion for more efficient paired electrolysis.

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Notes

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